

## Flows in two-dimensional non-autonomous phases in polycrystalline systems

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**Summary.** — The processes of transformation and mass transport in two-dimensional non-autonomous phases are considered. It is shown that an eddy structure appears in the creeping flow of liquid two-dimensional non-autonomous phase. This type of flow causes the chemical separation inside eddies in the non-autonomous phase. A comparison with the experimental results is made.

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### 1. - Introduction

Theoretical investigations of processes in condensed matter may be based on phenomenological models constructions or on the analysis on atomic level. The second one is now widely spread due to the development of experimental techniques and possibilities of computer simulation. It is a merit of the phenomenological approach that it allows one to use achievements of equilibrium and non-equilibrium phenomenological thermodynamics with powerful approaches of system macro descriptions. We shall deal with phenomenological models in this paper.

Two-dimensional non-autonomous phases play an important role in the process of polycrystalline-system evolution. We use the terminology of Defay and Prigogine [1,2], in accordance with which phases may be classified as autonomous and non-autonomous ones. The characteristic feature of an autonomous phase is that its volume is so great that it is not necessary to take into account the interaction between the molecules of the phase and the ones of the interface to determine thermodynamical characteristics of the phase. An absolutely different situation is in the case when the phase is a thin layer. Here the properties of the layer depend on composition and properties of neighbour layers. The number of molecules interacting with molecules of neighbour layers is not negligibly small with respect to the whole number of the layer molecules. Hence, thin layer is a non-autonomous phase. In principle, the definition of the non-autonomous phase may be extended to a case of objects of

another (one or three) dimension (because the characteristic feature is not the thickness, but the necessity to take into account the corresponding molecules interaction). The dimension is related to the number of basic directions for which the translation invariance property takes place. Examples of one-dimensional non-autonomous phases are grain edges and triple grain boundaries. Boundaries of autonomous phases including interfaces and grain boundaries may be considered as two-dimensional non-autonomous phases. Sublattices in crystal and electron gas in a metal are examples of three-dimensional non-autonomous phases.

The results of experiments and theoretical thermodynamic investigations of two-dimensional non-autonomous phases lead to some conclusions about their properties. Namely, their thickness ( $h_e$ ) is a function of the structure and thermodynamic properties of the autonomous phases which have common boundaries with the non-autonomous one, chemical consistence of the non-autonomous phase and temperature. Various types of temperature dependence of  $h_e$  ( $h_e(T)$ ) have been described in [3-7]. The generalization of these types of dependences is the following relation:

$$(1) \quad h_e(T) = \phi(\alpha(T_m - T - (T_{m2n} - T)H(T_{m2n} - T)\beta + \delta)).$$

Here  $T_{m2n}$ ,  $T_m$  are the melting points for the non-autonomous phase and for the autonomous phase of the same chemical consistence, respectively (for the case of two insoluble (one in another) autonomous phases it is the eutectic temperature),  $H(\ )$  is the Heaviside step function,  $\phi(x)$  is some function satisfying the condition:  $\phi(x) \xrightarrow{x \rightarrow +0} +\infty$  (usually,  $\phi(\ ) = -\ln(\ )$  or  $(\ )^{-1/n}$ ), the parameters  $\alpha$ ,  $\beta$ ,  $\delta$  depend on

$T$ , but the dependence is weak and constant parameters are a rather good first approximation. Expression (1) allows one to show that  $h_e$  increases when  $T \rightarrow T_m$  (if  $\delta = 0$ , then  $h_e \xrightarrow{T \rightarrow T_m} \infty$ ). That is, melting of a polycrystalline system may be considered as a process of autonomization of the liquid two-dimensional non-autonomous phase. The autonomization is a process which results in such an increase of the thickness of the liquid non-autonomous phase (in accordance with the temperature increase) that its volume reaches a value so great that the phase becomes an autonomous one in accordance with the definition. In this situation the size of grains in the polycrystalline system decreases, and after reaching the corresponding size values the grains should be considered as a non-autonomous phase. Since  $\delta \neq 0$ ,  $h_e(T_m)$  is significant but finite. It means that there are small crystalline particles in a liquid phase. This fact is in accordance with experimental data (see, e.g., [8]).

As mentioned above, the melting point for the two-dimensional non-autonomous phase differs from that for the corresponding autonomous one [9]:

$$(2) \quad T_{m2n} = (1 - \alpha_H)(1 - \alpha_S)^{-1} T_m = \gamma T_m.$$

Here  $\alpha_H$ ,  $\alpha_S$  depend on the enthalpic and entropic properties of the phases, respectively. The magnitudes of  $\gamma$  differ slightly for the substances of one type, for example,  $\gamma = 0.65 \pm 0.1$  for inorganic oxides. The value  $T_{m2n}$  coincides with the point of elastic-plastic transition for ceramic materials (for example, oxide ceramics exhibit such a behaviour under high temperature [10-12]) and with the activation temperature of processes of sintering and synthesis [7, 9, 13]. These phenomena are related to the uneven increase of the speed of diffusion in two-dimensional non-

autonomous phases for  $T > T_{m2n}$ . But there exist processes that cannot be described satisfactorily in the framework of the diffusion model of mass transfer. That is why the construction of new dynamical models of polycrystalline-system evolution seems to be useful.

## 2. - The model

Let the geometric configuration of the system be such as shown in fig. 1. The evolution of the polycrystalline system under the action of surface tension forces or external mechanical ones for a temperature greater than  $T_{m2n}$  may be treated as a combination of the following transformation and transport processes. For this temperature regime the two-dimensional non-autonomous phase having thickness  $h$ , becomes liquid. Under the action of contracting force  $F$ , the grains  $A$  and  $B$  come together squeezing the liquid-like substance from the region  $\Gamma_1$ . After this rapprochement the distances between the grains become less than the equilibrium ones, and the transformation of the crystal grain into the two-dimensional non-autonomous phase begins. The speed of transformation may be described by the formula [7]

$$(3) \quad v_{tr} = v_0 \left| (h_e - h) / h_e \right|^b,$$

where  $v_0$  and  $b$  are some parameters,  $h$  is the distance between grains 2 and 1 (or 3), see fig. 1 in dynamical situation. That is, the speed of the transformation is determined by the kinetic factors and by the difference between  $h$  and the equilibrium thickness  $h_e$ . Usually, the grains have different speeds of transformation but in this paper we shall assume that they are equal. The liquid-like substance flows out from the region  $\Gamma_1$  and spreads along the region  $\Gamma_2$  (fig. 1). During this process the width of the liquid-like layer  $\Gamma_2$  becomes greater than the equilibrium one. Hence, the transformation of the corresponding part of the liquid two-dimensional non-autonomous phase to the crystal phase begins. In the general case the transformation may be realized through the growth of the existing grains or through the formation of new grains. The latter way is preferable when  $h \gg h_e$  due to kinetic or thermodynamic reasons. In this paper we assume that the main way of the transformation

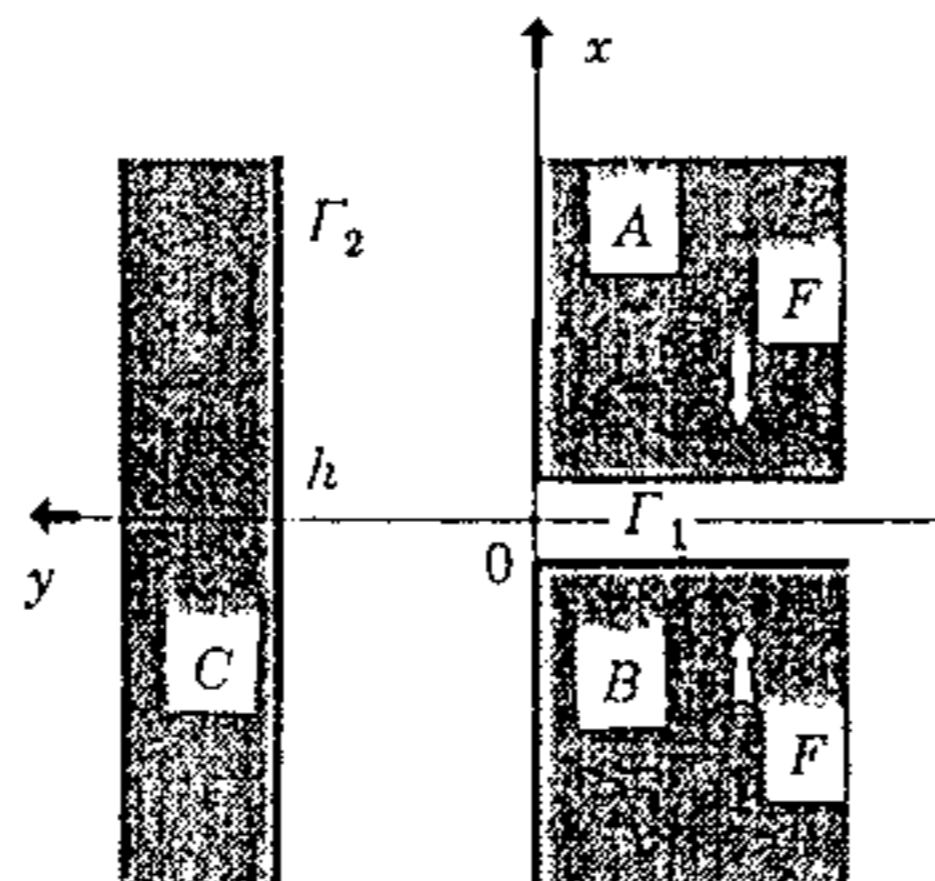


Fig. 1. - Geometrical configuration of the system:  $h$ : thickness of the two-dimensional non-autonomous phase,  $F$ : contracting force.

two-dimensional non-autonomous phase  $\rightarrow$  autonomous phase is the crystallization of the liquid non-autonomous phase on the grains surfaces. The speed of the transformation may be described by the same formula (3) with other values of the parameters  $v_0, b$ .

The flow in the two-dimensional non-autonomous phase has some peculiarities. In contrast to the isotropic liquids, the viscosity of the two-dimensional non-autonomous phase has anisotropic character due to the different mobility of components with respect to the orthogonal directions[14]. But for temperatures near the melting point (i.e. for a sufficiently big value of the thickness of the two-dimensional non-autonomous phase) one can believe that the liquid is an isotropic one. We deal with stationary flows with extremely small Reynolds number

$$(4) \quad \text{Re} = \rho v h / \mu \ll 1,$$

where  $v$  and  $\mu$  are the velocity and viscosity, respectively. As a result, the Navier-Stokes equations reduce to the biharmonic one,

$$(5) \quad \Delta^2 \varphi = 0,$$

for the stream function  $\varphi$  related with the velocity in accordance with the expressions

$$(6) \quad v_1 = \frac{\partial \varphi}{\partial y}, \quad v_2 = -\frac{\partial \varphi}{\partial x}.$$

It is a sufficiently complicated problem to describe the creeping flow in the domain in question (fig. 1) and it is useful to simplify the problem. We shall consider the flow in the domain  $\Gamma_2$  only. That is why we study the model in which the thin channel  $\Gamma_1$  is replaced by the point source at the boundary  $\partial\Gamma$ . We consider the creeping flow in a channel with straight boundaries ( $y = 0, y = h$ ) (it is acceptable because the inertial terms in the general equation are omitted) with a periodic set of point sources (singularities). The condition

$$(7) \quad \varphi|_{\partial\Gamma} = \frac{\partial \varphi}{\partial n} \Big|_{\partial\Gamma} = 0$$

is valid on the channel boundaries except for points where the sources are situated.

*Remark.* As for the boundary conditions, one can note that on the part of the surface between the sources the crystallization process takes place, hence it is more correct to put the condition  $(\partial\varphi/\partial x)|_{\partial\Gamma} = \text{const} \neq 0$ , where the  $x$ -axis is parallel to the boundary, instead of  $\varphi|_{\partial\Gamma} = 0$ . But we use the homogeneous condition because the intensity of the corresponding flow is sufficiently small in comparison with the source intensity.

To solve the model problem we use the operator version of the Stokeslet approach[15,16] based on the theory of self-adjoint extensions of symmetric operators (this approach gives us a correct mathematical model of singular perturbations and is analogous to the zero-range potential method in quantum mechanics[17,18] and zero-width slits model in diffraction theory[19]). Then the

solution of the problem is given by the following formula:

$$(8) \quad \varphi = 2\pi \operatorname{Re} \sum_{n=1}^{\infty} \left( A_n (2h^{-1}y - 1) \exp \left[ -\frac{1}{2} \lambda_n |x| \right] + B_n (2h^{-1}y - 1) \exp \left[ -\frac{1}{2} \mu_n |x| \right] \right).$$

Here

$$(9) \quad A_n(y) = \frac{y \sin(2^{-1} \lambda_n y) \cos(2^{-1} \lambda_n) - \sin(2^{-1} \lambda_n) \cos(2^{-1} \lambda_n y)}{\cos(\lambda_n) + 1},$$

$$(10) \quad B_n(y) = \frac{y \cos(2^{-1} \mu_n y) \sin(2^{-1} \mu_n) - \cos(2^{-1} \mu_n) \sin(2^{-1} \mu_n y)}{\cos(\mu_n) - 1},$$

$\lambda_n$  and  $\mu_n$  are the roots of the equations

$$(11) \quad \sin(\lambda_n) + \lambda_n = 0, \quad \sin \mu_n - \mu_n = 0.$$

One can now obtain a picture of streamlines for the flow as a simple consequence of this consideration (see fig. 2a). As plastical deformations in a polycrystalline body are accompanied by mass transfer in the two-dimensional non-autonomous phases, a shift flow exists in the domain  $\Gamma_2$ . Consequently, the solution takes the form  $\varphi + \varphi_0$ , where we choose the function  $\varphi_0$  in the following form:

$$(12) \quad \varphi_0 = w(2^{-1} h^{-2} y^2 - 3^{-1} h^{-3} y^3), \quad 0 \leq y \leq h,$$

$\varphi_0$  satisfies the boundary conditions  $\varphi_0 = \partial \varphi_0 / \partial n = 0, y = 0, \varphi_0 = \text{const}, \partial \varphi_0 / \partial n = 0, y = h$ .

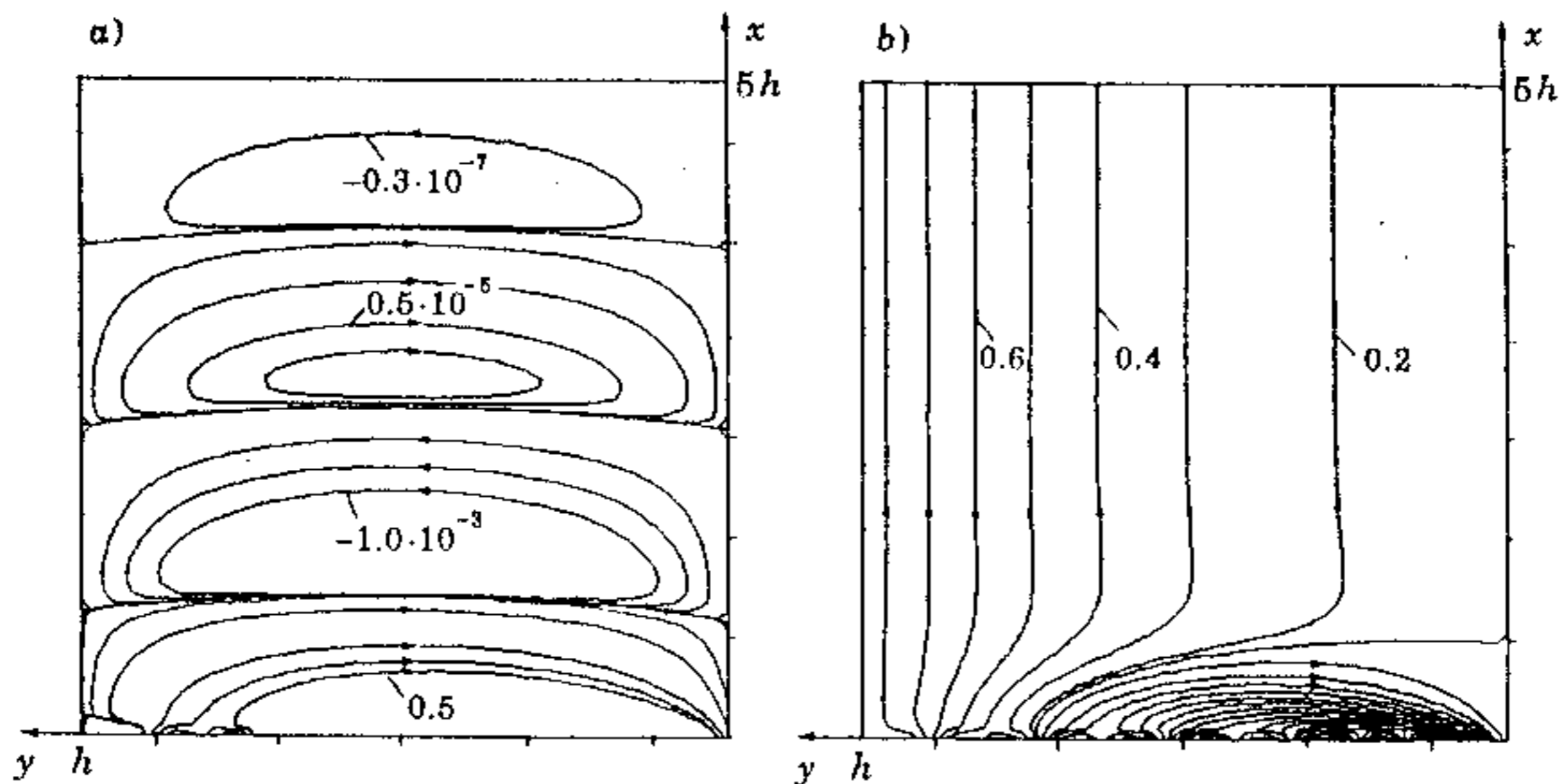


Fig. 2. - The picture of the flow (one half of the streamline picture is shown (for  $x > 0$ ), the whole picture is symmetric with respect to the  $y$ -axis): a)  $\varphi_0 = 0$ , b)  $\varphi_0 \neq 0$ .

The streamlines of the flow are computed using a simple superposition of the unperturbed flow  $\varphi_0$  and the stream function  $\varphi$  in (8). In the case of the absence of  $\varphi_0$  the far-field flow in the channel consists of an infinite set of eddies which are separated by zero streamlines. Each eddy of the far-field flow has a length (in the  $x$ -direction) of about  $2\pi(\text{Im}\lambda_1)^{-1}h \cong 1.4h$ ; moreover, owing to the presence of the exponential factor in expression (8), the flow at corresponding points in adjacent eddies (*i.e.* at points with the same  $y$ -coordinate but differing by approximately  $2\pi(\text{Im}\lambda_1)^{-1}$  in the  $x$ -coordinate) differs in speed by a factor approximately of  $\exp[\pi \text{Re}\lambda_1(\text{Im}\lambda_1)^{-1}] \cong 360$  and is in opposite directions. Hence, in the case of the presence of  $\varphi_0$  the far-field flow in the channel is similar to the unperturbed flow (without point source). One can see that in this case for the realistic values of the parameter  $w$  of the flow  $\varphi_0$  there exists only one eddy depicted in fig. 2b).

### 3. - Results and discussion

If the thickness of the two-dimensional non-autonomous phase exceeds its equilibrium value, then the transformation liquid two-dimensional non-autonomous phase  $\rightarrow$  solid autonomous phase begins (in accordance with (3)). This process is influenced by the cellular character of the flow. The presence of an eddy in the substance which transforms into the solid state leads to the appearance of a one-dimensional defect in the crystal, *i.e.* a dislocation. The experimental confirmation of this effect is given by the results concerning the distribution of the dislocation density in sintering bodies (see [20]), where some maxima of spatial distribution of the dislocation density are discovered). The intensity of the first maximum is approximately 100 times greater than the second one (and the analogous correlation is between the second and the third maxima). This picture is similar to the distribution of eddies and the correlation between its intensities (fig. 2a)).

The existence of eddies in the flow leads to the chemical stratification of the non-autonomous phase consisting of atoms (ions) of different types. The compounds with the greatest mass and strength of chemical bond will be collected in the centre of an eddy. A dynamical chemical structure forms, which may be sufficiently stable even after the transition to the static regime (after «freezing» of the polycrystalline system). The result of this process is that the thickness of the non-autonomous phase in the region of triple grain and phase boundaries in polycomponent systems is greater than the one for the corresponding pure one-component system (see the experimental data in [21]). This result is in some sense additional to the one in [22] where the influence of chemical processes on the hydrodynamic character of the flow in the interface considered as a two-dimensional Newtonian fluid is studied. Note that the described chemical process in the eddies has a different mechanism than chemical reactions in shear flows (see [23]).

The appearance of eddies in the region of triple grain and phase boundaries makes a slip of grains easier. Hence, it may be one of the causes of the effect of superplasticity in polycrystalline systems under high temperatures [10].

The obtained results show that the formation of a dynamical eddies structure in the flow of the two-dimensional non-autonomous phases influences the properties of the polycrystals.

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