

## Dorovskii V.N. Mass transfer in the magma containing surface active compounds

The United Institute of Geology, Geophysics and Mineralogy, Siberian Branch of RAS

*key words: [magma, surface active compounds, non-equilibrium thermodynamics]*

**Introduction.** In the petrological studies, an extraction and a transfer of major and minor components by the volatile phase in the magmatic systems is considered in the approximation of the diffusion exchange between separate gas bubbles and a melt. The magmatic melt is considered as a solution with concentration gradient, whose changing is governed by diffusion laws. In the same time, magmatic melts contain chlorine, fluorine, oxygen, sulfur, etc., whose concentration is able to significantly influence on a value of surface tension in the melt. The above constituents of the magmatic melts are known as the surface active compounds (SAC). In presence of the SAC, the process of extraction in the melts can be significantly different. There is an experimental evidence from the metallurgy for difficulties in explanation of extraction by diffusion exchange between the melt and the volatiles only: the time of the formation of metallurgical slag in the process of bubbling of heterogeneous melts by argon bubbles is by orders of magnitude lower than the characteristic diffusion time during the transfer of minor components [1]. It is shown [2] that the magmatic melt containing the SAC and particles, which are able to sorb the SAC, is always thermodynamically locally non-equilibrium system. The existing gradient of the surface tension, related to the unequal distribution of the particles, causes a displacement of the particles with respect to the melt. A complete system of equations describing the process of extraction is deduced. The qualitative analysis of the equation allowed to construct the following pattern of the developing of the extraction process. The spatial variation of the SAC concentration results in displacement of the particles in the melt. This process, in turn, causes the changes in the SAC concentration. The larger variations the larger velocities of displacement. The instability in the initial distribution of the particle concentrations appear. If some surface extracting the SAC is placed on the area boundary, we can obtain a mechanism of concentration both the SAC and particles. In the magmatic melts, such surfaces could be bubbles of some other gas. The characteristic times of such process, since the described instability, can be significantly lower than the diffusion times. If the above suggestion are justified, the following pattern of magma differentiation in cooling chambers on the stage of releasing of the gaseous phase and simultaneous, for instance, subliquidus liquid immiscibility can be seen. The tiny particles of new phase sorb the SAC on their surface. In turn, bubbles of the gaseous phase sorb the SAC as well. Thus, the particles are in inhomogeneous field of the SAC concentration. Because of the local thermodynamic non-equilibrium state, the particles begin to move on the surface of the bubbles, changing the spatial gradients of the SAC. The process continues until all the particles and the SAC would be removed from the magmatic melt. Thus, an assumption about the presence in the system of the relative velocity of magma motion and dependence of the energy

of the system on the surface energy of the particles-melt boundary leads to the principally new mechanism of extraction. The present paper is directed to solve the principal question on the characteristic times of the extraction of the particles on gas bubble. The study is fulfilled under support of the Russian Foundation for Basic Research (project no. 00-05-65454).

**Non-equilibrium thermodynamics of extraction.** It is shown [2] that the dependence of Gibbs potential of an element of the magmatic melt on the thermodynamic degrees of freedom, containing both the SAC and the particles is

$$d\Phi = -\left(S + J\zeta \frac{\partial\sigma}{\partial T}\right)dT + \mu d\rho + \rho\mu_1 dc - J\zeta \frac{\partial\sigma}{\partial c_*} dc_* - j_0 dw$$

where  $S$  – entropy of the unit melt volume,  $\rho$  – melt density;  $\mu$  – chemical potential,  $c$  – SAC concentration,  $T$  – temperature,  $J$  – density of the particles,  $w$  – velocity of displacement of the particles with respect to the melt,  $j_0$  – relative impulse,  $c_0$  – SAC concentration at the surface of the particle,  $\zeta$  – surface area of the particle. The surface tension  $\sigma$  depends on the SAC concentration in accordance with equation

$$\sigma = \sigma_0 - \Gamma_\infty RT \ln\left(1 + \frac{k}{\Gamma_\infty} c_*\right)$$

This formula includes constants, which characterize the compound.  $R$  – gas constant. The dependence of the surface tension on the SAC concentration and the above differential Gibbs equation for relatively low velocities of displacement of the particles allow to calculate a correction to the chemical potential

$$\mu_1 = -\frac{\zeta k}{2m} RT \frac{\Lambda}{\rho} \frac{c_*^2}{c^2} + RT \ln c + \mu_0(P, T), \quad \sqrt{\frac{w_0}{w}} = \Lambda.$$

The latter formula allows deduction of the simplest variant of equations, which describe the process of extraction of particles from the magmatic melt [2]

$$w = \frac{\zeta k}{m} \tau RT \nabla c,$$

$$\frac{\partial J}{\partial t} + \text{div}(Jw) = 0,$$

$$\frac{\partial c}{\partial t} = D \text{div}\left(-\frac{\zeta k}{2m} c \nabla \sqrt{\frac{w_0}{w}} + \nabla c\right).$$

Equations include the characteristic time  $\tau = m/(6\pi a \eta)$ , where  $a$  – the characteristic size of the particles,  $\eta$  – melt viscosity,  $m$  – its mass,  $D$  – diffusivity of the SAC in the melt.

**Characteristic times of extraction.** A motion of the particles onto the bubble of radius  $R_0$  in the spherical system of coordinates at the bubble boundary  $r = R_0 + y$  is

$$\frac{\partial c}{\partial t} = D \frac{\partial}{\partial y} \left( -\frac{\zeta k}{2m} c \frac{\partial}{\partial y} \sqrt{\frac{w_0}{w}} + \frac{\partial c}{\partial y} \right),$$

$$\frac{\partial J}{\partial t} + \frac{\partial}{\partial y} (Jw_r) = 0,$$

$$w_r = \frac{\zeta k}{m} \tau RT \frac{\partial c}{\partial y},$$

$$c(y=0, t) = c_0, \quad J(y=0, t) = 0, \quad J(y=\infty, t) = J_0.$$

It is evident, the system has a automodel solution

$$w = \sqrt[3]{\left(\frac{\zeta k}{m} \tau RT\right)^2} \sqrt[3]{\left(\frac{\zeta k}{m}\right)^2} \sqrt[3]{\frac{c_0^2 w_0}{36.0}} \frac{1}{\sqrt[3]{y^2}},$$

$$J = J_0 \frac{\sqrt[3]{y^2}}{\sqrt[5]{(5\varepsilon_0 t / 3 + \sqrt[3]{y^5})^2}}$$

The most interesting value is a density of flux of particles onto the bubble surface

$$W = Jw = (-W_0, 0, 0), \quad W_0 = \sqrt[5]{\left(\frac{\zeta k}{m} \tau RT\right)^2 \left(\frac{\zeta k}{m}\right)^2 \frac{c_0^2 D}{150\pi a}}$$

The total flux of the particles per surface unit is an increasing function of time

$$\int_0^t W dt = \sqrt[5]{\left(\frac{\zeta k}{m} \tau RT\right)^2 \left(\frac{\zeta k}{m}\right)^2 \frac{c_0^2 D}{150\pi a}} \cdot \frac{5J_0}{3} \sqrt[5]{t^3}$$

Thus, the principally new result is obtained: the density of the flux of the particles is proportional to  $\sqrt[5]{D}$ . The latter formula allows to do some basic estimations. Consider the cubic meter of the magmatic melt, which contains 10 % (volume content) of gas bubbles with the characteristic size  $R_0 = 0.01$  m. Evidently, the cubic meter of the melt contains

$$N = \frac{0.1}{4\pi R_0^3 / 3} \sim 2.4 \cdot 10^4 \text{ of bubbles. The total surface area}$$

of the bubbles is  $\Sigma = 4\pi R_0^2 N = 30 \text{ m}^2$ . Take the following values for parameters, characteristic for the melt, the particles, and the SAC

$$a = 2 \cdot 10^{-5} \text{ m}, \quad \eta = 5 \cdot 10^{-3} \text{ H} \cdot \text{c} / \text{m}^2,$$

$$\rho = 4 \cdot 10^3 \text{ kg} / \text{m}^3, \quad R = 8.31 \text{ J} / (\text{K} \cdot \text{mol}),$$

$$1.2 \cdot 10^{-8} \text{ m}^2 / \text{s}, \quad T = 1873 \text{ K}, \quad k = 0.26 \text{ mol} / \text{m}^2.$$

Thus, we have

$$\frac{\zeta k}{m} \tau RT \sim 10.8 \text{ m}^2 / \text{s}, \quad \frac{\zeta k}{m} \sim 0.16,$$

$$D / a \sim 6 \cdot 10^{-4} \text{ m/s.}$$

Consequently,  $N$  bubbles accumulate the total amount of particles  $I = 4J_0 c_0^{2/5} t^{3/5}$  for the period  $t$ . Define  $t^* = 0.1/c_0^{2/3}$  as a characteristic time, when the bubbles accumulate on their surface all particles, which are present in the melt volume in the initial time  $t = 0$ . If the starting concentration is  $c_0 = 10^{-3}$ , then  $t^* = 10$  s. An abrupt decrease of the characteristic time of extraction is observed.

Thus, the total time to remove all the particles from the melt is proportional to  $D^{-1/3}$ , whereas the characteristic time of extraction in accordance with the diffusion rule is proportional to  $D^{-1}$ . Since the diffusivities are small, the fractional negative power corresponds to the abrupt decrease of the characteristic time of extraction. It should be noted, that the metallurgical de-oxidation of steel supports the above times of extraction [1]. The above estimations, as a result of the analysis of the relaxation process of the thermodynamically non-equilibrium melt, allow to state, that the above mechanism of extraction allows another view on the processes of the magma differentiation contrasting to the classical petrology.

#### References:

1. V.A. Grigoryan, L.N. Belyanchikov, A. Ya. Stomakhin (1987) Theoretical basis of the electrical steel melting processes. Moscow, Metallurgy.
2. V.N. Dorovskii (2001) Dynamics of the exchange between the phases in magma containing the surface active compounds. Geology and Geophysics, N 8.