

# Spinodal decomposition of solutions during crystallization

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## Abstract

The modern theory of phase transitions cannot explain the results of many experiments of interphase mass transfer. One reason for this is the assumption that during crystallization the solution is in the metastable state. The decomposition of the solution occurs by binodal scenario in this case. Crystallization nuclei form and grow in solution. The purpose of this study to show that in many cases the solution during crystallization is in an unstable state. The unstable condition leads to decomposition the solution by spinodal scenario

## Keywords

decomposition, solution, reverses diffusion, spinodal, phase diagram

## Introduction

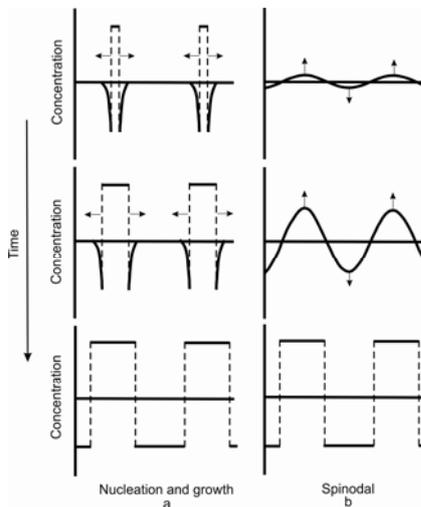
The subjects of this study are eutectic composites, which are obtained by crystallization of a homogeneous liquid solution. The original homogeneous melt is moved through the area of crystallization. A crystal with a periodic distribution of components is formed as a result of crystallization. Eutectic composites represent a periodic alternation of rods, plates or colonies of one phase, located in the volume of the other, matrix phase.

Let us consider at the differences in the mechanisms of decomposition of metastable and unstable solutions [1]. The physical meaning of binodal decomposition is that in supercooled solution clusters of a new phase are constantly forming and decomposing. The cluster continues to grow and forms a new phase, if it reaches a critical size. The new phase has a sharp boundary, as shown in the figure 1a.

Two facts are important for further discussion. Firstly, the solution decomposes not throughout the entire volume simultaneously, but growth of individual clusters of the new phase occurs. And secondly, during decomposition at the interface there is a jump of concentration. The magnitude of the concentration jump depends on the difference of the components solubility in liquid and solid solutions.

Spinodal decomposition is of other nature. Spinodal decomposition is associated with the dependence of the interaction potentials of the solution particles on the environmental conditions. Some thermodynamic conditions lead to a homogeneous distribution of the

components throughout the entire volume of the solution. In this case, an excess of one of the components in any area will lead to diffusion of this component, and the solution will remain homogeneous. The other thermodynamic conditions lead to decomposition of the solution to the phases having different concentration. In this case, any arbitrarily small fluctuations of concentration (or temperature) lead to the situation when the particles of different varieties will diverge. A homogeneous solution will decompose to two solutions with different concentrations of the components (figure 1b).

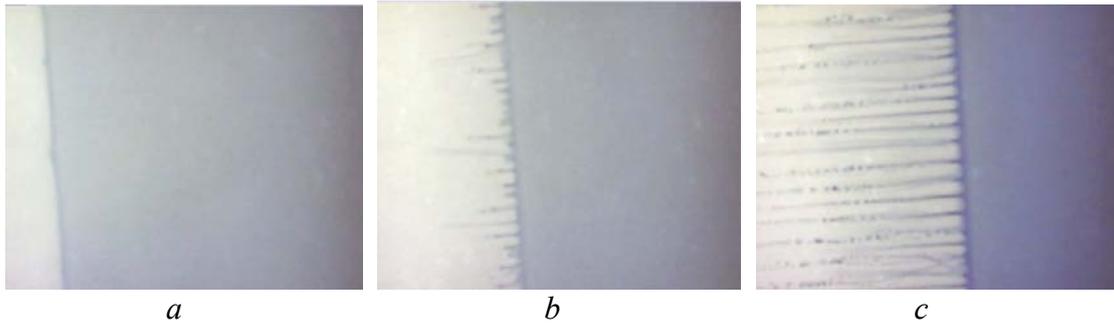


**Fig. 1:** . Scheme of solution decomposition by binodal (a) and spinodal (b) scenario.

It is important to note that in the case of spinodal decomposition any energy barrier does not exist. The system is unstable to arbitrarily small fluctuations. Decomposition starts immediately after transfer of the solution into the unstable state. The particles immediately begin to diffuse into the area in which there was an excess of this component. Concentration of the excess component in this area increases gradually, without sharp boundaries. The unstable solution decomposes immediately in all the unstable area. Decomposition of the solution ends with formation of the equilibrium phases with sharp boundaries between them. The scheme of the start and the end of the solution decomposition is shown on figure 1. The diagram shows that the decomposition scenarios differ at the beginning and in the process of decomposition. The result of both scenarios is the same. Therefore, it is difficult to distinguish between binodal and spinodal decomposition by the end result of decomposition. The process of spinodal decomposition, however, occurs by continuous changes in concentration of the entire volume of the unstable solution. In this it differs from the process of decomposition of solution decomposition by binodal scenario. This difference gives one the opportunity to determine the mechanism of decomposition of the solution decomposition, observing the process of decomposition itself.

## Result of experiments

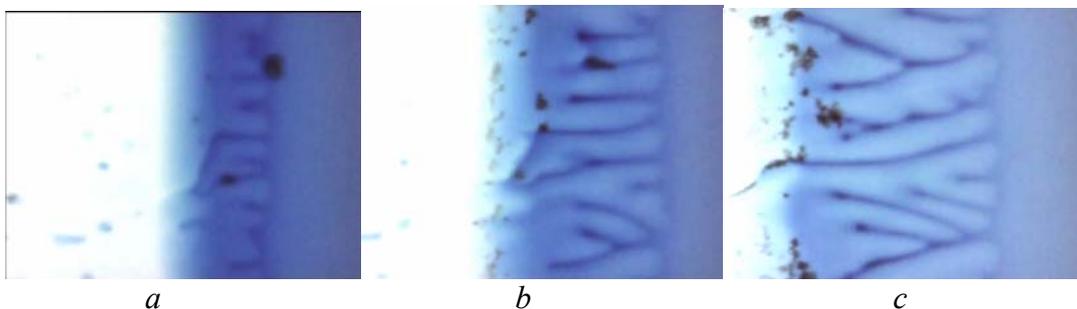
Now we shall demonstrate the experiments result in which spinodal decomposition of the solution in the process of its crystallization was observed. The cuvette with the solution is moved between the refrigerator and the heater [2]. The temperature of the refrigerator is lower than the temperature of crystallization. As a result the solution freezes, and the interface moves with a given speed of cuvette movement. Bromthymol blue dye aqueous solution is used in order to observe the process of decomposition of the solution decomposition. This solution decomposes to the phases of different colors. One phase is almost pure water, colorless and transparent. The other phase is blue. At first the experiment shows a homogeneous liquid solution. The forming interface appears after some period of time on the



**Fig. 2:** Formation of periodic structure during solidification of an aqueous solution bromthymol blue. a - flat interphase boundary, b - emergence of concentration distortion, c - formed periodic structure.

left (figure 2a). The interface is flat at the beginning. It becomes unstable then. Spatial distortions appear at the interface (figure 2b). The amplitude of these distortions increases. The solution decomposes into two phases in front of the interface. The Spatial distortions transform into strips with different phases. Then these strips form into the periodic structure (figure 2c). The experiment shows that crystallization occurs after formation of the periodic structure. There is no equilibrium boundary between liquid and solid phases, as predicted by other theories. This experiment shows also the relation between instability of the interface and the period of the eutectic structure. Thus, the previously theoretically obtained result [3,4] is confirmed: the eutectic structure period is equal to the period of interface instability. It is difficult to show on this clip that decomposition of the solution occurs by spinodal scenario. This is demonstrated by the following experiment.

The cuvette with the solution was located so that the part of the solution was on the cold area of the device, and the other part was on the warm area in the following experiment. The solution was crystallized on the cold part of the device. A flat interface formed between the cold and warm parts of the device. The cuvette was set in motion after the boundary had become stationary. The figure 3 shows a successive change of the solution concentration. This figure shows that structure formation occurs under continuous, without jumps change in solution concentration. It is clearly seen here that concentration changes simultaneously throughout the entire area of solution decomposition. Periodically alternating strips with different composition are formed from a homogeneous concentration distribution. Decomposition occurs continuously in the vicinity of the interface. This experiment demonstrates that the change of concentration occurs by reverse diffusion. A homogeneous distribution of concentration simultaneously in the entire volume transforms to a modulated distribution in the form of strips of different colors. There are no sharp boundaries of



**Fig. 3:** The formation of periodic structures in a thin layer of an aqueous solution bromthymol blue. A - beginning of structure formation, b, c - process of structure formation.

concentrations. That is, decomposition of the solution occurs by spinodal scenario.

## Area of the unstable state of solution

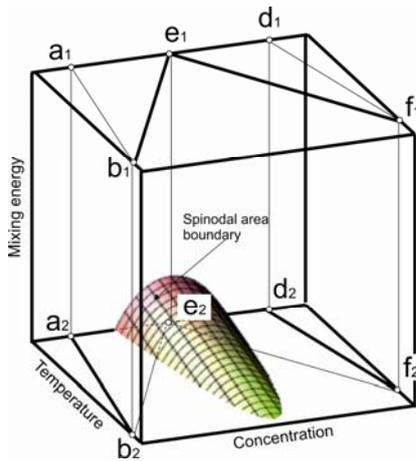
These experiments show that decomposition of the solution occurs by spinodal scenario. Let us show how the solution can get to the area of spinodal decomposition. For this purpose we shall use the locally configuration model of solutions. This model has been used for a qualitative analysis of crystallization processes for a long time [5]. The expressions for free energy of the solutions of the concentration  $c_i$  for this model have the form (1). Index  $i$  relates to the solid  $l$  and liquid  $2$  phases. These expressions correspond to the liquid and the solid.

$$G_i(c_i) = N \left[ U_i c_i (1-c_i) + \frac{U_{AA}^i (1-c_i)}{2} + \frac{U_{BB}^i c_i}{2} \right] + NkT \left[ c_i \ln(c_i) + (1-c_i) \ln(1-c_i) - \ln \beta_i \right] \quad (1)$$

$$U_0^i = U_{AB}^i - \left( \frac{U_{AA}^i}{2} + \frac{U_{BB}^i}{2} \right) \quad (2)$$

$$\frac{d^2}{dc_i^2} G_i(c_i) = -2NU_i + NkT \left( \frac{1}{c_i} + \frac{1}{1-c_i} \right) \quad (3)$$

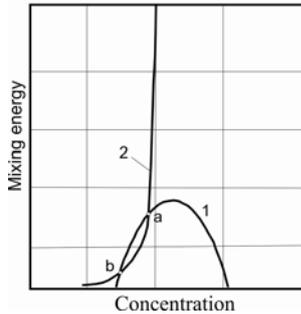
Here  $k$  is the Boltzman constant,  $N$  is total number of particles and position.  $\beta$  is the logarithmic dependence of entropy on free energy. This model includes the interaction potentials  $U_{AA}^i$ ,  $U_{BB}^i$ ,  $U_{AB}^i$ , between the particles of the solution. These interaction potentials change their values during transition from the liquid phase to the solid one. The locally - configuration model includes the parameter that uniquely identifies the boundary of the spinodal area. This parameter is mixing energy  $U_0^i$  (2). The boundary of the spinodal area is determined by the equation (3). This equation (3) contains only three variables of the parameter. These parameters are: concentration, temperature, and mixing energy. Therefore, the convenient state diagram of the solution can be built. For this purpose one needs to add one more coordinate, which is mixing energy. Therefore, the boundary of the spinodal area is uniquely defined at these coordinates. Such a diagram is depicted in the figure 4.



**Fig. 4:** Phase diagram of solution taking into account change mixing energy of component.

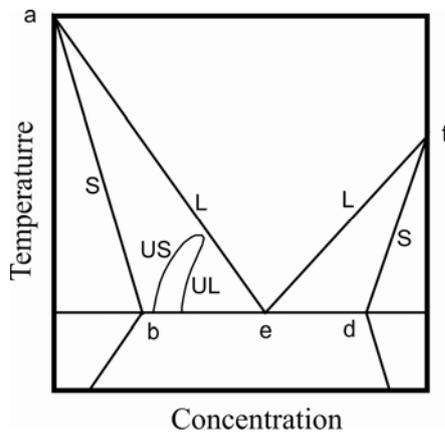
The liquidus lines  $b_1e_1$  and  $e_1f_1$  are in the plane corresponding to the value of the mixing energy in the liquid phase at these coordinates. The solidus lines  $b_2a_2$  and  $d_2f_2$  are in the plane corresponding to the value of the mixing energy in the solid phase. These planes are separated by the values of mixing energy. The border of spinodal decomposition area is built in this chart. The solution decomposes by spinodal scenario if in the process of phase transition it is getting in this area.

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**Fig. 5:** Phase diagram of solution taking into account change mixing energy of component.

trajectories intersects of the area of spinodal decomposition, we obtain the intersection curve of the surface of the system trajectories and the boundaries of the spinodal area. The system will be disposed on the trajectories that pass through this curve at different parameters of the stationary regime. This curve is a curve of dynamic equilibrium of the system. Let us construct the projection of the equilibrium curves of the liquid and solid phases, and also the dynamic equilibrium curve in a single plane with a constant mixing energy. Such a phase diagram is shown in the figure 6.



**Fig. 6:** Equilibrium phase diagram  $baefd$  and dynamic phase diagram  $US-UL$ .

The phase diagram includes the equilibrium phase diagram  $baefd$  and the curve  $US$ ,  $UL$  of dynamic equilibrium. The curve of dynamic equilibrium is similar to the curves of phase equilibrium for the analysis of phase transition.

Let us show some effects of this phase transition. For this we shall consider formulation of the steady isothermal problem of diffusion. The state of the solution changes successively as it passes between the liquid and solid phases, following this trajectory. The solution has a metastable state – the phase  $C_{ML}$ , after the liquid steady state. Then the solution becomes unstable – the phase  $C_U$ . The solution falls in the area of metastable state  $C_{SM}$  after the unstable state. Then the solution state becomes solid stable. Such a sequence of states of the

solution can be described by the isothermal diffusion problem. Let us use the diffusion equation with constant coefficients in order to find a concentration distribution. The area of existence of each state of the solution will be described by a separate equation. The example of the boundary conditions can be written as follows.

1. Concentration is setting on the outer boundary of the liquid phase by analogy with the known task of the Burton prima and Slichter.
2. The conditions of dynamic equilibrium of the liquid and unstable phases.
3. The condition of equality of the mass flow component of the liquid and unstable phases.
4. The condition of dynamic decomposition of the unstable phase between the  $C_U$  and  $C_{SM}$  phases.
5. The condition of equality of the mass flow component of the unstable and metastable phases.
6. The condition of equality of the mass flow component of the  $C_{SM}$  and solid phases.
7. The conditions of dynamic equilibrium of the metastable and solid phases.

This is a rough approximation, because the diffusion coefficients are continuous functions. They describe both direct diffusion and reverse diffusion.

### Coincides with experiment.

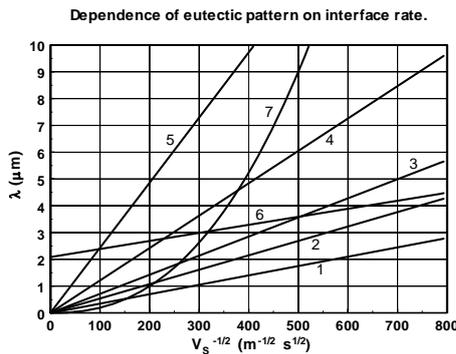
Let us look at three experimental results that give the solution to the problem of diffusion, taking into account spinodal decomposition of the solution. The dependence of period of the eutectic structure on the interface velocity

$$\lambda = \frac{2\pi(\chi' + \chi)}{\varepsilon\Lambda}(1 + \Lambda\Gamma) \quad (4)$$

$$\lambda_d = \frac{\pi(\chi' + \chi)}{\varepsilon\sqrt{h_d V_s}} + \frac{2\pi(\chi' + \chi)\Gamma}{\varepsilon} \quad (5)$$

$$\lambda_e = \frac{2\pi(\chi' + \chi)h_2}{\varepsilon V_s \ln\left(\frac{V_s}{h_1}\right)^2} + \frac{2\pi(\chi' + \chi)\Gamma}{\varepsilon} \quad (6)$$

(4) – (6) was found in the works [3,4]. The analytical dependences plotted in the figure 7.



**Fig. 7:** Dependences period of spatial perturbations on interface velocity for experimental dependences of [n].

Here it is plotted several dependences  $\lambda(V_s)$ . Values of constant correspond to the experimental dependence of the eutectic pattern period on the interface velocity reported in [6]. These dependences can be divided into three families. Most of them are straight lines coming from the origin. They correspond to plots 1 ( $Al_2O_3 - ZrO_2$ ), 2 ( $Pb - Sn$ ), 3 ( $ZrO_2 - MgO$ ), 4 ( $MgO - MgAl_2O_4$ ) and 5 ( $ZrO_2 - Y_2O_3$ ). For the plot 6 ( $CaO - NiO$  composition), the dependence is a straight line intersecting the axis of ordinates above the origin. For the plot 7 ( $Zn_5B_4O_{11} - ZnB_2O_4$  composition), the dependence is an increasing nonlinear curve. The

analytical dependences plotted in the figure 1 coincide with the experimental data [6] up an accuracy of construction.

However, these expressions were found at the two conditions, which contradict well-known theories of phase transitions. The first condition is the requirement that the segregation coefficient is close to one. This condition is necessary in order to get the expressions (4) - (6) from the dispersion equation [3,4]. The second condition is the requirement that the segregation coefficient is greater than one. This condition gives instability of the interface. Let us explain both of these conditions with the help of spinodal decomposition of the solution during formation of the periodic eutectic structure. For this purpose we shall consider the phase diagram that was obtained above. Let the solution passes through the area of spinodal decomposition during crystallization. The curve of dynamic equilibrium should be used instead of the liquidus line in this case. The curve of dynamic equilibrium is located between the liquidus line and the solidus line. Therefore, the segregation coefficient in this case is smaller than in the case without spinodal decomposition of the solution. It can be close to one in the limiting case. Hence the first condition is satisfied.

Now let us explain instability of the interface during spinodal decomposition of the solution. The cited above papers [3,4] explain instability of the interface by the dependence of the interface velocity on kinetic overcooling (7). Instability occurs when the segregation coefficient in the expression (8) becomes greater than one. Expression (7) can be written as (8), if approximate equality (9) is used.

$$\Delta T_k = T_{e0} + mC(0)(1-k) - T(0) \quad (7)$$

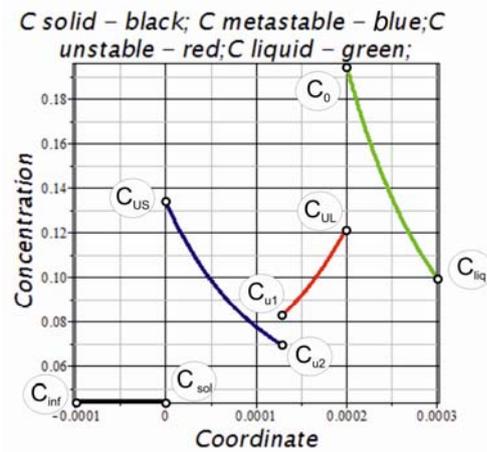
$$\Delta T_k = T_e - m\Delta k\Delta C(0) - T(0) \quad (8)$$

$$k \approx 1 + \Delta k \quad (9)$$

Let us pay attention to the expression (7). The change in  $k$  values larger than one to values less than one is equivalent to change in the sign of the coefficient  $m$ . If the phase diagram does not contain a curve of dynamic equilibrium, the sign of  $m$  is determined by the slope of the liquidus line and it is negative. If the phase diagram contains a curve of dynamic equilibrium, the sign of  $m$  is determined by the slope of the dynamic equilibrium line. In this case the sign of  $m$  can be positive. Therefore, the interface will be unstable if the segregation coefficient is less than one. Consequently, both the requirements of proximity of the segregation coefficient to one, and instability of the interfaces are explained by spinodal decomposition of a solution.

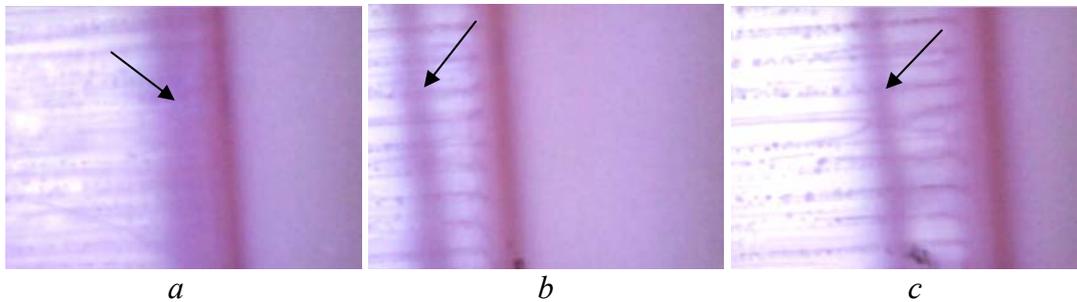
The obtained results explain the process of formation of the periodic eutectic structure. No additional assumptions are required in order to explain the sequence of formation of the periodic eutectic structure. A layer of the unstable solution occurs in front of the initially flat interface. The Interface becomes unstable during its movement. Perturbations of the concentration at the interface have a period which depends on the interface velocity. The solution in front of the interface decomposes by spinodal scenario. Thus, the solution will decompose according to the law, which is set by interface instability. Consequently, the period of decomposition of the unstable solution will depend on the interface velocity so as the period of instability of the interface depends on the velocity of its movement.

Now let's look at other experiments. The example of the boundary conditions was written above. Let consider the example of solution of such problem. The spatial dependencies of a concentration distribution in the phases of the solution are shown in graph of figure 8. This problem solution is illustrative. Therefore, the values of the parameters are not given. The graph shows that in front of the interface between the liquid and unstable phases extremum of concentration can exist. Such an extremum is observed in the experiments.



**Fig. 8:** Solution of a problem of diffusion taking into account a region of spinodal decomposition of solution.  $C_{inf}C_{sol}$  – solid phase,  $C_{US}C_{u2}$  – metastable solution,  $C_{u1}C_{UL}$  – unstable solution,  $C_0C_{liq}$  – liquid phase.

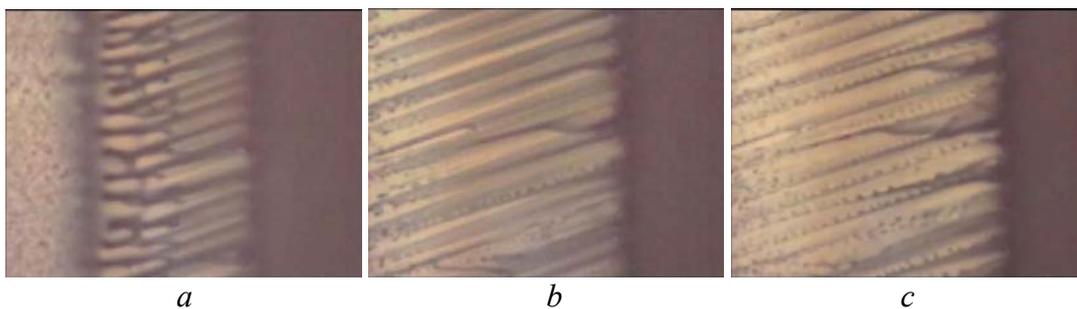
Let us look at the figures 9 with such experiment. The concentration extremum is noted arrow. Clearly visible high concentration of one component moves to the front of the liquid



**Fig. 9:** Extremum of component concentration between liquid and solid phase of the solution.

phase in this experiment. The considered here theory explains this phenomenon.

As shown above, the area of spinodal decomposition is located between the liquid steady state of the solution and the solid solution. The experiments show that in this zone there is formation of the eutectic structure. This zone is the mushy zone. A satisfactory theoretical description of mushy zones still does not exist. According to the modern theory formation of a dendritic structure occurs in a mushy zone. This fact is confirmed by our experiments. Figure



**Fig. 10:** Formation of dendrites in the interfacial area, a – formation of periodic structure at beginning of crystallization, b,c – formation of dendrites branches at interfaces of periodic structure.

10 demonstrates formation of dendritic structures. The flat interface between the solid and liquid phases was formed upon a stationary solution. Then the solution was set in motion, and the interface moved with a constant velocity. Let us turn our attention to the change of the moving interface (figures 10a-10c). The solution darkens in front of the interface at the beginning of its movement. The eutectic structure forms in this area (figure 10a). In approximately 1 minute from the start of movement of the flat interface branches of dendrites

are formed on these strips (figure 10b). That is, the boundary between the phases loses its stability. The periodic inhomogeneities of concentration arise on this boundary. The amplitude of these inhomogeneities is growing, and they form the branches of the dendrite (figure 10c). These experiments show that spinodal decomposition can play an important role in formation of a mushy zone. It can be assumed that many cases of segregation of components are associated with spinodal decomposition. Consequently, spinodal decomposition of the solution under phase transition explains occurrence of the mushy zone.

## Conclusions

A solution of a eutectic type can decompose by spinodal scenario during crystallization.

The states of dynamic equilibrium exists in solutions of the eutectic type. These states are described by the boundary of the unstable state of the solution – a spinodal. The line of dynamic equilibrium supplements the equilibrium phase diagram.

The periodic structure of eutectic composites is a result of interaction between instability of the interface, instability of the solution and kinetics of joining of particles to the growing solid phase. The interface instability defines the period of spinodal decomposition of the unstable solution. Kinetics of joining of particles to the growing solid phase determines the dependence of the period of the eutectic structure on the speed of the moving interface.

Spinodal decomposition of the solution explains observed in the experiments extremum concentration in front of the interface.

Spinodal decomposition of the solution explains existence of a mushy zone and formation of dendrites in this zone.

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