The capture of nanosized particles by the directional crystallization of sulfur

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ABSTRACT

High-purity sulfur used in nanotechnology, assumes a total impurity content at the level of $1 \cdot 10^{-3}$–$1 \cdot 10^{-4}$ wt% and also limiting impurities at the level of $1 \cdot 10^{-7}$–$1 \cdot 10^{-8}$ wt%, which include both molecular and heterogenous nanoparticles. The mathematical model for the efficiency of the capture of nanosized particles by the directional crystallization has been developed. The model was verified on the experimental data on the capture of nanosized particles (silver and germanium (30–60 nm)) by the crystallization front of benzene and then it has been used for calculation of sulfur purification process. It is found that the rate of the crystal growth increases, the energy of the particle that is due to the motion of the melt also increases and, consequently, the rate of transition of particles from the melt into the crystal increases too. It is found that as the rate of the crystal growth increases, the distribution coefficient decreases but at the rate greater than 1 cm/h it begins to increase. With an increase in the rate of crystallization, the rate of the transition of particles from the melt to the crystal increases exponentially with a linear increase of the crystallization rate. The calculations showed that the value of the potential of the disjoining pressure is determined by the values of interaction constant and particle size. Since the value of the particle distribution coefficient between the crystal and the melt in the process of the crystal growth differs from unity, crystallization methods can be sufficiently effective for sulfur high purification.

1. Introduction

High-purity sulfur is widely used as a component of chalcogenide glasses, which recently attracted an increased interest of researchers as a promising material for optical applications in the IR range, such as fiber lasers and amplifiers, nonlinear fiber-optical switching devices, and others [1–5] Modern requirements for high-purity sulfur used in nanotechnology suggest that the total content of impurities in sulfur should be at the level of $1 \cdot 10^{-3}$–$1 \cdot 10^{-4}$ wt% and also limiting impurities should be at the level of $1 \cdot 10^{-7}$–$1 \cdot 10^{-8}$ wt%. The most difficult to remove impurities in sulfur are carbon, arsenic and selenium [4,6].

When obtaining sulfur with a low total content of impurities, there are two main groups of problems. One of them, common to all high purity substances, is due to a low concentration of impurities. The purification process is limited by impurities from the material of the equipment in which the purification is carried out and also by impurities in the form of suspended particles of submicron size. For purification of substances from nanosize particles distillation [7–9] crystallization [5,6,10] and membrane methods [11,12] are used. Another group of problems arises from special properties of sulfur – its ability to

intramolecular allotropy, that is the formation of molecules with different numbers of atoms in them or with different structures [10]. To produce high-purity sulfur chemical, distillation and crystallization methods, as well as combinations thereof are used. The greatest development of the crystallization method for high purification of sulfur is recrystallization of its melt. For example, in the concentration range $(1–5) \cdot 10^{-4}$ wt%, the distribution coefficient for aluminium, magnesium, copper, iron, lead and nickel is 0.50–0.66 [10]. The data presented indicate that the crystallization methods for high purification sulfur will be effective only in the multistage mode. The greatest purification effect in obtaining high-purity sulfur can be achieved in a countercurrent column [6,10]. In addition, sulfur contains nanosized particles [2,10]. The behaviour of suspended nanosized particles as impurities in the process of purification by crystallization methods has not been practically investigated. The search for a solution to this problem of obtaining high-purity chalcogenide glasses is important since nanosized particles affect linear optical and physicochemical properties of glasses.

Therefore, this article is devoted to the development of a mathematical model for the efficient capture of nanosized particles by the crystallization front, which was verified on the experimental data on

the capture of nanosized particles by the crystallization front of benzene and has been used for calculation of sulfur purification process.

2. Theory

In the process of the crystal growth, when the particle is located ahead of the crystallization front in the melt, capture or repulsion of the particle is possible by the crystallization front. This is due to the fact that growing crystals are able to exert a mechanical effect on extraneous particle objects encountered in the way of their growth that is to develop a so-called disjoining pressure [13].

The nature of the interaction of particles with the crystal surface can be described by the disjoining pressure, which is determined both by the nature of the particles and the melt. The disjoining pressure can be any – both positive and negative. Disjoining pressure is positive when the pressure in the film is less than in the bulk liquid. In this case the liquid flow into the gap under the particle from a massive volume, and the particle is repelled by the surface. When the disjoining pressure is negative the interlayer under the influence of surface forces decreases and the particle is captured by the surface at any rate of crystallization. Therefore, purification from micron particles can be carried out only when the disjoining pressure between the particle and the crystal surface is positive. However, unlike micron particles, nanosized particles are in Brownian motion and due to the energy of thermal motion some nanosized particles can overcome the potential barrier of repulsive forces on the crystal surface and can be captured by it [14,15].

To characterize the capture of submicron and nanosized particles by the surface of the growing crystal, we introduce the value of the rate of transition of particles from the melt into a crystal V_n, equal to the ratio of the flow of particles to the crystal surface to their concentration in the melt [16–18]. To determine such values as these, we have considered the behaviour of particles in a boundary layer of thickness δ_F, in which the interaction forces between the particle and the crystal ($\delta_F = 10^{-5}$–10^{-6} cm) are significant [18]. In the general case the disjoining pressure consists of three components: dispersion, electrostatic and structural. For non-polar substances, the main contribution to the precipitation of nanosized particles on the crystal surface is provided by the dispersion forces.

For the stationary case for the boundary layer near the crystal surface the following equation is valid:

$$\frac{dy}{dt} = -\text{div} \quad J = 0,\tag{1}$$

where y is the particle concentration in the boundary layer of the melt, J is the flow of particles in the melt to the crystal surface. From Eq. (1) it follows that $J = \text{const}$.

For any fluid flow, whether it be laminar or turbulent, the flow rate tends to zero when approaching the interphase boundary between the liquid and solid phases, excluding the flow normal to the surface caused by the crystallization.

Thus, there is some region in the melt that adjoins the crystal surface, in which the main transport of impurities to the surface is due to diffusion. The thickness of this region is $\delta_t = 10^{-2}$–10^{-3} cm [18–20]. On the other side, the length at which the concentration of particles in the liquid phase changes in the case of the removal of the impurity only by diffusion is $\delta_D = 10^{-3}$–10^{-4} cm. Since $\delta_D \ll \delta_t$, the convective motion of the melt due to its mixing, can be neglected.

Taking into account only the diffusion transport of particles in the melt in front of the growing crystal of the surface, the total flow of particles normal to the crystal surface in the reference frame due to the surface of the crystallization front will be considered as having three components:

$J_D = -D(z)\frac{dy}{dz}$ – diffusion flow,

$J_F = -m(z)y(z)\frac{d\Phi}{dz}$ – flow due to molecular interaction forces,

$J_C = -Uy(z)$ – flow due to the motion of the melt near the solid surface.

Then the equation for the total flux of particles on the surface of the growing crystal is written in the form:

$$J = -D(z)\frac{dy}{dz} - m(z)\cdot y(z)\frac{d\Phi}{dz} - U\cdot y(z),\tag{2}$$

where z is the coordinate of the centre of the particle, measured along the normal to the surface, $y(z)$ is the concentration of particles (particles in cm^3); $\Phi(z)$ is the interaction potential of a particle with the solid surface due to van der Waals forces; $D(z) = m(z)kT$ is the diffusion coefficient of particles in the boundary layer; k is the Boltzmann constant; T is the absolute temperature; $m(z) = f_b(z)/6\pi\mu R_p$ is the mobility of particles in the boundary layer; μ is the viscosity of the melt; R_p is the radius of the particle; $f_b(z)$ is the Brenner correction factor, which takes into account the difference in mobility of the particle near the surface from its mobility in the volume [21]; $U = V\rho_s/\rho_l$ is the velocity of the melt about the crystal surface; V is the rate of the crystal growth; ρ_s and ρ_l are the densities of the solid and liquid phases, respectively.

When solving Eq. (2), it should be taken into account that the concentration of particles at the crystal surface as a result of their deposition on the crystal surface is zero. However, the calculation formula for the forces of the disjoining pressure and the Brenner correction factor is valid if the film between the particle and the crystallization front contains at least several molecular layers [18]. Therefore, it is assumed that a particle is captured by the crystal surface if the distance between them is less z_m. The transition of particles from the crystal surface to the melt is neglected, thereby determining the maximum separation effect.

Then the boundary condition is determined:

$$y(z_m) = 0\tag{3}$$

We introduce the dimensionless variable $l = (z - R_p)/(z_m - R_p)$, $h_m = z_m - R_p$.

Since $h = z - R_p \ll R_p$, the Brenner correction factor can be determined [21]:

$$f_b(h) = \frac{h}{R_p} \text{ or } f_b(l) = \frac{l \cdot h_m}{R_p}\tag{4}$$

For our system, the wavelength of the characteristic radiation $\lambda = 5\cdot10^{-5}$ cm [22] is greater than the width of the boundary layer. The interaction potential in the particle-melt-crystal system for the case of small distances (without taking into account the electromagnetic delay) can be written in the form [22,23]:

$$\Phi(l) = \frac{E_0 R_p}{l},\tag{5}$$

where E_0 is a constant depending on the dielectric properties of the materials.

Solving the linear differential Eq. (2) with the boundary condition $y(1) = 0$ [18], we obtain an equation for determining the particle concentration at the outer boundary of the boundary layer:

$$y(l_\delta) = -\frac{JR_p}{D_0}\exp\left[-\frac{Q(l_\delta)}{kT}\right]\int_1^{l_\delta} l^{-1}\exp\left[\frac{Q(l)}{kT}\right]dl\tag{6}$$

where $l_\delta = (\delta_F - R_p)/h_m$ is the dimensionless thickness of the boundary layer on the crystal surface and the value

$$Q(l) = \Phi(l) + kT\frac{UR_p}{D_o}\ln(l)$$

The value of $Q(l)$ is the interaction potential of the particles with the growing crystal surface. The first term determines the interaction energy of the particles with the crystallization front. For nonpolar substance, it is determined by Eq. (5).

The second term determines the energy of the particle due to the