Crystallization and melting are phase transitions of first type, which can proceed with a finite rate only at finite declination from equilibrium [1]. The parameters determining the direction and the rate of phase transition are the declination of pressure, temperature and concentration from equilibrium value. The rate of crystal→liquid phase transition at equilibrium is equal zero. It is impossible to reach a complete equilibrium under any experimental conditions, as it takes an endless time. The deviation from equilibrium in such transition leads to origin gradients of temperature and concentrations in a liquid phase close to the liquid-crystal interface. These gradients result in mass and heat transfer towards and away from the interface [2]. The heat transfer in a silicate melts in the absence of forced convection takes place mainly due to heat conductivity, and mass transfer is carried out by diffusion of components (ions) in the melt [3]. Local (“mosaic”) equilibrium is attained between the liquid and surfaces of crystals only in certain limited layer at the phase boundary. The thermodynamics of disequilibria systems, physicochemical hydrodynamics, and the theory of dimensions give an opportunity for describing that boundary layer [2, 3, 4].

The crystallization and the melting in experiments proceed under steady-state conditions, when the temperature, pressure, supercooling degree, or crystal growth rate remain unchanging over a long period of time. The steady state plays the same role in disequilibria thermodynamics as that played by thermodynamics of equilibrium processes [2]. Thus, understanding the processes that control the crystallization requires clarifying as to how a deviation from equilibrium under steady-state conditions affects the rate and mechanism of crystallization.

The growth rates of crystals from melt depend on the supercooling degree (∆T), which is equal to the difference between the equilibrium liquidus temperature for a given liquid T₀ and its actual temperature T, i.e. ∆T=T₀ -T≥0 (Fig.1). Rate equations can also be expressed through the oversaturation of melt with respect to one of its components – ∆C郦≥0 (Fig. 1). Oversaturation is defined as the difference between the concentration of component B in the melt, C郦 at a temperature T and the concentration of this component C郦₀ on the liquidus line at a temperature T₀, i.e. ∆C郦 = C郦₀ - C郦. At thermodynamic equilibrium in still liquid, ∆T=0 and ∆C郦=0, and, hence, the growth rate of crystal is equal to zero. Minute liquid motions (flows) and changes in its temperature and concentrations of components from point to point signify deviations from thermodynamic equilibrium [2, 4].

In hydrodynamics and the theory of mass and heat transfer, the dimensionless proportions of sizes of a body and characteristic physical parameters of a given phenomenon are termed similarity criteria or numbers [4, 5]. Certain external (critical) values of similarity numbers allow determination of the character and mechanism of mass and heat transfer. By the means of these criteria it is shown that multicompontent melt which consists of i components (ions) can be subdivided into two regions: (a) a volume of constant concentration of ion i in the melt C郦₀i away the interface crystal-liquid, where the convective flux of ion i is dominant, and (b) a region (a thin zone) where diffusion flux dominates and the concentration of ion i varies from C郦₀i to C郦 at the interface. The melt region dominated by the diffusion transport of ion i is referred to as the diffusion or concentration boundary layer δ郦. Since diffusion coefficients of different ions vary over broad intervals, the width of the diffusion boundary layers of distinct ions in a melt may differ by one to two orders of magnitude. The existence of diffusion boundary layers around crystals growing from the silicate melts was well known and was confirmed experimentally and found in natural samples.

In a multicomponent melt, the composition of crystallized solid phase does not coincide with the composition of the liquid, because the equilibrium partition coefficients of its components (ions) are never equal to one: K郦=С郦0/С郦≠1. If K郦<1 (Fig. 2), the diffusion boundary layer is enriched in ions y and C郦>郦₀; if K郦>1, the boundary layer becomes depleted in ions z and C郦<郦₀ (Fig. 2). It was shown [3, 4] that the width of the diffusion boundary layer δ郦 for any ion i in a liquid is:

\[ δ郦 = D_i |C郦₀ - C郦|/j_i \]  

(1)

where D_i is the diffusion coefficient for ion i, and j_i is the density of flux for ion i to or away from the crystal surface. The origin of the diffusion boundary layer changes the equilibrium value K郦 up to its
effective value $K_i^{\text{eff}}, K_y^{\text{eff}} > K_y$ and $K_z^{\text{eff}} < K_z$. The values $K_i^{\text{eff}}$ and $K_y^{\text{eff}}$ are connected with the next equation: [6]:

$$K_i^{\text{eff}} = K_i [1 - (1 - K_i) \exp (v \delta_z / D_i)]$$

where $v$ is the linear rate of crystal growth. It follows from equations (1) and (2), that if $|C_{i0} - C_i|$ and $v$ are reduced then the value $K_i^{\text{eff}}$ is as much as possible close to $K_i$. It provides an opportunity at steady $v$ [7] to calculate the duration of the experiment, which secures an optimum value $K_i^{\text{eff}}$.

Fig.1. Melt composition on the liquidus line at equilibrium ($C_{i0}$) and supercooling ($C_B$) in a system system with solid solutions. $\Delta T$ is supercooling, $\Delta C_B$ is oversaturation.

Fig.2. Variations in the concentrations of components $z$ and $y$ near the interface. $K_z$ and $K_y$ are the partition coefficients of components $z$ and $y$: $K = C^o / C^l$. $C_{i0}$ and $C_{i0}^o$ are the concentrations of $z$ and $y$ in liquid far from interface; $C_i^l$ and $C_y^l$ are the concentrations of $z$ and $y$ in liquid at the interface. $C_i^c$ and $C_y^c$ are the concentrations of $z$ and $y$ in the crystal; $\delta_z$ and $\delta_y$ are the diffusion boundary layers.

References