Numerical simulation of hydrogen-methane mixture flow through the cylindrical channel in vacuum

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Abstract. Algorithm of the direct simulation Monte Carlo method for the flow of the hydrogen-methane mixture through a cylindrical channel has been developed. Heterogeneous reactions on tungsten channel surfaces and gas-phase reactions are included into model. The influence of the channel length on the degree of hydrogen and methane dissociation in the gas mixture have been analyzed. The obtained results can be useful for optimization of gas-dynamic sources of activated gas diamond synthesis.

1. Introduction

The Hot Wire Chemical Vapor Deposition (HWCVD) method is widely used to deposit thin films from an activated precursor gas, including for the synthesis of diamond structures from a mixture of hydrogen with carbon-containing gases [1-3]. The gas-jet modification of this method has been actively developed in recent years [4-6]. It is based on the thermal activation of a hydrogen-methane mixture flowing through a heated tungsten channel. A specific feature of this approach is the use of heterogeneous processes of dissociation of hydrogen due to multiple collisions of molecules with the hot surface [3, 6, 7]. Optimal conditions for diamond synthesis by this method are not known.

Deposition of diamond-like structures by the gas-phase method is a multi-parameter problem [1-3, 6]. In experiments, some parameters of the process can be accurately controlled: flow rates of methane and molecular hydrogen, temperatures of the activating surface and target, and pressure in the expansion chamber. Despite the developed measurement tools, measurements in the gas phase are rather complicated and involve certain constraints on accuracy and localization. Therefore, it is important to use numerical simulation of gas mixture flows for effective search for optimal deposition modes. Under prescribed conditions on the surface, it is determined by the ratio of the concentrations of atomic hydrogen and fragments of decomposition of methane (in our case, methyl) colliding with the surface [1-3]. The probability of methyl formation in the interaction of methane with heated tungsten is rather small [8], therefore gas-phase reactions are the main source of methyl.

In the presented work, the direct simulation Monte Carlo (DSMC) method [9] was used for studying the dynamic of chemical reactions in the hydrogen-methane mixture flow. The study was carried out for different ratios of the channel length to its radius. In the course of the simulation, special attention was paid to the evaluation of the effect of the hydrogen dissociation and recombination coefficients on the degree of hydrogen and methane dissociation at the channel outlet. The influence of various conditions for supplying the mixture into the channel on the simulation results was studied.
2. Statement of the problem

The formulation of the problem was chosen close to the experiments of [4-6]. A gas mixture CH₄/H₂ with an initial temperature of 1800K is injected into a cylindrical channel with diameter D and length L_{cold} + L (figure 1). The channel consists of two parts: input cold section (domain 1) and output hot section (domain 2). The wall temperature is 1800 K in the input section and 2500 K in the output one.

On the right of the channel there is a calculated area in the form of a second cylindrical channel (domain 3). It ensures the correct simulation of gas outflow into vacuum. The diameter of the second channel is D_{1} > D, and its length is L_{1}. At a distance L_{1} from the exit from the hot section of channel there is a circular substrate of diameter D_{s}. The substrate temperature T_{s} is taken to be 1100 K. Particles move freely from one channel to another. If a particle hits the wall of the second channel, it is absorbed.

To describe the process of particle interaction with the surface the model of specular-diffuse reflection [9] was used. Using this model requires accommodation coefficient α, which allow one to describe the process of gas/surface interaction: the particle is reflected from the surface in a diffuse manner with complete accommodation of momentum and energy with a probability α, and specular particle reflection occurs with a probability (1-α). In collision with the wall of the channel a hydrogen molecule can dissociate into two atoms, and two hydrogen atoms can recombine into a molecule: H₂ ↔ 2H. To describe the processes of dissociation and recombination, we use coefficients α_d and α_r: the hydrogen molecule splits with probability α_d into two atoms, which are reflected from the surface with complete accommodation of momentum and energy; and with probability (1 - α_d), it remains a molecule. Similarly, the hydrogen atom recombines with probability α_r to the molecule, which is reflected from the surface with complete accommodation of momentum and energy, and with probability (1 - α_r), it does not recombine. The particles that have not entered into chemical reactions are reflected from the surface according to the accommodation coefficient.

In the gas phase, the following reactions were simulated:

\[ H + H + H_2 \leftrightarrow H_2 + H_2, \]  
\[ H + CH_4 \leftrightarrow CH_3 + H_2. \]  

Two values were used to evaluate the dissociation degree of hydrogen and methane:

\[ K_{d_H} = \frac{n_{H}}{2n_{H_2} + n_{H}}, \quad K_{d_C} = \frac{n_{CH_4}/n_{CH_3} + n_{CH_3}}{n_{CH_4}}. \]

Here n_H and n_{H_2} are densities of atomic and molecular hydrogen, and n_{CH_4} and n_{CH_3} are densities of methane and methyl, respectively.

3. Computation method

In the present work, the DSMC [9] is used for a flow numerical analysis. The DSMC method is based on splitting of the continuous motion of particles and their collisions into two successive steps:

- motion of particles within a time interval Δt, according to their velocities;
– simulation of collisions between particles within a time interval \( \Delta t \) (using a selected procedure for simulation of collisions).

In this work, the axisymmetric algorithm of the DSMC method was adapted to the calculation of flows in a cylindrical channel and behind it (figure 1). To describe the collisions of particles, a variable soft sphere model (VSS) was used [9]. The different accommodation coefficients were specified for the cold and hot parts of the channel. The choice of dissociation and recombination coefficients for hydrogen on channel surface was carried out on the basis of a numerical technique [7, 8]. The recombination of atomic hydrogen and the partial absorption of methane were simulated on the substrate surface [3, 10]. Only recombination was simulated in the hydrogen interaction with the cold channel surface, while dissociation simulating was included in the interaction with the hot one.

A more detailed description of the parameters of the DSMC method can be found in [10]. To organize the simulation of gas-phase reactions (1)-(2), the approach from the work [11] was used.

The determining parameters of the problem are the Knudsen number \( Kn = \lambda / D \) (\( \lambda \) is the mean free path in the undisturbed flow of molecular hydrogen with the density \( n_0 \) and the temperature \( T_0 = 1800 \)), the temperature ratio \( T_r \) of the channel length to its diameter \( L/D \), initial mixture composition, the accommodation coefficients \( \alpha \), the coefficients of dissociation and recombination of hydrogen on channel surface \( \alpha_d \) and \( \alpha_r \). The flow macroparameters (the density, the velocity, the temperature) were calculated. The value \( n_0, T_0, \lambda \) and the most probable molecular thermal velocity of molecular hydrogen at the temperature \( T_0 \) were used as reference values to reduce the problem to non-dimensional one.

Obtaining more detailed information about the concentrations of particles approaching the substrate requires data on the degree of methane decomposition into fragments. In our case, it is possible to use a one-dimensional approach [12] for calculating the changes in the mixture composition along the flow axis by means of solving a system of chemical kinetics equations. A mixture of 11 components is considered: \( \text{H}_2, \text{H}, \text{CH}_4, \text{CH}_3, \text{CH}_2, \text{CH}_2(S), \text{CH}, \text{C}_2\text{H}_2, \text{C}_3, \) and \( \text{C}_2\text{H} \). The computations are performed for 13 forward and backward chemical reactions.

### 4. Results and Discussion

The calculations were carried out for the transition regime (Knudsen number \( Kn = 1 \)) and for hydrogen- methane mixture (3% of methane). At first, the impact of the length of the channel cold part on the mixture flow was investigated. The increase in the length of the cold part leads to an increase in the number of simulated particles, an increase in the time to reach the steady-state regime, and, correspondingly, an increase in the computational costs for obtaining the result with a given accuracy. A short cold part of the channel (or its absence) results in a distortion of the flow macroparameters, especially for short channels.

Figure 2 shows the values of the density, velocity and translational temperature of molecular and atomic hydrogen, methane and methyl averaged over channel cross-section at the entrance to the hot part of the channel. The data are presented for three values of the length \( L_{\text{cold}} \) (0, 3\( \lambda \), 8\( \lambda \)) and two values of the ratio \( L/D \). The obtained data indicate that an increase in the cold part from 3 free mean paths to 8 free mean paths did not lead to a significant change in the flow parameters at the entrance to the hot part. Therefore, the length of the cold part 3\( \lambda \) was used in subsequent calculations. Particles “forget” their initial distribution function sufficiently rapidly because of collisions with other particles [13] and with the channel walls.

The concentration of atomic hydrogen is one of the determining parameters for the gas-phase deposition of diamond-like structures. Atomic hydrogen participates in the gas-phase decomposition of methane and in the formation of diamond structures on the substrate. It is formed as a result of heterogeneous dissociation on the heated surface of tungsten. Its recombination on the tungsten surface is also possible. To simulate heterogeneous hydrogen reactions on the channel surface, values of the dissociation and recombination coefficients \( \alpha_d = 0.27 \) and \( \alpha_r = 0.068 \) determined by the procedure from the works [7, 8] and the experimental data [14, 15] are used.
Since the probability of methane decomposition on the channel surface is small [8], heterogeneous reactions involving methane on the channel surface were not simulated. Note that the dissociation rate of hydrogen on the surface significantly depends on the ratio of the number of free activation sites on the tungsten surface and the frequency of collisions of hydrogen molecules from the gas phase with the surface. It has long been known that the concentration of atomic hydrogen near a hot wire increases with an increase in pressure and reaches a maximum at a pressure of ~10–20 Torr; then the concentration stabilizes (see, for example, [16]). In order to explain this fact, a two-step model of the heterogeneous interaction of hydrogen with a tantalum surface (a metal that is similar in many properties to tungsten) was proposed in work [17]. An important feature of this model which allows describing the processes of dissociation and recombination of hydrogen over a wide range of pressures is the inclusion of a decrease in the number of free activation sites due to their occupation by hydrogen atoms. Note that within this model the fraction of occupied activation sites on the tantalum surface decreases with increasing temperature. It became insignificant at a temperature of 2500 K. The values of dissociation and recombination coefficients used in our work were determined for low pressures (< 1 Torr).

Figure 3b shows the mixture composition averaged over the channel cross-section. In order to verify the correctness of using the only reactions (1) - (2) for analysis of the change in the mixture composition, the calculations by the one-dimensional approach [12] were fulfilled in the parameter range under consideration. Figure 3b shows the mixture composition during flow through a long channel L/D = 6. It can be noted that methyl remains the predominant carbon-containing component of the mixture. Therefore, taking into account reactions (1) - (2) is sufficient for the analysis of the flow in the parameter range under consideration. According to the literature data [18, 19], tungsten carburization is insignificant at a temperature of 2500 K, which assumes the preservation of its catalytic activity. However, the flow of methane through the channel for a long time can lead to a decrease in the catalytic activity of the surface (a decrease in the number of free activation sites). To estimate the effect of this process on the degree of hydrogen and methane dissociation at the channel outlet, calculations were carried out for three variants of dissociation and recombination coefficients. In this case, the decrease in the number of free activation sites was taken into account through a decrease in dissociation and recombination coefficients.
The dissociation degrees of hydrogen and methane at the outlet from the channel for three variants of dissociation and recombination coefficients for different values of the channel length are shown in figure 4. Here, line 1 corresponds to a "clean" surface ($\alpha_d = 0.27$, $\alpha_r = 0.068$), line 2 corresponds to the variant in which the number of free activation sites decreased by half ($\alpha_d = 0.135$, $\alpha_r = 0.034$), and line 3 corresponds to the variant in which the number of free activation sites decreased three-fold ($\alpha_d = 0.09$, $\alpha_r = 0.0226$). The calculations show that the increase in the degree of hydrogen dissociation slows down with an increase in the channel length and practically stops at $L/D > 6$. The sensitivity of the hydrogen dissociation degree to a decrease in the surface catalytic activity is maximal for short channels and decreases with an increase in the channel length. Reducing the amount of atomic hydrogen in the flow slows down the decomposition of methane. Numerical experiments show that the channel length has a significant effect on the degree of methane dissociation as it grows rapidly with an increase in channel length.

**Figure 3.** a) Axial distribution of the density and velocity of the mixture components. b) Distributions of the molar fractions of the mixture components along the flow axis. $L/D = 6$.

**Figure 4.** Dissociation degree of hydrogen $K_{dH}$ (a) and methane $K_{dC}$ (b) at the outlet from the channel for three variants dissociation and recombination coefficients. Line 1 corresponds to $\alpha_d = 0.27$, $\alpha_r = 0.068$, line 2 corresponds to $\alpha_d = 0.135$, $\alpha_r = 0.034$, and line 3 corresponds to $\alpha_d = 0.09$, $\alpha_r = 0.0226$. The dissociation degrees of hydrogen and methane at the outlet from the channel for three variants of dissociation and recombination coefficients for different values of the channel length are shown in figure 4. Here, line 1 corresponds to a "clean" surface ($\alpha_d = 0.27$, $\alpha_r = 0.068$), line 2 corresponds to the variant in which the number of free activation sites decreased by half ($\alpha_d = 0.135$, $\alpha_r = 0.034$), and line 3 corresponds to the variant in which the number of free activation sites decreased three-fold ($\alpha_d = 0.09$, $\alpha_r = 0.0226$). The calculations show that the increase in the degree of hydrogen dissociation slows down with an increase in the channel length and practically stops at $L/D > 6$. The sensitivity of the hydrogen dissociation degree to a decrease in the surface catalytic activity is maximal for short channels and decreases with an increase in the channel length. Reducing the amount of atomic hydrogen in the flow slows down the decomposition of methane. Numerical experiments show that the channel length has a significant effect on the degree of methane dissociation as it grows rapidly with an increase in channel length.
5. Conclusions
In this study, the algorithm of DSMC method is used to investigate the hydrogen-methane mixture flow through a cylindrical channel. The effect of heterogeneous and gas-phase reactions on flow has been analyzed. The influence of the channel length on the degree of hydrogen and methane dissociation in the gas mixture at the channel outlet is shown. The analysis of the results obtained provides insight into the most probable chemical processes in the gaseous phase under nonequilibrium conditions of gas-jet deposition. A one-dimensional approach based on the solving of the equilibrium chemical kinetics equations is used to analyze gas-phase methane decomposition. Obtained results can be useful for optimization of gas-dynamic sources of activated gas for diamond film synthesis.

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