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PLASMA INVESTIGATIONS

Efficiency of the Plasma-Chemical Method of Preparation of Silicon from Quartz in an Argon-Hydrogen Flow

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Abstract—A kinetic model of nonequilibrium chemical processes in gas mixtures of Si, O, H, and Ar and a model of the calculation of the main parameters of plasma facilities for the implementation of the plasma-chemical method of the direct preparation of silicon from quartz in argon–hydrogen gas-plasma flows have been formulated. The criteria and general conditions at which the maximal yield of silicon is achieved were determined. The main mode and construction parameters of plasma facilities were determined. It is shown that at the consumed electrical power of a stationary plasmatron of 100 kW the calculated efficiency of the facility (over vapor Si) could be on the order of 10^{-2} g/s.

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INTRODUCTION

The known plasmachemical methods of the preparation of silicon from quartz SiO_2 [1, 2] are implemented in two stages: first there occurs the reduction in argon plasma of gaseous silicon monoxide SiO by hydrocarbons or hydrogen and, then, the reduction of silicon from gaseous SiO. Technical problems may arise from the practical implementation of these methods associated with the transport of prepared gaseous SiO from the region of its preparation in the reduction zone.

In [3] a one-stage plasma-chemical method of the preparation of silicon from a quartz concentrate was proposed and studied experimentally. In this method the process of the transformation of the initially solid quartz particles into polycrystalline silicon occurs in the same flow of argon–hydrogen plasma. Finely disperse solid SiO_2 particles are introduced simultaneously with hydrogen in argon plasma of the discharge created by a stationary electric arc or induction plasmatron. Then the three main zones in which different physicochemical processes occur can be singled out downstream the formed heterophase flow in accordance with the level of the values of its bulk temperature.

The first zone (homogenization zone) is the high-temperature part of the plasma flow from the place of the input of quartz particles (where the bulk temperature of the flow is maximal, 8.0–12.0 kK) into the region in which the temperature of mixture decreases to 6.5 kK (the temperature of the beginning of the formation of molecules). In this zone solid SiO_2 particles evaporate (with the formation of silicon vapors) and all molecular compounds decay into atoms; i.e., an atomic gas mixture of Ar, H, O, and Si is formed.

In the second zone, the zone of gas-phase chemical transformations, the formation of molecular compounds in the cooling gas flow and, first of all, association of free oxygen atoms with hydrogen under the condition of the absence of the production of molecules of gaseous silicon monoxide should take place. The length of this zone is determined by the length on which the bulk temperature of the gas-phase flow decreases from 6.5 kK to 2.0–2.5 kK, i.e., to the temperature of the beginning of heterophase chemical reactions. This region of the channel, which directly follows after the homogenization zone, is called the gas-chemical reactor (GCR).

In the third zone, the condensation zone, the volume condensation of silicon vapors is implemented with the formation of polycrystalline silicon particles. These processes occur at a flow temperature below 2.0 kK in the insulated channel of the reactor-condenser connected directly to the GCR.

Experimental studies [3] performed using the electric arc plasmatron with power comsumption up to 3.0 kW confirmed the possibility of the implementation of this plasma-chemical method. Polycrystalline silicon in the shape of spherelike particles with a purity from 99.8 to 99.9% and average sizes from 100 to 200 μm was prepared during processing of quartz particles (with an initial size of no larger than 100 μm and a total content of impurities of about 10^3 ppm). The primary analysis of these experimental results showed that the product yield and the efficiency of the plasma-chemical method depend on the conditions of the organization of the main physicochemical processes in all three zones.

In this work on the basis of theoretical studies processes in the first two zones, which limit to the greatest extent the efficiency of this plasma-chemical method,

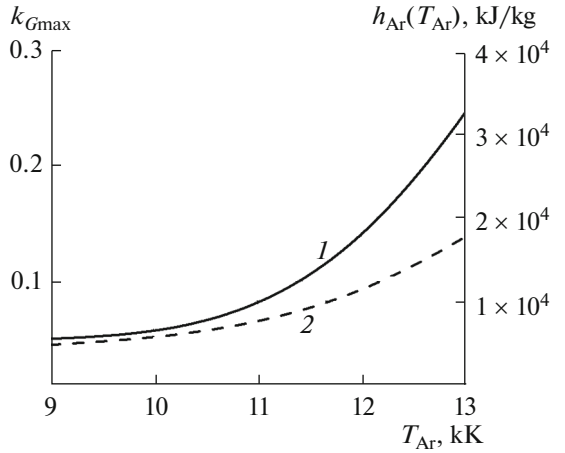

Fig. 1. Dependence of the maximum value of the relative consumption of processed disperse quartz $k_{G\max}$ (*1*) and the enthalpy of argon plasma $h_{\mathrm{Ar}}(T_{\mathrm{Ar}})$ (*2*) on its temperature T_{Ar}.

the criteria and the general conditions of effective implementation of the method were established and the main geometrical and mode parameters of plasma-chemical facilities for processing quartz concentrates into silicon were determined.

THEORETICAL ANALYSIS OF THE MAIN PROCESSES OF THE PLASMA-CHEMICAL METHOD

Study of Processes in the Homogenization Zone

From the energy point of view, the processes in the homogenization zone may be considered as processes of mixing of two flows. The first is the flow of argon plasma with the temperature T_{Ar} (enthalpy $h_{\mathrm{Ar}}(T_{\mathrm{Ar}})$) and mass consumption G_{Ar}; the second is the flow of the mixture of gaseous hydrogen (with the mass consumption G_{H_2}) and solid quartz particles (with the mass consumption G_{SiO_2}) at the temperature $T_n = 298$ K. At the exit of the zone, there should be formed a homogeneous flow of atomic gases (Ar, H, O, and Si) with the mass consumption G_Σ, temperature $T_0 = 6.5$ kK, and enthalpy $h(T_0)$. Mixing of subsonic flows occurs in the isobaric mode in the adiabatically isolated cylindrical channel, and the parameters of flows in the input ($T_{\mathrm{Ar}} = 8.0$–12.0 kK) and output ($T_0 = 6.5$ kK) cross sections of the homogenization zone are related by the laws of mass and energy conservation

$$\begin{gathered} G_\Sigma h(T_0) = G_{\mathrm{Ar}} h_{\mathrm{Ar}}(T_{\mathrm{Ar}}) + G_{\mathrm{SiO}_2} h_{\mathrm{SiO}_2}(T_n), \\ G_\Sigma = G_{\mathrm{Ar}} + G_{\mathrm{SiO}_2} + G_{\mathrm{H}_2}. \end{gathered} \quad (1)$$

It was taken into account in (1) that hydrogen comes into the mixing zone at standard conditions so that its enthalpy $h_{\mathrm{H}_2}(T_n) = 0$.

From the condition that the amount of hydrogen should provide (in accordance with the reaction $SiO_2 + 2H_2 = Si + 2H_2O$) bonding of all oxygen initially contained in SiO_2 molecules, the mass consumption of molecular hydrogen is determined from the formula

$$G_{\mathrm{H}_2} = \lambda_{\mathrm{H}} G_{\mathrm{SiO}_2}, \quad (2)$$

where $\lambda_{\mathrm{H}} = 1/15$.

With allowance for (2), relation (1) can be written in the form

$$h(T_0, k_{G\max}) = \frac{h_{\mathrm{Ar}}(T_{\mathrm{Ar}}) + k_{G\max} h_{\mathrm{SiO}_2}(T_n)}{1 + k_{G\max}(1 + \lambda_{\mathrm{H}})}, \quad (3)$$

where $k_{G\max} = G_{\mathrm{SiO}_2\max}/G_{\mathrm{Ar}}$ is the maximum value of the relative consumption of processed disperse quartz at which the mixture is completely homogenized and has the temperature $T_0 = 6.5$ kK.

Assuming that the state of the mixture at the output from the homogenization zone is thermodynamically equilibrium, for the given value of the argon plasma temperature from the range of $T_{\mathrm{Ar}} = 8.0$–12.0 kK according to formula (3), one can find the maximal value $k_{G\max}$, given in Fig. 1 as the function T_{Ar}. Figure 1 also shows the temperature dependence of the specific enthalpy of argon plasma $h_{\mathrm{Ar}}(T_{\mathrm{Ar}})$, through which one can determine the consumed power of plasmatron $P_{\mathrm{pl}} = G_{\mathrm{Ar}} h_{\mathrm{Ar}}(T_{\mathrm{Ar}})/\eta_{\mathrm{pl}}$ (here η_{pl} is the efficiency of the plasmatron). It can be seen that at T_{Ar} on the level of 11.0–12.0 kK the value $k_{G\max}$ is about 0.1. This means that, e.g., at electrical power $P_{\mathrm{pl}} = 100$ kW consumed by the plasmatron (with $\eta_{\mathrm{pl}} = 40\%$) and the consumption of the plasma-forming gas $G_{\mathrm{Ar}} = 3.0$ g/s, the maximum consumption of processed quartz can be $G_{\mathrm{SiO}_2\max} = 0.3$ g/s. Here it is necessary to note that allowance for nonadiabaticity of the homogenization process leads to a 1.3- to 1.5-fold decrease in $k_{G\max}$.

The efficiency of the course of the homogenization process of the initial heterophase flow depends not only on the consumption but also on the size of quartz particles processed: the evaporation time of the particle in the plasma flow proportional to the square of the diameter should be less than the time of the stay in the homogenization zone. The fulfillment of this condition depends on the type and energy-power parameters of the plasmatron. The calculations [4] showed that in flows generated by electric arc plasmatrons with the consumed electrical power from 3.0 to 30.0 kW and the characteristic time of the stay of the particle in the homogenization zone on the level of 10^{-4}–10^{-3} s, quartz particles with an initial size not larger than 10–30 μm evaporate almost completely. The use of induction plasmatrons with a consumed power of ~100 kW as plasma sources makes it possible to provide a time of stay of quartz particles in the high-temperature zone on the level of 10^{-2} s and to evaporate particles with an initial size of up to 100 μm completely.

Table 1. Main chemical reactions in the gas mixture of Si, O, H, and Ar

No.	Reaction	No.	Reaction
1	$Si + O + Ar \rightleftarrows SiO + Ar$	7	$H + H + Ar \rightleftarrows H_2 + Ar$
2	$Si + H + Ar \rightleftarrows SiH + Ar$	8	$OH + H + Ar \rightleftarrows H_2O + Ar$
3	$Si + O + H \rightleftarrows SiO + H$	9	$O_2 + H \rightleftarrows OH + O$
4	$Si + OH \rightleftarrows SiO + H$	10	$O + H_2O \rightleftarrows OH + OH$
5	$SiH + O \rightleftarrows SiO + H$	11	$H + H_2O \rightleftarrows OH + H_2$
6	$O + O + Ar \rightleftarrows O_2 + Ar$	12	$O + H_2 \rightleftarrows OH + H$

Table 2. Rate constants of gas-phase chemical reactions $q = 1$–12 at $T = 2.0$–6.5 kK and $p = 1$ atm.; m^3/s (dimensionality of $k_q^+(\tilde{T})$ for $q = 1$–3 and 6–8—m^6/s)

Reaction no.	$k_q^+(\tilde{T})$	$k_q^-(\tilde{T})$
1	$8.5\times10^{-48}\exp(-0.25/\tilde{T})$	$3.6\times10^{-17}\tilde{T}^{-0.5}\exp(-14.6/\tilde{T})$
2	$1.2\times10^{-45}\exp(-0.15/\tilde{T})$	$1.0\times10^{-16}\tilde{T}^{-0.5}\exp(-5.23/\tilde{T})$
3	$2.44\times10^{-44}\tilde{T}^{-0.52}$	$9.26\times10^{-14}\tilde{T}^{-0.833}\exp(-14.7/\tilde{T})$
4	$4\times10^{-16}T^{0.5}\exp(-9.0/\tilde{T})$	$3.35\times10^{-15}\tilde{T}^{0.5}\exp(-14.7/\tilde{T})$
5	$1.55\times10^{-15}\tilde{T}^{0.5}\exp(-8.57/\tilde{T})$	$3.35\times10^{-15}\tilde{T}^{0.5}\exp(-14.7/\tilde{T})$
6	$4.2\times10^{-47}\tilde{T}^{-1}$	$2.0\times10^{-16}\exp(-8.31/\tilde{T})$
7	$2.7\times10^{-46}\tilde{T}^{-1}$	$3.6\times10^{-16}\exp(-7.45/\tilde{T})$
8	$9.2\times10^{-45}\tilde{T}^{-2}$	$2.7\times10^{-13}\exp(-8.77/\tilde{T})$
9	$6.8\times10^{-17}\tilde{T}^{0.91}\exp(-1.28/\tilde{T})$	3.0×10^{-17}
10	$5.6\times10^{-16}\tilde{T}^{1.14}\exp(-1.34/\tilde{T})$	$5.6\times10^{-17}\tilde{T}^{1.14}$
11	$9.6\times10^{-16}\tilde{T}^{1.6}\exp(-1.45/\tilde{T})$	$2.1\times10^{-16}\tilde{T}^{1.6}\exp(-0.26/\tilde{T})$
12	$1.1\times10^{-15}\tilde{T}^{2.0}\exp(-0.58/\tilde{T})$	$4.6\times10^{-16}\tilde{T}^{2.0}\exp(-0.43/\tilde{T})$

The results given in this subsection show that physicochemical processes in the homogenization zone do not pose any fundamental limitations on the efficiency of the plasma-chemical method. At an increase in the power P_{pl} (and, respectively, G_{Ar}) of high-frequency induction plasmatrons, an increase in the consumption $G_{SiO_2\,max}$ and in the size of the processed quartz particles is possible.

Study of Processes in the Zone of Gas-Phase Chemical Transformations

To study processes of gas-phase kinetics in the GCR channel, the kinetic model of processes in the high-temperature gas mixture initially consisting of Ar, Si, O, and H atoms was formulated. Gas-phase reactions determining the kinetics of the main components of the gas mixture are given in Table 1.

The rate constants of direct $k_q^+(\tilde{T})$ and inverse $k_q^-(\tilde{T})$ reactions $q = 6$–12 (where q is the number of the reaction and $\tilde{T} = T/T_0$ is the dimensionless mixture temperature) were determined on the basis of known experimental data [5].

Experimental information about the rate constants of reactions $q = 1$–5 is absent. Their values were established using known theoretical models [6]. The rate constants $k_q^-(\tilde{T})$ of all inverse reactions $q = 1$–5 were determined from the model of the one-quantum stepwise excitation for $q = 1$ and 2, on the basis of the diffusion model for the reaction $q = 3$ and with application of the model of "reacting solid spheres" for reactions $q = 4$ and 5. Rate constants $k_q^+(\tilde{T})$ of all direct reactions $q = 1$–5 were calculated from equilibrium constants $K_{qn}(\tilde{T})$ of these reactions from the formula $k_q^+(\tilde{T}) = k_q^-(\tilde{T})K_{qn}(\tilde{T})$.

The found rate constants in the temperature interval from 2.0 to 6.5 kK were approximated by the generalized Arrhenius dependence and are given in Table 2.

The values of the rate constants make it possible to estimate the scales of characteristic times of the formation of separate components of the chemically reacting gas mixture in GCR and to estimate qualitatively the effect of any mode parameter on the efficiency of the method. The method can be implemented if the bonding of free oxygen atoms with hydrogen (with the formation of water vapors) will take place in the cooling gas flow during the characteristic time of stay of the mixture $t_x = l/W_0$ in the GCR with the length l and the bulk velocity at the input W_0 under the condition of the absence of the production of gaseous silicon monoxide molecules, i.e., with fulfillment of the inequality

$$t_{[H_2O]} \le t_x \ll t_{[SiO]}, \quad (4)$$

where $t_{[SiO]}$ and $t_{[H_2O]}$ are the characteristic times of the formation of gaseous SiO and H_2O molecules. Inequality (4) indicates that the process of the formation of H_2O should be the fastest and be implemented in a quasi-equilibrium manner, and the process of the production of SiO should be the slowest and take place in a nonequilibrium manner for the time of the passage of the GCR channel by the mixture. It was taken into account in the formulation of condition (4) that, as the estimates showed, losses of Si are mainly associated with the formation of SiO and the efficiency of the formation of other silicon-containing molecules (e.g., SiH) in the specified conditions is low.

When estimating $t_{[SiO]}$ and $t_{[H_2O]}$, the rate constants of the corresponding processes were calculated at the mixture temperature $T^* = 4.0$ kK, at which, as the calculations showed, the reactions of the formation of molecular components proceed most intensively.

The study of relaxation processes in the system of reactions (Table 1) made it possible to relate the characteristic time scales of the formation of water vapors $t_{[H_2O]}$ and hydrogen molecules $t_{[H_2]}$ (in the reaction $q = 7$) by the relation

$$t_{[H_2O]} = 7\times10^{-3} k_G^{-0.62} t_{[H_2]}, \quad (5)$$

where $t_{[H_2]} = \left[k_7^+(T^*) n_H(T_0) n_{Ar}(T_0)\right]^{-1}$; $n_H(T_0)$, $n_{Ar}(T_0)$ are the concentrations of H and Ar vapors at the input in GCR (at the temperature T_0).

The formation of silicon monoxide in accordance with the assumed model of chemical processes most effectively occurs in reactions $q = 1$ and 3 with the participation of Ar and H atoms as a buffer. The considerable difference in the masses of particles of the buffer gas can lead, as noted in [6], to a considerable difference in the rate constants of the corresponding reactions and characteristic times of the production of SiO. The time scale of the production of monoxide $t_{[SiO]}$ is determined by the minimum value of these two times.

Estimates show that in processing quartz with the relative consumptions $10^{-3} \le k_G \le k_{G\max} \approx 0.1$ in the flow with the hydrogen consumption corresponding to (2), the time scale of the production of monoxide $t_{[SiO]}$ is determined by the reaction $q = 3$ and can be estimated as

$$t_{[SiO]} = \left[k_2^+(T^*) n_{Si}(T_0) n_H(T_0)\right]^{-1}, \quad (6)$$

where $n_{Si}(T_0)$ is the concentration of Si vapors at the input in the GCR.

In accordance with (5) and (6), the relation between the characteristic times of the production of SiO and H_2O depends on the relative consumption of the processed quartz k_G. At the maximum consumptions $k_G \sim k_{G\max} \approx 0.1$ of the processed quartz and hydrogen, the value $t_{[SiO]}/t_{[H_2O]} \sim 1$. In this case the characteristic time scales of the formation of SiO and H_2O are comparable and the condition of the efficiency of the course of processes in the GCR (4) can be violated.

Here we note that at $k_G \sim k_{G\max} \approx 0.1$ the increase in the hydrogen consumption (in comparison with the stoichiometric value (2)) leads to the fact that the value $t_{[SiO]}/t_{[H_2O]}$ becomes already less than unity and the condition of the effective bonding of oxygen vapors by hydrogen (4) is guaranteed to be violated. It follows that the proposed method cannot be implemented in a purely hydrogen gas-plasma flow and the presence of the argon buffer in the corresponding amount is required.

When the consumption of processed quartz decreases (and, consequently, the hydrogen consumption) below $k_{G\max}$, the characteristic time scales of the formation of the main molecular components of the mixture vary essentially. For example, at $k_G \sim 0.01$ they take the values $t_{[H_2O]} \sim 1.5\times10^{-2}$ s and $t_{[SiO]} \sim 2.0\times10^{-1}$ s. The characteristic time scales of the formation of SiO and H_2O already differ considerably. $t_{[SiO]} \gg t_{[H_2O]}$, and at the corresponding choice of t_x, the condition (4) can be fulfilled.

The quantitative analysis of the course of the chemically reacting gas mixture in the GCR was performed for the laminar mode (at the characteristic value of the Reynolds number averaged over the GCR length $Re_l \approx 10^2$–10^3; see below) of the flow of the gas mixture in the cylindrical (with the diameter d) cooling channel with a constant wall temperature within the one-dimensional stationary model "reactor of the ideal displacement" [7]. Within this model it is assumed that in the flow the complete transverse mixing of reacting components takes place in the absence of their longitudinal mixing.

The continuity equation of the i-th (for all but Ar) component is written in the dimensionless form

$$\tilde{W}\frac{dy_i}{d\tilde{z}} = \mathrm{Da}\tilde{R}_i. \quad (7)$$

Here $\tilde{W} = W/W_0$ is the dimensionless velocity of the mixture flow in the cross section with the dimensionless axial coordinate $\tilde{z} = z/l$, counted from the cross section in which the flow temperature $T_0 = 6.5$ kK; $y_i = n_i/n_{\mathrm{Si}}(0)$ is the dimensionless concentration of the i-th component ($n_{\mathrm{Si}}(0)$ is the concentration of silicon vapors at the input of the GCR); $\mathrm{Da} = t_x/t_{[\mathrm{H}_2]}$ is the Damkohler number. The Ar concentration was found from the thermal equation of state, and the flow velocity was calculated using the continuity equation for the whole flow.

The dimensionless rate of the formation of the i-th component $\tilde{R}_i$ was determined from the formula

$$\tilde{R}_i = \sum_q \left(\nu_{iq}^- - \nu_{iq}^+\right)\left(k_q^+(\tilde{T})\prod_l y_l^{\nu_{lq}^+} - k_q^-(\tilde{T})\prod_l y_l^{\nu_{lq}^-}\left(n_{\mathrm{Si}}(0)\right)\sum_l\left(\nu_{lq}^- - \nu_{lq}^+\right)\right) \times t_{[\mathrm{H}_2]}\left(n_{\mathrm{Si}}(0)\right)\sum_l \nu_{lq}^+ - 1, \quad (8)$$

where ν_{lq}^- and ν_{lq}^+ are the stoichiometric coefficients of l-th components of the mixture in the q-th reaction.

The energy equation is written in the dimensionless form

$$\frac{d\tilde{T}}{d\tilde{z}} = -\mathrm{Da}\left[\sum_i \tilde{H}_i\left(\tilde{T}\right)\tilde{R}_i + 4B_\alpha\left(\tilde{T} - \tilde{T}_w\right)\right]. \quad (9)$$

Here, $\tilde{H}_i(\tilde{T}) = H_i(T)/H_0$ is the dimensionless enthalpy of the i-th component determined in terms of the characteristic scale $H_0 = \overline{\mu C_p}T_0$, where $\overline{\mu C_p}$ is the mean integral molar heat capacity of the mixture; $\tilde{T}_w = T_w/T_0 = \mathrm{const}$ is the dimensionless wall temperature; $B_\alpha = \mathrm{Nu}\bar{a}t_{[\mathrm{H}_2]}/d^2$, where Nu is the Nusselt number; and $\bar{a}$ is the mean integral coefficient thermal diffusivity of the gas mixture. The first term in (9) containing the criterion Da characterizes the intensity of the volume heat sources as a result of the passing chemical reactions. The second term in (9) containing the criterion $B_\alpha\mathrm{Da}$ is responsible for the heat dumping through the walls of the GCR channel.

As the boundary conditions to the system of equations (7)–(9) at the input to the GCR at $\tilde{z} = 0$, we set the dimensionless mixture temperature $\tilde{T} = 1$ and the relative concentrations of components of the mixture (the hydrogen concentration was set in accordance with (2))

$$y_{\mathrm{Ar}}(0) = \left(m_{\mathrm{Ar}}k_G/m_{\mathrm{SiO}_2}\right)^{-1}, \quad y_{\mathrm{Si}}(0) = 1, \quad y_{\mathrm{O}}(0) = 2, \quad y_{\mathrm{H}}(0) = 4,$$

where m_{Ar} and m_{SiO_2} are the masses of argon and quartz molecules. The concentrations of molecular components are zero. The obtained system of equations was solved numerically using backward differentiation formulas (BDFs) [8].

The condition of reaching the temperature $T = 2.0$ kK by the flow at the coordinate $\tilde{z} = 1$, at which the GCR zone is terminated, makes it possible to establish the functional relationship between criteria Da, B_α, and k_G, which on the basis of the results of the calculations performed can be interpolated approximately by the formula

$$B_\alpha = \frac{f(k_G)}{\mathrm{Da}}, \quad (10)$$

where $f(k_G) = 0.162 + 1.43k_G^{0.44}$.

The Da and k_G values determine the intensity and character of the heat and mass transfer processes in the mixture flow passing through the GCR. First of all, we note the features of the spatial (along $\tilde{z}$) distributions of the concentrations of the main components.

At small values $\mathrm{Da} < 10^{-3}$ and $k_G = 10^{-3}$–10^{-1}, the characteristic time of the stay of the flow in the GCR channel is less than the characteristic time scale of the production of any molecular component of the mixture. The condition (4) is violated, which is equivalent to the inequality $\mathrm{Da} \ll 7\times10^{-3}k_G^{-0.62}$. This mode corresponds to the condition of the fast passage of the mixture through the GCR zone. Almost no chemical reactions occur in the flow, and at the output from GCR, a nonequilibrium system is formed containing silicon and oxygen vapors. Obviously in the reactor-condenser in this mixture, the heterophase processes of the formation of silicon oxides will occur, which leads to a decrease in the efficiency of the method. At $\mathrm{Da} > 10$ and $k_G = 10^{-3}$–10^{-1}, the inequality (4) is also violated, but now $\mathrm{Da} \gg t_{[\mathrm{SiO}]}/t_{[\mathrm{H}_2]}$. All the main processes occur in a quasi-equilibrium manner. At the output from the GCR (Fig. 2a) (as in the thermodynamically equilibrium process) almost the complete oxidation of free Si vapors to SiO takes place with the formation of water vapors (with the concentration equal to the SiO concentration). Free oxygen is absent, but silicon vapors are also absent. In such a mode of processing the gas mixture prepared at the output from GCR, further cooling in a thermodynamically equilibrium manner in the reactor-condenser zone should be transformed in the initial heterogeneous system consisting of Ar, H_2, and condensed

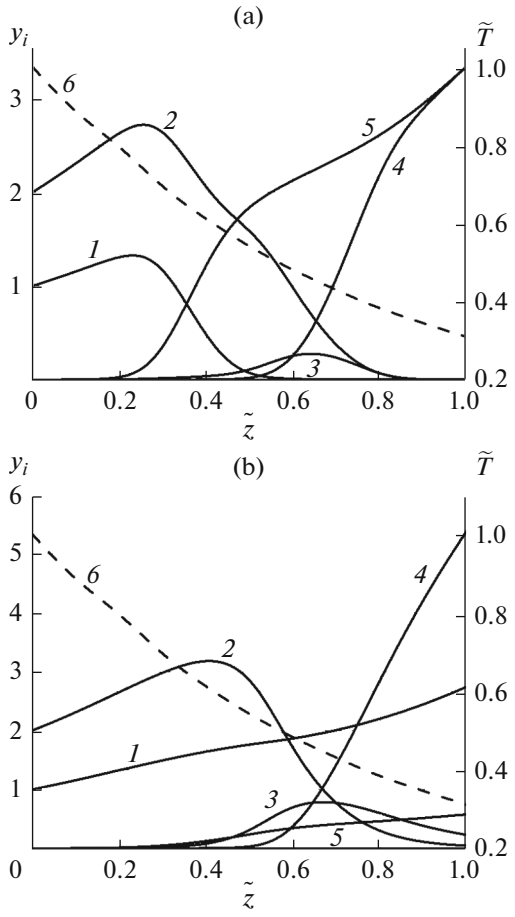

Fig. 2. Dependence of dimensionless concentrations y_i of some components of the mixture and the dimensionless bulk temperature $\tilde{T}$ of the flow on $\tilde{z}$ at Da = 10^2 (a), 10^{-1} (b) and $k_G = 10^{-2}$: *1*—y_{Si}, *2*—y_O, *3*—y_{O_2}, *4*—y_{H_2O}, *5*—y_{SiO}, and *6*—$\tilde{T}$.

SiO_2. At Da = 10^{-3}–10 and $k_G = 10^{-3}$–10^{-1}, condition (4) is fulfilled and can be presented in the form $7\times10^{-3}k_G^{-0.62} \le \mathrm{Da} \ll t_{[SiO]}/t_{[H2]}$. Then the mode in which the process of the formation of SiO is nonequilibrium is implemented (the production of SiO is low), and the reaction of the formation of H_2O occurs with a high velocity in a quasi-equilibrium manner coupling almost all free oxygen (see Fig. 2b). As the calculations have shown, H_2O is produced most efficiently in the GCR region in which the flow temperature varies from 4.5 to 2.0 kK. The composition of the mixture, i.e., silicon and water vapors in an argon medium obtained in this mode at the output from the GCR, excludes processes of the oxidation of Si in the condensation zone providing the conditions of the formation of polycrystalline silicon with the maximum efficiency.

One can introduce the following integral index of the efficiency of the plasma-chemical method: $\varepsilon = \eta_{Si}\eta_{H_2O}$, where $\eta_{Si} = G_{Si}(\tilde{z} = 1)/G_{Si}(\tilde{z} = 0)$ is the ratio of the mass consumptions of silicon vapors, respectively, at the output $G_{Si}(\tilde{z} = 1)$ and input of GCR $G_{Si}(\tilde{z} = 0)$; $\eta_{H_2O} = G^{(O)}_{H_2O}(\tilde{z} = 1)/G_O(\tilde{z} = 0)$ is the ratio of the mass consumption of oxygen transported by water vapors formed at the output of the GCR to the total consumption of oxygen at the input to the GCR. The η_{Si} value determines the amount of free Si vapors at the output of the GCR. The η_{H_2O} value makes it possible to determine the amount of free oxygen and silicon monoxide in the mixture at the output of the GCR and indicates what part of silicon vapors prepared at the output of the GCR in the reactor-condenser can be condensed into polycrystalline silicon. The η_{H_2O}, η_{Si} values and, respectively, ε may vary from 0 to 1. The larger η_{Si} and η_{H_2O}, the higher the concentration of vapor silicon and the lower the concentration of oxygen-containing compounds such as SiO, O, and O_2 at the output of the GCR, and, consequently, there are no conditions for the formation of SiO_2 from them in the reactor-condenser zone. Thus, the efficiency of the method on the whole is maximal at the maximal ε value (i.e., the Si losses are minimal).

Calculations show that at fixed k_G, the parameter ε depends on Da nonmonotonically (see Fig. 3). At values Da < 10^{-3}, Si vapors and free oxygen at the output of the GCR are present in the maximum amounts, so that $\eta_{Si} \approx 1$, but $\eta_{H_2O} \approx 0$ and the efficiency of the process is small ($\varepsilon \ll 1$). The efficiency of the process at Da > 10 is also close to zero ($\varepsilon \ll 1$), since at the output of the GCR silicon vapors are absent ($\eta_{Si} \approx 0$) due to the presence of quasi-equilibrium processes in the

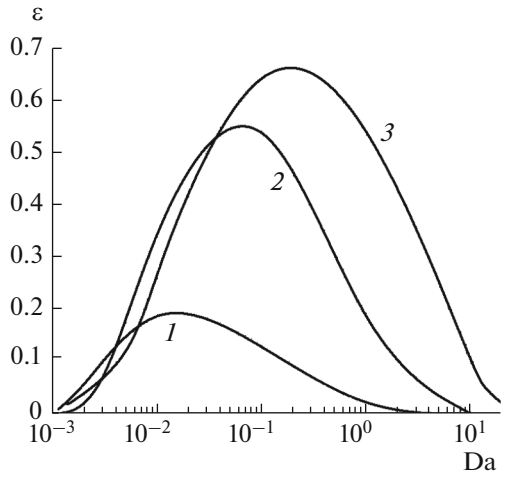

Fig. 3. Dependence of the integral index of the efficiency ε of the plasma-chemical method on Da at different k_G: (*1*) 10^{-1}, (*2*) 10^{-2}, and (*3*) 10^{-3}.

production of gaseous silicon monoxide and water ($\eta_{H_2O} \approx 0.5$). In the range of Damkohler numbers $Da = 10^{-3}$–10, there is an optimum Da_{opt} value at which the index of the efficiency of process ε_{max} has a maximum. The Da_{opt} value, like ε_{max}, depends on k_G: the increase in k_G leads to a decrease in ε_{max} and the displacement of Da_{opt} to the side of lower values. At the increase in k_G from 10^{-3} to 10^{-1}, the value ε_{max} decreases from 0.65 to 0.2. The dependence Da_{opt} on k_G (in the specified interval) can be approximated by the function $Da_{opt}(k_G)Da_{opt}(k_G) \approx 7\times10^{-3}k_G^{-0.5}$.

The decrease in ε_{max} with the increase in k_G means that the efficiency of the method decreases and the value of the consumption of processed quartz is limited. In accordance with the results obtained, one can recommend the range of optimal values $k_{G\text{opt}} = 10^{-2} - 5\times10^{-2}$. Here it should be noted that $k_{G\text{opt}}$ is less than the maximum value of the relative consumption of processed quartz $k_{G\max}$, which is determined by the homogenization process (see Fig. 1).

From relation (10) it is possible to determine the value of the diameter d of the GCR channel for modes with the maximum efficiency of processing (i.e., at $Da = Da_{opt}$) of the quartz concentrate with the relative consumption k_G

$$d \approx \sqrt{\frac{\overline{a}\mathrm{Nu}t_{[H_2]}\mathrm{Da}_{\mathrm{opt}}(k_G)}{f(k_G)}}. \qquad (11)$$

Using relations $l = W_0 t_x = W_0 \mathrm{Da}_{\mathrm{opt}}(k_G) t_{[H_2]}$ and $G_\Sigma = \rho_\Sigma(\tilde{z}=0)W_0\pi d^2/4$, with allowance for (11), the length l of the GCR channel can be calculated from the formula

$$l \approx \frac{4f(k_G)(1+k_G)}{\pi}\frac{G_{\mathrm{Ar}}}{\overline{a}\mathrm{Nu}\rho_\Sigma(\tilde{z}=0)}, \qquad (12)$$

where $\rho_\Sigma(\tilde{z}=0)$ is the mixture density at the input into the GCR.

Figure 4 shows dependences d and l on k_G, calculated from (11), (12). When estimating d and l, the Nusselt number Nu was chosen to be 3.66 [9] and the value of the mean integral coefficient of heat diffusivity $\overline{a}$ and mixture density $\rho_\Sigma(\tilde{z}=0)$ were determined for the equilibrium mixture of Ar, H, O, and Si according to the technique of [10]. It can be seen that the optimum diameter of the GCR channel depends only on the relative consumption of processed quartz k_G being the monotonically decreasing function k_G. The modes with the maximally allowed $k_G \approx k_{G\max} = 0.1$ should be implemented at the channel diameter $d \approx 0.4 \pm 0.1$ cm. The transition to processing of less concentrated mixtures with $k_{G\text{opt}} = (1-5)\times10^{-2}$ required an increase in the GCR channel diameter to the values $d \approx 2 \pm 1$ cm. It should be recalled that the index of the efficiency of the plasma-chemical method increases to $\varepsilon_{max} = 0.55$. The length of the GCR channel l is a monotonically increasing function of k_G and is proportional to the consumption of the plasma-forming gas G_{Ar}. It follows from Fig. 4 that the range of optimum lengths of the GCR channel at $G_{Ar} = 1$–3 g/s (the electrical power of the plasmatron $P_{pl} = 30$–100 kW) and $k_G \approx 10^{-2}$ is within 30–100 cm.

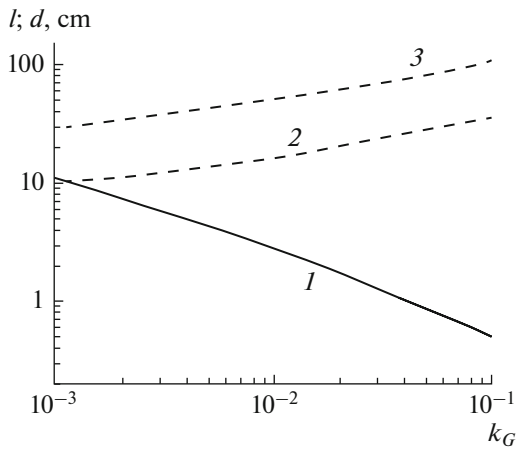

Fig. 4. Dependence of the length l and diameter d of the GCR on k_G for Da_{opt}: (*1*) d, (*2*) l at $G_{Ar} = 1$ g/s, and (*3*) l at $G_{Ar} = 3$ g/s.

As a result, it is possible to recommend the following values of the main mode and construction parameters of the plasma facility for the preparation of silicon: the maximum consumed electrical power of the plasmatron $P_{pl} = 100$ kW, the consumption of the plasma-forming gas $G_{Ar} = 3$ g/s, the consumption of processed quartz $G_{SiO_2} = 3\times10^{-2}$ g/s, and the diameter and the length of the GCR channel $d = 3$ cm and $l = 50$ cm. At the specified parameters, it is possible to implement the process of plasma-chemical processing of the quartz concentrate into silicon with the index of the efficiency of the process on the level $\varepsilon_{max} \approx 0.55$ and rough efficiency (over Si vapor) $G_{Si} \approx 10^{-2}$ g/s. The energy expenses on the implementation of this method are close to the expenses of other existing plasma methods [1, 2], and the practical implementation is simpler.

CONCLUSIONS

On the basis of the calculation-theoretical studies of thermal and chemical processes in the homogenization and gas-phase chemical transformation zones of a plasma facility for the preparation of silicon, it was

established that the efficiency and productivity of the process depends essentially on the values of criteria B_α, Da, and the relative consumption of the processed quartz k_G. It is shown that the optimum values of these quantities are $B_{\alpha\text{opt}} = \left(0.162 + 1.43k_{G\text{opt}}^{0.44}\right)\Big/\text{Da}_{\text{opt}}$, $\text{Da}_{\text{opt}} = 7 \times 10^{-3}k_{G\text{opt}}^{-0.5}$ and $k_{G\text{opt}} = (1-5)\times 10^{-2}$. For optimal modes of plasma processing of quartz, the main parameters of the plasma facility were chosen on the basis of the stationary plasmatron with a consumption of electrical power up to 100 kW providing for the preparation of silicon vapors with an efficiency of up to 10^{-2} g/s and a maximum index of the efficiency on the level $\varepsilon_{\max} \approx 0.5$–$0.6$.

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REFERENCES

1. Bibikov, M.B., Demkin, S.A., Zhivotov, V.K., Zaitsev, S.A., Moskovskii, A.S., Smirnov, R.V., and Fateev, V.N., *High Energy Chem.*, 2010, vol. 44, no. 1, p. 58.
2. Afanas'ev, V.D., Gorokhov, A.D., Gribov, B.G., Evdokimov, B.A., Zinov'ev, K.V., and Krasnikov, G.Ya., RF Patent 2367600, 2009.
3. Grishin, Yu.M., Kozlov, N.P., and Skryabin, A.S., *High Temp.*, 2012, vol. 50, no. 4, p. 459.
4. Grishin, Yu.M., Kozlov, N.P., and Skryabin, A.S., *Inzh. Zh.: Nauka Innovatsii*, 2013, no. 5. http://engjournal.ru/catalog/machin/criogen/716.html.
5. *Combustion chemistry*, Gardiner, W.C., Jr., Ed., Springer, 1984.
6. *Fiziko-khimicheskie protsessy v gazovoi dinamike* (Physical and Chemical Processes in Gas Dynamics), Losev, S.A. and Chernii, G.G., Eds., Moscow: Mosk. Gos. Univ., 1995, vol. 1.
7. *Fiziko-khimicheskie protsessy v gazovoi dinamike* (Physical and Chemical Processes in Gas Dynamics), Losev, S.A. and Chernii, G.G., Eds., Moscow: Mosk. Gos. Univ., 2002, vol. 2.
8. Beers, K.J., *Numerical Methods for Chemical Engineering: Applications in MATLAB®*, New York: Cambridge Press, 2007.
9. Lyakin, M.V., Suris, A.L., and Postnikov, V.M., *Inzh.-Fiz. Zh.*, 1989, vol. 56, no. 1, p. 71.
10. Trusov, B.G., *Inzh. Vestn.*, 2012, no. 8. http://engbul.bmstu.ru/doc/483186.html.

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