МНОГОФАЗНЫЕ СИСТЕМЫ

Penetration of a Silicon Vapor through Residual Gaseous Medium during Siliconizing of a Carbon Composite Material

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A new physical and mathematical approach is proposed for the description of a silicon vapor high-temperature transfer from the melt mirror to the surface of absorbing carbon porous medium in an atmosphere of residual gas under moderate vacuum conditions. The general hydrodynamic equations are simplified as much as possible and lead to the model, which is intended for further numerical implementation in the course of simulation the non-stationary three-dimensional process of high-temperature siliconizing of porous carbon products of arbitrary shape and under the condition of complex distribution of silicon sources and sinks. The physical and mathematical model of transport consists of only one non-linear differential equation in partial derivatives for the silicon vapor concentration in the atmosphere of argon or any other residual gas. The main achievement consists of obtaining two stationary analytical solutions for plane and cylindrical geometry in one-dimensional formulation of the problem, which explain the anomalously large silicon vapor flux into the porous material in full-scale experiments. The exact solutions for the studied gas mixtures are expressed in terms of the well-known verified values of material parameters. The high degree of the model usability is supported by numerical simulation in a non-steady two-dimensional case. It has shown that despite the low saturation density of gaseous silicon, the vapor-liquid phase process of high-temperature siliconizing of the carbon material is physically possible in a reasonable time.

Keywords: high temperature processes, rare gaseous medium, transfer of silicon vapor, diffusive and convective transport

1. Introduction

All currently known technologies of the production of high-temperature composite materials are being improved constantly and, due to their increasing complexity, require the implementation of more perfect approaches at different stages [1–3], including the very first one — the construction of new physical and mathematical models for the process occurring. One of the current problems in this area is the numerical simulation of the gaseous silicon transfer from the melt surface to the product during high-temperature siliconizing of a carbon porous material. For real production conditions, the complex system of differential equations in partial derivatives must describe this process. The adequate modelling of this process requires taking into account many complicating factors, including compressibility of the medium. At the same time, the technology is essentially three-dimensional and requires a highly detailed computational mesh due to the presence of many crucibles with the melt in retort and their complex location in the working space of the furnace. As the result, it is not yet possible for a technologist to carry out quickly full-fledged 3D numerical simulation of this process. At the moment, existing models for describing the transfer of

gaseous silicon in a working space of the industrial installation during high-temperature siliconizing are limited to the simplest approaches [4]. Namely, due to the fact that this process is carried out under conditions of moderate vacuum and at extremely high temperatures above the melting point of silicon, it is believed that the diffusion plays decisive role in ensuring the transport of gaseous silicon from the melt surface to the product [5]. In other words, to simulate this process, the simplest diffusion equation is always used without taking into account additional mechanisms, like convective transport. At the same time, it turns out that the use of real values of the diffusion coefficient in this equation does not allow us to ensure the supply of silicon amount observed in the experiment, which is necessary for complete siliconizing of the product. As the result, there is a paradoxical situation, because the facts speak for themselves: in experiments, under certain conditions, the product can still be saturated with the required amount of silicon but calculations based on diffusive model predict impossibility of this process. This means that all the physical conditions, necessary for the successful implementation of this process, still remain not fully understood.

2. Diffusive and Convective Transport in Gases

2.1. Statement of the problem

At first, let us ignore the details of real industrial technology and consider the process in the simplest model formulation, when the surfaces of the product and the silicon melt represent two parallel planes located at a distance L from each other (Figure 1,a). The working space of retort is filled up with a residual gas, the role of which the argon plays. The conditions of medium vacuum are maintained in the retort and correspond to the partial pressure about 100 Pa [6, 7]. The temperature exceeds the melting point of silicon. The product 1 is saturated by silicon vapour which is generated by the melt 2 (Figure 1,a). There is a task to study the transfer of silicon vapor from the melt surface to the product through residual gas. Characteristic size of the retort accounts for about 1–2 m, therefore in our statement we can neglect the effect of gravity (quantitative estimation of this effect will be given in section 2.2). At first, let us begin the discussion about phenomenon description from the analysis of the classical diffusion equation, which has in the three-dimensional case the following form

$$\frac{\partial C}{\partial t} = D \left(\frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2} + \frac{\partial^2 C}{\partial z^2} \right), \qquad (1)$$

where D is the diffusion coefficient, C is the mass concentration of gaseous silicon. This is a standard second order partial differential equation of parabolic type. In the stationary case ($\partial/\partial t = 0$), the problem (1) is simplified and reduced to the Laplace's equation $\Delta C = 0$.

The non-applicability of this equation for the simulation of silicon vapor transfer becomes obvious in a limiting case of one-dimensional statement ($\partial/\partial y = \partial/\partial z = 0$). For the simplest homogeneous boundary conditions

$$C(0) = 0, \quad C(L) = C_s, \qquad (2)$$

only linear distribution of silicon concentration satisfies to

the one-dimensional Laplace's equation

$$C(x) = \frac{C_s}{L} x. \qquad (3)$$

Here C_s is the concentration of silicon vapor on the melt surface. Obviously, this value can't exceed the concentration of saturation for given thermodynamic conditions. The zero value of concentration on the left boundary means complete absorption of gaseous silicon by the porous medium. Characteristic distance L between the melt surface and the product in the course of the technological process is equal about 0.5–1 m. The saturated vapor pressure for silicon at the temperature not much higher than the melting point of silicon is very small and accounts in order of magnitude to $p_s = 10$ Pa [8, 9]. Thus, the number of silicon atoms per unit of volume for conditions of saturation is estimated using the state equation for the ideal gas

$$n_s = \frac{p_s}{kT} = \frac{10}{1.38 \cdot 10^{-23} \cdot 1800} = 4.03 \cdot 10^{20} \ \ 1/m^3, \quad (4)$$

where k is the Boltzmann's constant. The characteristic working temperatures lie near $T = 1800-1900$ K. It is important to compare the theoretically predicted silicon flux density with the weight gain of the product observed in experiment. In fact, by definition the flux density of a substance is the mass transferred per a unit time through a unit area. If silicon transport is determined only by the diffusion, then in this case the Fick's law describes silicon flux density

$$\mathbf{j}_{Si} = -\rho D \nabla C = -D \nabla \rho_{Si}. \qquad (5)$$

Let us make the estimation of diffusion coefficient using the well-proven formula of molecular-kinetic theory [10]:

$$D = \frac{3}{8} \frac{kT}{\sigma_{12} p} \sqrt{\frac{\pi kT}{2\mu_{12}}} = \frac{3}{8} \frac{(kT)^{3/2}}{d_{Si}^2 p \sqrt{\pi m_0}}. \qquad (6)$$

Here σ_{12} is the effective scattering cross-section for two particles, μ_{12} is the equivalent mass. For two approximately equal masses and sizes for silicon atom and argon one, we
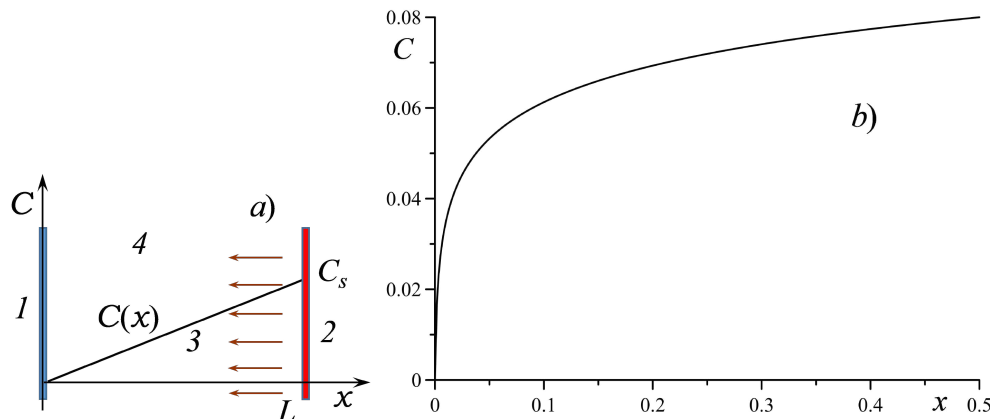
Figure 1. *a)* Plane geometry of the problem: 1 − product surface (carbon material), 2 − surface of silicon melt (melt mirror), 3 − linear distribution according to the standard diffusion model, 4 − working space of retort; *b)* Analytical solution of modified diffusion equation for $L = 0.5$ m

apply $\sigma_{12} \approx \pi d^2$, $\mu_{12} \approx m_0/2$; where m_0 is the mass of one silicon atom $m_0 = M_{Si}/N_A = 0.028$ kg/Mole / $6.02 \cdot 10^{23}$ 1/Mole = $4.7 \cdot 10^{-26}$ kg (M_{Si} is the silicon molar mass). In addition, the diameter of this atom accounts about $d_{Si} = 0.23 \cdot 10^{-9}$ m. The resulting value of the diffusion coefficient is $D = 0.7$ m^2/s. Despite of so giant and unusual value of diffusion coefficient, the formula (5) for constant gradient C_s/L predicts a very low value of silicon flux density $j_{Si} = 2.62 \cdot 10^{-5}$ kg/m^2 s (silicon density on the melt mirror is $\rho_{Si} = p_{Si}M_{Si}/RT = 1.87 \cdot 10^{-5}$ kg/m^3, where R is the universal gas constant).

According to the estimations of technologists involved in the siliconizing of carbon products, this is clearly not enough to block the pores completely in a reasonable time for existing porosity of the material. Moreover, today there is a situation when the moving to a new workpiece shape or new heating conditions, the process cannot be predicted whether it will be successful. However, in reality, if certain conditions are found experimentally, the product of any shape is still successfully saturated with silicon. Thus, an assertion can be reliably established according to which all failures during the technological process are determined not by the diffusive resistance of residual gas and the large distance from the melt surface to the product, but by absolutely another factors.

2.2. Convective transport in residual gas

Thus, it is necessary to explain the anomalously intensive transport of gaseous silicon from the melt to the product surface, which takes place in experiments. The more general equation of admixture transfer in continuous media mechanics, taking into account an additional convective mechanism of the transport [11], is written in the form

$$\frac{\partial C}{\partial t} + (\mathbf{V}\nabla)C = D\Delta C. \qquad (7)$$

Here $\mathbf{V}$ is the macroscopic mean-mass velocity of a physically small fluid element. The main problem of the equation usage is in the absence of mathematical completeness, since the velocity field is an additional unknown quantity. It seems that convective mechanism is the next significant factor after diffusion in the course of silicon mass transfer.

Within the framework of continuous media mechanics, the dynamics of fluid is determined generally by the Navier–Stokes equation [11]. In three-dimensional case, there are three evolutionary nonlinear partial differential equations for velocity components V_x, V_y and V_z. These equations include in addition two variables — the pressure and the density, which need to be determined also. As the result, two supplementary equations are added to the system: the law of mass conservation for compressible medium in differential form and the equation of state. Thus, the final system of equations becomes extremely cumbersome and difficult to solve.

Currently, direct numerical simulation of the processes under consideration in a full three-dimensional formulation is very difficult, even with the help of high-performance supercomputers. The task is to reformulate

the problem more simply. On the one hand, it is important to take into account all the physical factors necessary for the adequate description of the process under consideration, and on the other hand, to avoid the use of overly complex models. It is desirable to construct a new physical model that can permit to carry out our calculations in a reasonable time and would not require an excessive computing power.

To realize these perspectives let us follow the approach, which is implemented in the theory of porous media. Residual gas is not generated at the melt surface and is not absorbed by the product. It permits to suppose that the transfer of silicon vapor through the residual gas is analogous to filtration of a fluid through porous medium, and this average flow is not reduced to the diffusion phenomenon. Then, let us take the momentum equation for filtration in its primary formulation (Wooding, 1957) and evaluate the contribution of each term in it. In the hydrodynamics of porous media, it is necessary to distinguish between the intrinsic velocity $\mathbf{v}$ and the seepage velocity $\mathbf{u}$. The seepage velocity is determined through the total fluid flow rate and is related to the pore velocity by the ratio $\mathbf{u} = \phi\mathbf{v}$. Here ϕ is the material porosity. For intrinsic velocity in the porous medium mechanics, we can use the equation of the fluid motion in first rough approximation [12], neglecting by Brinkman's and Vafai's comlexifications

$$\rho_f \left(\frac{\partial \mathbf{v}}{\partial t} + (\mathbf{v}\nabla)\mathbf{v} \right) = -\nabla p - \frac{\eta}{\kappa}\mathbf{u} + \rho_f\mathbf{g}. \qquad (8)$$

Here ρ_f is the density of the pumped fluid, η is the dynamic viscosity, κ is the permeability. Turning completely to the seepage velocity, we get the equation in the form of Dupuit-Forchheimer

$$\rho_f \left(\phi^{-1}\frac{\partial \mathbf{u}}{\partial t} + \phi^{-2}(\mathbf{u}\nabla)\mathbf{u} \right) = -\nabla p - \frac{\eta}{\kappa}\mathbf{u} + \rho_f\mathbf{g}. \qquad (9)$$

Now it is needful to evaluate the terms containing velocity in the left and right parts of this equation. The most non-trivial parameter in this equation is permeability. In relation to the mobile atoms of the residual gas (argon), we can only talk about the model nature of this matter as a porous medium with some effective permeability. Namely, we mean a model according to which the gaseous silicon, as a kind of fluid, is filtered through a carrier medium due to the fact that silicon vapors are scattered on dotty argon atoms, which heavier than silicon atoms, but nevertheless mobile. Due to the extreme rarefaction of the carrier medium, it is expected that the permeability has anomalously large value.

Indeed, the value of mean free path corresponding to the conditions of moderate vacuum is equal

$$l = \frac{kT}{\sqrt{2}\pi d^2 p} = \frac{1.38 \cdot 10^{-23} \cdot 1800}{\sqrt{2}(1.4 \cdot 10^{-10})^2 100} = 2.8 \cdot 10^{-3} \text{ m.} \quad (10)$$

The value of mean free path permits to calculate the Knudsen number. It plays key role in the mechanics of rare gases. The distance between the product and the melt mirror determines characteristic spatial scale. In our case

$L \sim 1$ m. Following to definition, the Knudsen number can be estimated as

$$Kn = \frac{l}{L} \sim l = 2.8 \cdot 10^{-3} \text{ m}.$$

One can conclude that Knudsen number satisfies condition $Kn \ll 1$, that leads to the ability of continuum media mechanics application. On the other hand, this value close to the limits of applicability of this approach. This is the actual reason of the paradoxical situation that demands taking into accounts of additional factors to describe anomalously intensive transfer of silicon vapour.

Nevertheless, let us apply the Kozeny–Karman formula to estimate the permeability of this artificial porous medium. For partial pressure of argon 100 Pa and porosity $\phi = 1 - v_0 n_{\text{Ar}} = 0.9999999979$, the permeability has the value

$$\kappa = \frac{\kappa_0 \phi^3}{(1-\phi)^2} = 2 \cdot 10^{-3} \text{ m}^2, \tag{11}$$

where v_0 is the volume of one argon atom, κ_0 is the Kozeny–Karman constant. It has supposed in our calculation that following estimation is valid for this parameter $\kappa_0 \sim a^2$; where a is the characteristic size of the obstacle (for spherical argon atom $a \sim 10^{-10}$ m).

Another important quantity is the macroscopic mean-mass velocity of the gas element $\mathbf{V}$. We have to distinguish later among three velocities: the mean-mass velocity $\mathbf{V}$, which appears in equation (7), the seepage velocity $\mathbf{u}$ and the intrinsic one $\mathbf{v}$, that enter into equation (8). Note that the values of seepage velocity and intrinsic one are approximately equal to each other because our medium is rare and its porosity is extremely close to unit. It can be assumed for estimation that during evaporation, silicon atoms detach from the melt surface with a root-mean-square speed

$$u = \sqrt{3kT/m_0} \approx 1250 \text{ m/s}. \tag{12}$$

An averaging this velocity over all directions gives the mean value of the silicon flux density out of the melt in projection on the normal $j_{\text{Si}} = \rho_{\text{Si}} u/2$. The definite part of the vapor momentum is transmitted to the scattering centers therefore the equality for the mean-mass velocity takes place $\rho_{\text{Si}} u/2 = (\rho_{\text{Si}} + \rho_{\text{Ar}})V$. As the result, the mean-mass velocity is defined by the formula $V = \rho_{\text{Si}} u/2(\rho_{\text{Si}} + \rho_{\text{Ar}}) = 41$ m/s (for partial pressure of argon $p_{\text{Ar}} = 100$ Pa the density is equal to $\rho_{\text{Ar}} = \rho_{\text{Ar}} M_{\text{Ar}}/RT = 2.67 \cdot 10^{-4}$ kg/m^3). This evaluation means that convective mechanism makes the significant contribution to the general transfer of gaseous silicon during the process under consideration.

Let us estimate now the value of each term in equation (9), taking into account that the porosity of such medium is close to unit. In our statement, the flux and the seepage velocity of gaseous silicon have only one component along x-axis, which can depend on all three coordinates, therefore $\mathbf{v}\nabla\mathbf{v} \neq 0$ for compressible fluid. On the other hand, the conditions for steady transfer are settled extremely quickly. Thus, we can assume $\partial\mathbf{v}/\partial t = 0$ for steady regime of transfer. Thus, the non-linear term, viscous one and gravity

force in (9) are equal in order of magnitude to following values

$$\left| \rho_f \phi^{-2} (\mathbf{u}\nabla)\mathbf{u} \right| \sim \rho_f \frac{\mathbf{u}^2}{L} = 1.87 \cdot 10^{-5} \frac{625^2}{1.0} = 7.3,$$

$$\left| \frac{\eta\mathbf{u}}{\kappa} \right| = \frac{3.5 \cdot 10^{-4} \cdot 625}{2 \cdot 10^{-3}} = 110, \tag{13}$$

$$\left| \rho_f \mathbf{g} \right| = 1.87 \cdot 10^{-5} = 1.87 \cdot 10^{-4}$$

and satisfy the condition

$$\left| \frac{\eta\mathbf{u}}{\kappa} \right| \gg \left| \rho_f \phi^{-2}(\mathbf{u}\nabla)\mathbf{u} \right| \gg \left| \rho_f \mathbf{g} \right|. \tag{14}$$

One can see that there is no parity between these three terms. Comparison of these quantities permits to neglect by the inertial term and gravity influence in equation (9). As the result, the Darcy's law follows from this equation

$$\mathbf{u} = -\frac{\kappa}{\eta} \nabla p_{\text{Si}}. \tag{15}$$

Due to the incessant evaporation on the melt surface and absorption on the product, we have a certain average density gradient of silicon vapor. Since the pressure in the ideal gas is proportional to density, this causes a silicon pressure gradient, which can act as an additional driving force differing from diffusion. The partial pressure of silicon according to the equation of the ideal gas state is equal to

$$p_{\text{Si}} = n_{\text{Si}} kT, \tag{16}$$

where $n_{\text{Si}} = N_{\text{Si}}/V$ — number of silicon atoms per unit volume. Let us express n_{Si} over the mass concentration C. By definition, we introduce mass concentration over the formula

$$C = \frac{\rho_{\text{Si}}}{\rho_{\text{Ar}} + \rho_{\text{Si}}}. \tag{17}$$

Silicon density is expressed from (17) in terms of relative mass concentration as follows

$$\rho_{\text{Si}} = \frac{C}{1-C} \rho_{\text{Ar}}. \tag{18}$$

Let's rewrite equation (16) in terms of silicon density, i.e. substitute relation (18) into (16) at second step:

$$p_{\text{Si}} = \frac{RT}{M_{\text{Si}}} \frac{C}{1-C} \rho_{\text{Ar}}. \tag{19}$$

Then, we substitute this result into Darcy's law (15), for simplicity neglecting the spatial inhomogeneities of argon density and temperature. Let's also take into account the fact that the silicon mass concentration never actually reaches the unit. Argon, as a residual gas, always presents in the retort, and their concentration is approximately an order of magnitude higher than the concentration of silicon vapor. As the result, we expand the factor $C/(1-C)$ into a series in small C and limit ourselves in the final expression to the first non-vanishing term. Darcy's law (15) takes the final form

$$\mathbf{u}_{\text{Si}} = -\frac{\kappa}{\eta} \nabla p_{\text{Si}} = -\frac{\kappa}{\eta} \frac{RT\rho_{\text{Ar}}}{M_{\text{Si}}} \nabla C. \tag{20}$$

However, it is necessary to substitute the average-mass velocity into equation (7), which is calculated as

$$\mathbf{V} = \frac{\rho_{Ar}\mathbf{u}_{Ar} + \rho_{Si}\mathbf{u}_{Si}}{\rho_{Ar} + \rho_{Si}} = \frac{\rho_{Si}\mathbf{u}_{Si}}{\rho_{Ar} + \rho_{Si}} \approx \frac{\rho_{Si}\mathbf{u}_{Si}}{\rho_{Ar}}. \quad (21)$$

In this approximation the argon is immovable $\mathbf{u}_{Ar} = 0$. According to our model, the silicon vapour is filtered through the stationary argon. Substituting this expression into the generalized equation (7) for impurity transfer, we finally obtain the equation

$$\frac{\partial C}{\partial t} - \frac{\kappa R T \rho_{Si}}{\eta M_{Si}}(\nabla C)^2 = D\Delta C. \quad (22)$$

Now this is a more complex partial differential equation of diffusion with nonlinearity like the square of the concentration gradient. Note that similar diffusion equations with nonlinearities that are quadratic to the concentration gradient are quite common in various fields of physics. Thus, in works [13, 14] it is shown that a nonlinear term of this type quite significantly changes the transport diffusion properties of the material, which is played by a lithium niobate crystal, and makes it possible to explain some of the observed effects associated with the saturation with hydrogen of the material under consideration. For stationary conditions, equation (22) is reduced to the form

$$-(\nabla C)^2 = \psi \Delta C, \quad (23)$$

where ψ is a positively definite, dimensionless parameter responsible for the contribution of the convective term to the overall transport of silicon vapor

$$\psi = \frac{\eta M_{Si} D}{\kappa R T \rho_{Si}}. \quad (24)$$

It is important to estimate the value of the new introduced parameter. Let us use the values of dynamic viscosity and diffusion coefficient as in the works [6, 7]. These parameters were assessed in relation to our siliconizing process with the help of the well-known formulas of the molecular kinetic theory [10]. There is the formula for dynamic viscosity for a rare gas

$$\eta = \frac{1}{3}\left(\frac{2}{\pi}\right)^{3/2}\frac{(m_0 kT)^{1/2}}{d^2}. \quad (25)$$

Here d is the diameter of atom; m_0 is the atom's mass. Formula (25) gives the same magnitude of dynamic viscosity: $\eta = 3.5 \cdot 10^{-4}$ m²/s. Thus, according to (6), (11), (25) parameter ψ quantitatively has the value

$$\psi = \frac{3.5 \cdot 10^{-4} \cdot 28 \cdot 10^{-3} \cdot 0.7}{2 \cdot 10^{-3} \cdot 8.31 \cdot 1800 \cdot 1.87 \cdot 10^{-5}} = 0.012. \quad (26)$$

Note that this complex is an initially dimensionless parameter in the problem (23) and characterizes the relationship between diffusive and convective transport. The smallness of this parameter in (23) means that the new nonlinear term in the left part of the equation has an essential role in our model.

Of cause, the parameter (24) in most cases is greater. This parameter is small only for conditions of medium vacuum during product siliconizing in the course of technological process. At normal conditions, the density of carrying gas becomes significantly bigger and this leads to the diminution of permeability. It is seen from formula (24) that this parameter at lower temperature becomes also greater. As the result, the parameter ψ increases and we have purely diffusive transfer.

3. Exact Solutions of Equation for Concentration

3.1. Plane one-dimensional geometry

Thus, we have only one closed equation (22) for silicon vapor transfer with well-known parameters. Owing to the comparative simplicity of this equation, the pleasant ability exists to find an exact analytical solutions in several actual statements. The first one is one-dimensional stationary distribution of silicon vapor in Cartesian coordinate system with boundary conditions of the first kind. The equation (23) in this case has the form

$$-\left(\frac{\partial C}{\partial x}\right)^2 = \psi\frac{\partial^2 C}{\partial x^2}. \quad (27)$$

It is supplemented with the Dirichlet boundary conditions

$$C(0) = 0, \quad C(L) = C_s. \quad (28)$$

Using procedure the change of variable [15], the integration of equation of (27) with boundary conditions (28) gives the solution

$$C(x) = \psi \ln\left(\frac{x}{L}(\exp(C_s/\psi) - 1) + 1\right). \quad (29)$$

The functional dependence (29) is presented in Figure 1b for $C_s = 0.08$ and $\psi = 0.012$. This dependence qualitatively different from the linear solution (3). It means that the silicon vapor tends to fill up completely the working space of retort. Derivative of (29) on the product surface is determined by formula

$$\frac{\partial C}{\partial x}\Big|_{x=0} = \frac{\psi(\exp(C_s/\psi) - 1)}{L}. \quad (30)$$

It can be seen that this derivative is significantly greater than the same one for the linear solution. Thus, one can explain the anomalously intensive absorption of gaseous silicon by the product during silicification. In the limiting case of small ratio C_s/ψ the exponent can be expanded into series and we have got the derivative for linear solution (3), which is equal to C_s/L.

3.2. Cylindrical one-dimensional case

Analogical problem can be solved in cylindrical coordinate system. Using conditions of concentration uniformity on azimuthal angle and axial coordinate, we have the equation

$$-\left(\frac{\partial C}{\partial r}\right)^2 = \frac{\psi}{r}\frac{\partial}{\partial r}\left(r\frac{\partial C}{\partial r}\right). \tag{31}$$

As before, the Dirichlet boundary conditions can be imposed in our case

$$C(R_1) = 0, \quad C(R_2) = C_s. \tag{32}$$

This boundary value problem describes steady transfer of silicon vapor form external uniform sources located at distance $R_2 - R_1$ to the product of cylindrical form with radius R_1 (Figure 2,a).

As the result of statement with cylindrical symmetry, the integration of equation (31) for boundary conditions (32) gives superlogarithmic solution

$$C(r) = \psi \ln\left(\frac{(\ln(r/R_2) - \exp(C_s/\psi)\ln(r/R_1))}{\ln(R_2/R_1)}\right). \tag{33}$$

Derivative of (33) at $r = R_1$ is determined by expression

$$\frac{\partial C}{\partial r}\bigg|_{z=R_1} = \frac{\psi}{R_1}\frac{(1 - \exp(C_s/\psi))}{(\ln(R_1/R_2) - \exp(C_s/\psi))}. \tag{34}$$

It is seen that in the case of modified equation (22) the values of derivative as for rectangular coordinate system as for cylindrical one are evidently greater than analogical one for classical diffusion equation (1). The distinction can exceed the whole order. Note that the mass flux is proportional to the derivative of concentration. Thus, it means that the vapor-liquid phase method could be soundly applied for silicification of carbon porous materials and our theory confirms ability of the technology realization.
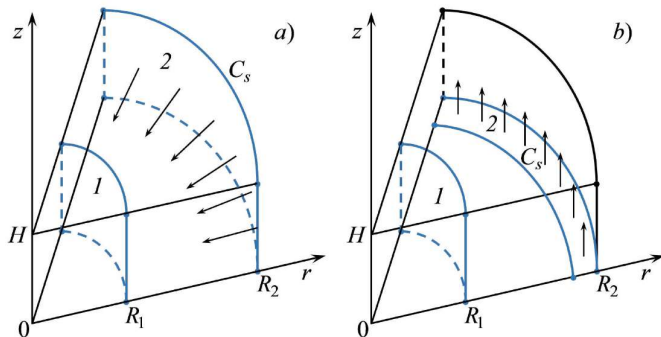

Figure 2. *a)* Cylindrical geometry of the problem with vertical melt mirror: 1 – product surface, 2 – melt mirror, R_2, R_1 – radii of cylindrical shells, C_s – concentration of saturation; *b)* Cylindrical geometry with horizontal melt mirror

4. Numerical Simulation in Two-dimensional Statement

4.1. Two-dimensional problem with the axial symmetry

The problem of silicon vapor transfer looks more realistic for the systems with cylindrical symmetry. The simplest configurations are presented in Figure 2, where one can see two coaxial cylindrical shells with different radii R_2 and R_1, corresponding to the melt surface and cylindrical product. Now let us consider the general case of time-dependent statement to observe also the formation and motion of concentration front. On the other hand, we simplify the statement assuming the condition of axial symmetry of the system. Thus, the equation (22) for unknown function $C(r, z, t)$ in cylindrical coordinates can be written as

$$\frac{\partial C}{\partial t} - D_c\left[\left(\frac{\partial C}{\partial r}\right)^2 + \left(\frac{\partial C}{\partial z}\right)^2\right] =$$
$$= D\left(\frac{\partial^2 C}{\partial r^2} + \frac{1}{r}\frac{\partial C}{\partial r} + \frac{\partial^2 C}{\partial z^2}\right). \tag{35}$$

Here D_c is the dimensional parameter, which characterizes the intensity of convective transfer in comparison with diffusion. Note, that there is no necessity to introduce non-dimensional quantities in our problem because this parameter has the same dimension $[\text{m}^2/\text{s}]$ as diffusion coefficient. There is a mathematical ability to compare D_c and D. By definition, this new parameter is equal to

$$D_c = \frac{\kappa R T \rho_{\text{Si}}}{\eta M_{\text{Si}}}. \tag{36}$$

Further, we shall call it as the parameter of convective transport, which appears in physics for the first time. For our conditions it has the value $D_c \approx 58 \text{ m}^2/\text{s}$ (see estimation ψ). Besides of the sectors with sources and sinks the impermeable boundaries of retort appear in this statement. Thus, two sets of boundary conditions take place for corresponding configurations, which are shown in Figure 2:

$$1) \quad C(R_1, z) = 0, \quad C(R_2, z) = C,$$
$$\frac{\partial C}{\partial z}\bigg|_{z=0} = \frac{\partial C}{\partial z}\bigg|_{z=H} = 0.$$
$$2) \quad C(R_1, z) = 0, \quad \frac{\partial C}{\partial r}\bigg|_{r=R_2} = 0, \quad \frac{\partial C}{\partial z}\bigg|_{z=H} = 0; \tag{37}$$
$$R_1 \leqslant r \leqslant R_s : \quad \frac{\partial C}{\partial z}\bigg|_{z=0} = 0,$$
$$R_s < r \leqslant R_2 : \quad C(r, z = 0) = C_s.$$

According to the first statement, the surfaces of product and melt mirror are opposite to each other. Under the second set of boundary conditions, the surface of the melt mirror is horizontal and surrounds the vertical product shell like in an experiment.

4.2. The method of numerical simulation

Now we have an evolutionary differential equation (35) in partial derivatives, which is solved numerically by the standard method of finite differences [16]. It is important to use the method that can be applied in a future for automatization of technological process. The method of finite differences is the most suitable for this purpose realization. An explicit scheme of first-order accuracy by time is applied to simulate the evolution of the system. In calculation algorithm, the spatial derivatives have different accuracy to provide the stability of the scheme. We use central second-order accuracy formulas for derivatives approximation along axial coordinate z and first-order accuracy backward differences along radial coordinate r. The solution of equation (35) with boundary conditions (37) is found for reasonable values of dimensional parameters $H = 0.4$ m, $L = R_2 = 0.9$ m, $R_1 = 0.2$ m, $D = 0.7$ m²/s, $D_c = 58$ m²/s (L is the full retort radius, which can distinguish from the radius of the shell with the melt). The time step is chosen in dependence on spatial one to obtain the stability of the numerical procedure (the Courant criterion). The author's computer code has implemented in the FORTRAN-90 programming language. The space of retort is initially empty, which means that at the beginning the concentration of the silicon vapor is equal zero in calculation domain. There is used a numerical grid with the number of nodes along radial and axial coordinates 85(121):41; along radial axis 85 nods – for vertical melt surface (Figure 2,a), 121 — for horizontal one (Figure 2,b). The ratio of the retort radius L to the product height H has been varied in the interval 2−4.

4.3. Numerical results and discussion

Two-dimensional numerical calculations show some complementary features of the process. This computation permits to ascertain the characteristic time of the settling of silicon vapor distribution in retort. The fields of silicon concentration in section (r,z) are presented in Figure 3 for two moments of time in the case when the surfaces of melt and product are opposite (Figure 2,a). Following values of time points correspond to these realizations: $t_1 = 0.008$ s, $t_2 = 0.5$ s.

At initial stage the concentration front of silicon vapor originates on the external boundary and moves inside to the product surface. It is visible that the gaseous silicon propagate quickly through the entire space of retort. One can see that the settling of stationary concentration profile occurs approximately over the time $t = 0.5$ s. At the final steady stage, the diminution of concentration is only observed near the product surface, which absorbs the silicon vapor according to the boundary condition. The profile on the Figure 3,b looks like the analytical solution (33). Also it corresponds qualitatively to the solution with plane geometry (29) which is shown in Figure 1b,.

It must be emphasized that in the case of cylindrical symmetry, one can observe the more strong effect of wave front steeping in comparison with the plane statement. In the system with cylindrical symmetry the streamlines are concentrated during the motion of gaseous silicon from the periphery to the centerline therefore the additional increasing of flux density on the surface product is observed owing to the topological convergence effect.

Then, let us consider the problem with more realistic statement, when the mirror of silicon melt is horizontal and the product surface, as early, is vertical (Figure 2,b). The width of the melt ring is equal $\Delta R = L/3$. The fields of silicon concentration are shown in Figure 4. At first stage the gaseous silicon becomes to evaporate vertically upward (Figure 4,a). After that the streamlines turn to the product surface and the silicon vapor begins again to fill up quickly the working space of the retort.

It can be concluded that the filling of the working space in the retort by the atoms of gaseous silicon occurs after the beginning of evaporation less than for the second. Mainly due to the convective transfer, the concentration of silicon in the volume quickly amounts to the value, which is close to the one near the melt surface. If conditions of silicon condensation take place on the product surface, the high gradient of concentration originates at this boundary after
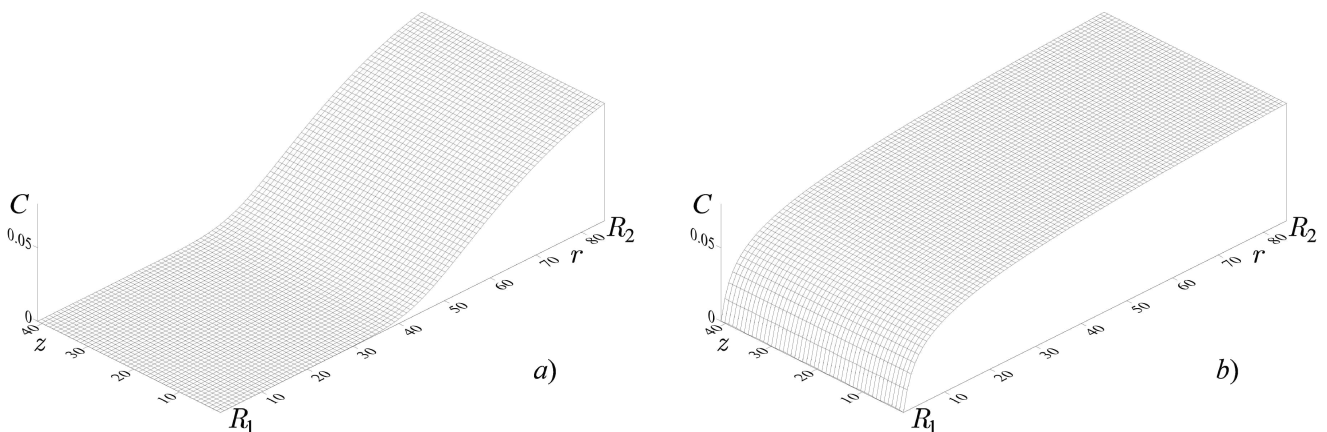

Figure 3. The concentration of silicon vapor in vertical section for the opposite surfaces of the melt and product for two moments of time; $a) - t_1$, $b) - t_2$
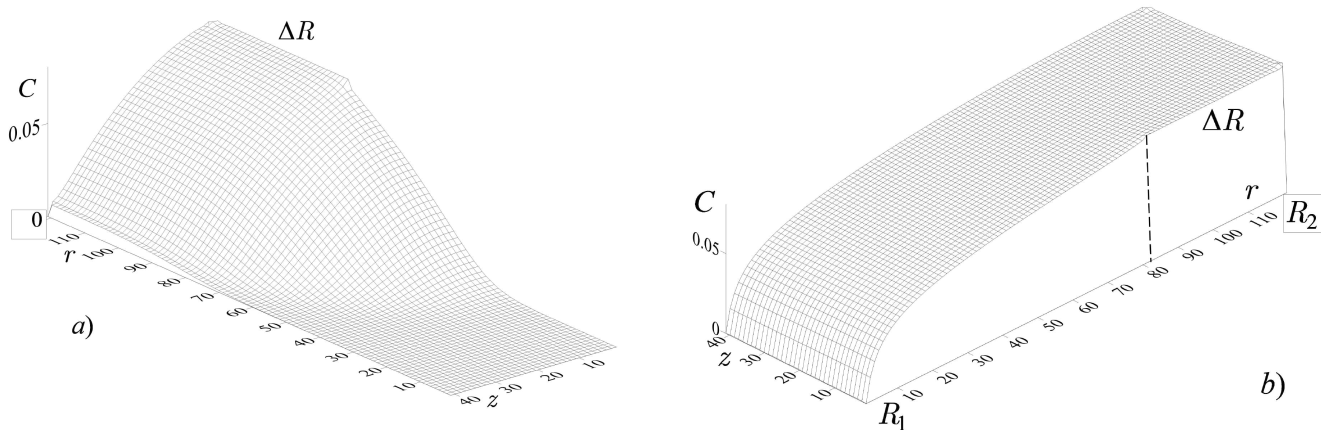
Figure 4. The concentration of silicon vapor in vertical section for the horizontal surface of the melt mirror for two moments of time $a)$ − $t_1 = 0.005$ s, $b)$ − $t_2 = 0.1$ s

the settling of steady state. The pressure flow is realized in this system because of the intensive evaporation at the melt surface. So, not only diffusion causes silicon transport through the residual gas but also convective transfer.

Theoretical works [4, 5] predicted the impossibility of silicon transfer in sufficient quantities for the realistic time. In the result of solution of the classical diffusion equation, the estimation of the full siliconizing time is equal 20−30 hours [4, 5]. The time of the siliconizing is proportional to the derivative of concentration at the surface of the product, see formulas (30) and (34). Our calculations demonstrate that the concentration derivative at the product boundary is ten times greater than in the case of pure diffusion. Thus, we prognosticate the siliconizing time 2−3 hours that conforms experimental data very well.

5. Conclusion

In the results of analytical and numerical calculations, one can summarize that there is no necessity to approach the crucibles as possible to the product during technological process in order to overpass the diffusive barrier of residual gas. This point of view could be valid only for linear distribution of gaseous silicon concentration in retort. Indeed, in this case the technologist have to move crucibles closer to the product in order to increase as possible the concentration derivative on the sample surface.

It has proved analytically, and additional numerical calculations confirm this result, that the convective transfer of gaseous silicon makes considerable contribution into the full mass flux in real technological conditions.

It is shown theoretically, that silicon vapor tends to occupy quickly the whole working space in retort therefore near the product surface there is always sufficient amount of silicon for successful realization of the siliconizing process. The simplicity of numerical procedure realization confirm an efficiency of suggested new non-linear diffusion equation for description of silicon transfer in the conditions of medium vacuum.

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