Controlled conditions of heat and mass transfer during crystallization as stimulating factors for improving the properties of metallic materials

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Abstract. The emergence of critical conditions in a meta-stable melt is considered under the influence of two main factors: pre-crystallization super-cooling and overcooling rate. The average density of free energy in such conditions is highly inhomogeneous. External impacts are considered as factors controlling the properties of materials. The solidification of the overcooled meta-stable melt is considered in a quasi-chemical approximation, assuming a transition state corresponding to an ideal solution type system. The finite time of existence of the meta-stable state is taken into account. The dimensions of the structural cell are determined by the ratio between the rate of diffusion and heat removal. The obtained estimate of the structure parameter is in qualitative agreement with the experimental dependence.

1. Introduction
Metallurgical materials have signs of natural self-organized behavior when certain types of boundary conditions affect on them. Understanding the mechanisms of self-organization is necessary for the development of technologies for creating materials with controlled properties for power engineering [1–5].

With a decrease in the temperature gradient ahead of the crystallization front below the critical value, the columnar growth of crystals transforms into dendrite type [6, 7]. Branches of free-growing dendrites do not grow together. This feature results in non-uniform properties of this crystal structure. However, if the trunks of dendrites are intentionally formed from a single substrate, then a single-crystal structure is formed with directional structurally sensitive properties. This method was embodied in the manufacture of gas turbine engine blades [6].

In technology, one usually deals with a non-uniform structure with uniform properties. When a critical situation occurs, the space of the meta-stable melt self-organizes into a system of micro-spaces of uniform size [8].

In unstructured mode, the critical behavior of particles (atoms) of the segregation zone continues to be determined by the density of surface energy. At this moment, in accordance with local gradients of heat sink and mass transfer, the formation of structural elements of the new phase will occur. However, their translation will be limited by the disorder of heat and mass transfer. When approaching the ultimate non-equilibrium, a non-dendrite structure is formed with a sub-fine grain and high-angle grain boundaries. For example, in aluminum alloys, a non-dendrite structure is formed at a cooling rate of 10–2 K/s and above. Meanwhile, at low cooling rates, an axial structure is formed with a larger grain and
different levels of dendrite crystallization. The boundaries of these grains have the structure of dendrite branches.

So, it is necessary to consider the pre-crystallization super-cooling and the cooling rate of a meta-stable melt.

2. The critical state of the meta-stable melt

A metal melt in a meta-stable state, including a critical non-equilibrium situation, is a system whose focus and integrity are maintained by internal order that determines the equilibrium of its parts and their connection [9, 10].

The difference between the free energies of the meta-stable liquid melt (L) cooled below the equilibrium melting temperature and the solid phase (S) is determined by the ratio

$$
\Delta g = \Delta h \frac{\Delta T}{T_{eq}},
$$

where $\Delta h$ is the enthalpy of melting, $T_{eq}$ is the equilibrium phase transition temperature (melting point), $\Delta T = T_{eq} - T$ is overcooling.

In a critical situation, there is a finite probability $I$ of microscopic behavior, which determines the transition of a meta-stable system through the energy barrier $\Delta g$ by fluctuations into the solid phase [11],

$$
I = K \exp \left( - \frac{\Delta g}{kT} \right),
$$

where $k$ is the Boltzmann constant, $K$ is the kinetic coefficient determining the energy exchange in the composition of the medium.

Drawing on experimental data, it becomes possible to associate the probability $I$ with the rate of nucleation and the rate of growth of a new phase.

To date, however, a number of significant aspects remain unexplained. Among them is a micro-tuning of the melt components hidden from direct observations. Although the model scheme of such a process involves the reaction with the non-equilibrium state of the components of the melt, it remains unclear the reason for the natural ability to abruptly ensure the formation of a new molar composition and physical properties.

Figure 1. Model diagram of the local fragment and segregation zone.

In a weakly non-equilibrium situation, directional valence bonds can predictably develop. In this case, the central atom has the ability to form bonds with the particles (atoms) of the near environment. It is necessary to establish a mechanism that operates in a meta-stable melt when selecting and placing components in segregation zones. For the meta-stable state of the melt, the interactions of atoms with the nearest environment are stable. Ascending diffusion transfers atoms to the segregation zone (Figure
1). Self-similar local spaces have a structural organization that is inherited from the melt. The structure of the segregation zone is determined by the fact that the incoming substance is in a state of pure component.

3. Structure formation mechanism in a meta-stable melt and spatial scale

In studies of the conditions of hardening of metals and alloys, the dependence was found [12]:

\[ d = a v_c^{-n}, \]

where \( d \) is the distance between the branches of the second order dendrite (dendrite parameter); \( v_c \) is the melt cooling rate, \( a \) and \( n \) are empirical constants.

The non-dendrite (axial) structure is formed along with the dendrite one at high cooling rates. When treating the melt with modifiers, it is formed even at low cooling rates. The size of the non-dendrite grain is comparable with the dendrite parameter in a wide range of cooling rates.

Today, the fundamental dependence (3) is used in the estimations of the structure and other properties of alloys in technological calculations. Attempts were made to associate the constants \( a \) and \( n \) with the properties of the alloy and its components (diffusion coefficients, parameters of the structure of the crystallization front, etc.) [13–16]. However, an unambiguous influence of the characteristics of the alloy has not yet been found. One can speak only about the tendency of an increase in \( n \) with an increase in the diffusion coefficient and a decrease in alloy doping. According to experimental data, the value of \( n \) is in the range from 0.2 to 0.5. The range of \( n \) is apparently related to the conditions of nucleation and the formation of a new phase. For example, for axial crystallization, \( n \approx 1/3 \).

In the study of packing in the inter-atomic space of particles (atoms) connected by the short and long order, using the renormalization group method [16], it was shown that the fluctuation energy is used by atoms to overcome the energy barrier, which makes it possible to “find the path” to the package with their mutual symmetric arrangement corresponding to symmetry in the electronic exchange interaction.

Characteristic phenomena during solidification are ascending diffusion and segregation of melt components. The localization of these phenomena is associated with a dendrite parameter, which can be considered as a parameter of the structure of a meta-stable metal system. In this study, we consider the possibility of estimating the dendrite parameter and establishing a connection with the properties of the melt. To do this, consider the ratio \( V/S \) of the system, consisting of similar structural elements (cells), where \( V \) is the volume of the cell, \( S \) is the area of its surface.

Any phase is considered meta-stable. It is taken into account that the transition to a new state takes place over a certain characteristic lifetime of the meta-stable phase. In physical material science, it is customary to characterize the meta-stable state of the melt by the overcooling \( \Delta T \) relative to the equilibrium liquidus. Let’s assume that at a temperature below the equilibrium liquidus, the system is cooled with a final rate \( v_c \). The characteristic cooling time (lifetime of the meta-stable phase) can be represented as

\[ \tau_c = \frac{\Delta T}{v_c}, \]

where \( \Delta T_c \) is the pre-crystallization overcooling of the meta-stable melt.

A particle (atom) of a condensed medium can change the energy state and bonds with neighboring particles (atoms) due to the flow of thermal energy and by diffusion. When assessing the level of energy variations, we assume that before solidification, the meta-stable solution evolves to an “ideal solution” type system. Such an approach is known as a quasi-chemical approximation. The necessary relationship between the processes of heat and mass transfer within the framework of the accepted consideration is carried out for regions of a meta-stable melt, the spatial scale of which is commensurate with the dendrite parameter.

In the case of equilibrium coexistence of the initial liquid and the solid phase that has arisen, it is considered that their chemical potentials are equal. At an equilibrium phase transition temperature \( T_{eq} \), a change in the phase composition can occur for an infinite duration of the process. In reality,
solidification takes place in a finite time determined by the rate of cooling. Note that overcooling is a necessary condition for solidification, ensuring the removal of the heat released by overcooled melt and a phase transition. The resulting non-equilibrium gives rise to non-compensated thermodynamic forces, the action of which can lead to the formation of structures localized in certain regions of the meta-stable melt.

Since we are supposed to evaluate the formation of these structures in the melt, we will not resort to considering the conditions for the formation of new phase nuclei. Imagine the volume of the melt as a set of cells with a common boundary, which is adjacent to the segregation zone, enriched with the most active particles. In overcooled melt, particles whose state corresponds to the highest energy level have the highest activity and mobility. The state of a pure component possesses the greatest energy. Groups of non-associated particles (central atom with close neighbors) have an excess of free energy, which allows them to form a configuration in which the nearest neighbors are arranged symmetrically.

Considering that the concentration of non-associated particles in the segregation zone is high, one can imagine the melt as an ideal solution with chemical potential

\[ g \approx g^*(T, p) + RT \ln C, \]

where \( g^*(T, p) \) is the chemical potential of the pure component, \( R \) is the universal gas constant, \( C \) is the mole fraction of non-associated particles (\( C \sim 1 \)).

Presumably, the transfer of non-associated particles to the segregation zone is carried out by diffusion. The transfer rate is consistent with the cooling rate. The diffusion time \( \tau_D \) of particles from the volume \( V \), bounded by the surface of area \( S \), we estimate from the ratio

\[ \frac{CV}{\tau_D} \approx \frac{D \Delta C}{r} S, \]

where \( \Delta C \) is the change in the mole fraction of non-associated particles within the segregation zone, \( r = V/S \) is the characteristic size.

Therefore, the inverse diffusion time is

\[ \tau_D^{-1} \approx \frac{D \Delta C}{r^2 C}. \]

Equating the cooling and diffusion times one obtains

\[ r \approx \sqrt{\frac{D \Delta T_c \Delta C}{v_c C}}. \]

Assuming \( \Delta C \ll C \), we get

\[ \Delta g \approx RT \Delta C / C. \]

As a result, we obtain an estimate of the spatial scale in the following form:

\[ r \approx \sqrt{\frac{D \Delta g \Delta T_c}{RT v_c^{1/2}}}. \]

The physical meaning of the parameter \( r \) indicates that its value is determined from the condition of matching with the rate of accumulation of unassociated particles in the segregation zone, since the mobility of the particles (atoms) themselves is limited by the diffusion coefficient \( D \). It is known that if the growth process of a new phase is limited by diffusion, then the spatial scale is determined by the value of the dendrite parameter \( d \). If we assume that the growth of dendrite branches occurs in the segregation zone, then we can approximately assume that \( d \approx 2r \). It can be seen that the estimate (10) is in qualitative agreement with the experimental dependence (3), and the value of the exponent \( n \) belongs
to the range indicated for Eq. (3). Eq. (10) can be considered as a limiting estimate. The value of \( \Delta g \) can be taken equal to the activation energy of diffusion \( A \).

The quantitative correspondence of Eq. (10) will be considered on the example of the ZhS26 nickel alloy. We use the following values: \( T = 1820 \) K, the activation energy of nickel diffusion \( A = 270 \) kJ/mol, the diffusion coefficient of nickel in the liquid phase \( D = 10^{-9} \) m\(^2\)/s. For comparison, we use the data obtained at cooling rates of \( \nu_c = 1.5, 2, \) and \( 2.5 \) K/s and overcooling \( \Delta T_c = 0.7, \) 0.8, and \( 0.9 \) K, respectively. The comparison in Figure 2 shows the acceptable agreement of our assessment.

![Figure 2. The change in the dendrite structure parameter of the alloy ZhS26 depending on the cooling rate: according to the empirical dependence (3) with \( n = 1/3 \) (dotted), the boundaries of the range for products obtained under production conditions (solid), and calculation by the formula (8) (rhombuses).](image)

The fact that compared with the proposed dependence (10) in experiments, a smaller value of \( n \) is observed due to the approximate nature of our estimate, which does not take into account the presence of large temperature gradients at high cooling rates. In addition, taking into account the temperature dependence of the parameters under the square root sign in (10) with an increase in the cooling rate also leads to a deviation from the 1/2 law.

4. Conclusions
To address effectively the issues of morphology, physical and chemical properties of new phases and conditions of translation of structural units, it is necessary to take into account the changes that are created during isomorphic and polymorphic transformations in metals and alloys. Isomorphism implies the similarity of the properties of the atoms of a substance of a soluble additive to its nearest neighbors in the interatomic configuration based on: 1) the identity or proximity of the electronic structure; 2) proximity of atomic, ionic or covalent radii; 3) proximity of ionization energies and other properties. The similarity leads to the possibility of replacing one isomorphic component with another. This principle can be used as a basis for the detailed development of the system of shifts in the chemical potentials of interatomic configurations of a meta-stable melt in a critical situation created by pre-crystallization super-cooling.

The theoretical significance of the analysis is in explaining the instability of interatomic configurations of a meta-stable melt in a critical situation created by pre-crystallization super-cooling, which makes it possible to evaluate the crystallization of metals and alloys from the standpoint of thermodynamic equilibrium and to solve the problems of improving their operational properties.

References
[1] Elinson V M, Shchur P A, Kirillov D V, Lyamin A N, Silnitskaya O A 2018 Journal of Surface Investigation 12 357
[2] Dvoretskiy A E, Magnitsky I V, Odinabekov F R, Sergeeva E S, Tashchilov S V 2018 *IOP Conf. Series: Materials Science and Engineering* **307** 012063

[3] Golub V V, Zhilin Yu V, Rylov S A 2018 *Instruments and Experimental Techniques* **61** 453

[4] Pozdnyakova E D, Maslennikova E V, Komshin A S, Orlova S R 2019 *IOP Conf. Series: Materials Science and Engineering* **489** 012008

[5] Reznik S V, Prosuntsov P V, Mikhailovskii K V 2019 *Journal of Engineering Physics and Thermophysics* **92** 89

[6] Svetlov I L, Kuleshova E A, Monastyrskiy V P, et al. 1990 *Izvestiya AN SSSR. Metally* **186** (in Russian)

[7] Alexandrov D V, Galenko P K 2014 *Phys.-uspekhi* **57** (8) 771

[8] Berry R S, Smirnov B M 2005 *Phys.-uspekhi* **48** (4) 345

[9] Brazhkin V V 2006 *Phys.-uspekhi* **49** (7) 719

[10] Kukushkin S A, Osipov A V 2014 *Phys. Solid State* **56** 792

[11] Martynov G A 1999 *Phys.-uspekhi* **42** (6) 517

[12] Dantzig J A, Rappaz M 2009 Solidification. EPFL Press, Lausanne.

[13] Morris D G 1982 *Metal science* **16** (9) 457

[14] Herlach D M 1994 *Mater. Sci. Eng.* **R12** (4–5) 177

[15] Herlach D M, Galenco P, Holland-Moritz D 2007 Metastable solids from undercooled melts. Elsvier, Amsterdam.

[16] Ma S - K 1989 Modern Theory of Critical Phenomena. Addison-Wesley, New York.