

Modeling the flow of activated $H_2 + CH_4$ mixture by deposition of diamond nanostructures

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Abstract. Algorithm of the direct simulation Monte Carlo method for the flow of hydrogen and methane mixture in a cylindrical channel is developed. Heterogeneous reactions on tungsten channel surfaces are included into the model. Their effects on flows are analyzed. A one-dimensional approach based on the solution of equilibrium chemical kinetics equations is used to analyze gas-phase methane decomposition. The obtained results may be useful for optimization of gas-dynamic sources of activated gas diamond synthesis.

The method of Hot-Wire Chemical Vapor Deposition (HWCVD) is widely used for diamond deposition from an activated precursor gas. Its main feature is activation of a gas precursor on metallic surfaces: wires, placed in a virtually resting gas [1] or in high-speed flows [2], as well as cylindrical channels [3]. The presented work is devoted to the numerical study of gas-dynamic aspects of the rarefied gas flow in a hot tube with dissociation and recombination on the surface. The algorithm of direct simulation Monte Carlo (DSMC) method [4] with majorant frequency scheme [5] is used for the numerical analysis and optimization of approaches to deposition of diamond-like films using the hot tubes. In [6-8] the importance of taking into account dissociation and recombination in the analysis of flows in the tubes was shown. The use of a cylindrical channel as an activator provides better gas dissociation due to multiple collisions with the surface [6-8] in comparison with the case of interaction of the supersonic flow with a wire obstacle [9,10]. A one-dimensional approach based on the solution of equilibrium chemical kinetics equations was used to analyze gas-phase methane decomposition.

The main goal of the presented work is to analyze the influence of the determining parameters on the composition and energy state of the gases flowing to the substrate. Particular attention is paid to the behavior of atomic hydrogen, one of the main components that determine the synthesis of diamond structures.

1 Computation methods

The mixture of molecular hydrogen with methane [1, 11] is used as the initial gas. The VSS molecular model [4] was adopted for simulation of molecular hydrogen, atomic hydrogen, and methane. Data for molecular hydrogen and methane are taken from [4]. To describe

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interaction of the gas particles with the surface, the model of specular-diffuse reflection was used [4]. 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 $(1 - \alpha_d)$, 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 $(1 - \alpha_r)$, it does not recombine. The particles that have not entered into chemical reactions are reflected from the surface according to the accommodation coefficient.

Different accommodation coefficients were specified for the cold and hot parts of the channel. The choice of dissociation and recombination coefficients for hydrogen was carried out based on a numerical technique [7] using experimental data [12, 13]. A more detailed description of the DSMC method parameters is given in [14]. Only recombination was simulated in hydrogen interaction with cold channel surface, while dissociation simulating was included in the interaction with the hot one. The analysis showed that under the involved conditions, gas-phase hydrogen dissociation and recombination make a negligible contribution to the result in comparison with the heterogeneous reactions. Consequently, gas-phase reactions of hydrogen can be neglected.

Obtaining more detailed information about the concentrations of particles approaching the substrate requires data on the degree of methane decomposition into fragments. The flow analysis shows that the flow macroparameters are distributed fairly uniformly over the radius. In this case, it is possible to use a one-dimensional approach for calculating the changes in the mixture composition along the flow axis by means of solving a system of chemical kinetics equations. Following [15], a mixture of 11 components is considered in solving the equations of equilibrium chemical kinetics: H_2 , H, CH_4 , CH_3 , CH_2 , $CH_2(S)$, CH, C, C_2H_2 , C_3 , and C_2H . The computations are performed for 13 forward and backward chemical reactions. The rate constants of reactions are calculated on the basis of the data obtained in [16].

2 Numerical experiments

Gas mixture of $H_2 + CH_4$ with temperature of 1200 K flows through the cylindrical channel into a chamber with a substrate (Fig. 1). The channel consists of two parts: inlet part $L_{cold} = 10$ mm with the cold wall ($T = 1500$ K) and outlet part $L_{hot} = 15$ mm with the wall temperature of 2400 K. The cylinder diameter is 3 mm, and the substrate diameter is 14 mm. The substrate temperature is 1300 K, and the distance to the substrate is $L_{sub} = 10$ mm. The hydrogen flow rate is 1500 sccm. Methane concentration is 10%. The chamber is initially filled with molecular hydrogen with background pressure $P = 0, 2$ and 20 Torr. Such conditions correspond to typical experiments on gas-jet deposition of diamond-like films [17-19].

The number density and streamlines of methane for $P = 0$ are shown in Fig. 2. The spatial distributions in Fig. 2 give a general notion about the features of the flow under consideration. Here and below, planes $X = 0.06$ and $X = 0.07$ correspond to the cutoff of the hot tube and to the substrate position, respectively. Four areas can be distinguished: the cold and the hot parts of the channel, the outflow into the vacuum, and the compressed layer near the substrate. An increase in the background pressure up to 2 Torr has a negligible effect on the flow in the tube. The presence of a background gas leads to the formation of the denser compressed layer. Axial distribution of the degree of hydrogen dissociation $K = n_H / (2n_{H_2} + n_H)$ is shown in Fig. 3. Here n_{H_2} and n_H are the number densities of molecular and atomic hydrogen. The distribution of relative concentration of mixture components along the flow axis for the case of outflow to vacuum is shown in Fig 4.

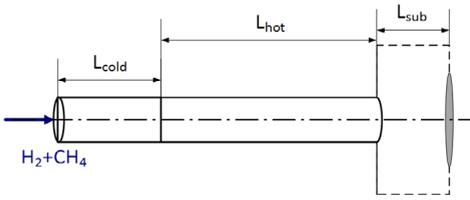


Fig. 1. The computational domain.

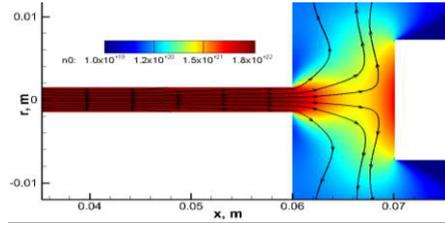


Fig. 2. The number density and streamlines of methane for the background pressure $P = 0$.

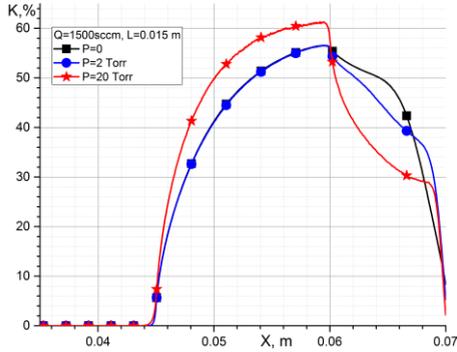


Fig. 3. Axial distribution of the degree of hydrogen dissociation for different background pressure.

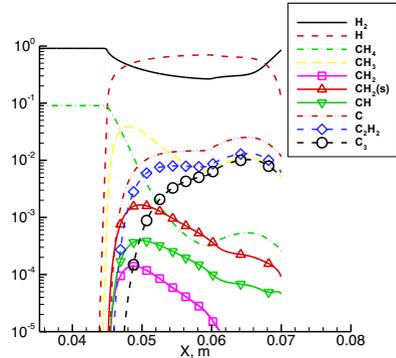


Fig. 4. Axial distribution of relative concentration of mixture components.

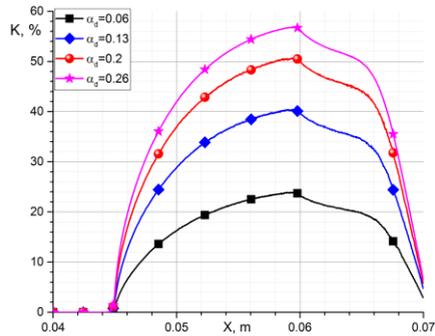


Fig. 5. Axial distribution of the degree of hydrogen dissociation for the vacuum outlet and different dissociation coefficients on tube surface.

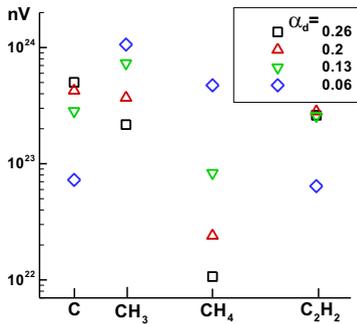


Fig. 6. nV for the four components of the mixture for the vacuum outlet and different dissociation coefficients on tube surface.

Data are obtained from the one-dimensional approach. Methane rapidly decomposes into separate fragments in the hot part of the tube. For the case under consideration, the predominant fragments are carbon, methyl, acetylene, and C_3 . There is some stabilization of the mixture composition in the region of gas expansion in the chamber. One of the problems of the deposition technique under consideration is associated with the possibility of carburizing of the tungsten channel [20, 21]. In this case, catalytic activity of the tungsten surface decreases, while the rate of methane decomposition significantly depends on the amount of atomic hydrogen. Therefore, numerical experiments were conducted to assess the influence of the "catalyticness" of tungsten surface on the degree of hydrogen dissociation and methane decomposition. Axial distribution of the degree of hydrogen dissociation is shown in Fig. 5. The probability of dissociation $\alpha_d = 0.26$ corresponds to a

"clean" surface. The fluxes of various mixture components near the substrate are presented in Fig. 6. The decrease in dissociation probability leads to the expected decrease in the hydrogen dissociation degree at the channel outlet. It results in a decrease in the methane decomposition, and its amount in the mixture grows up. Calculations show that in the cases under consideration atomic hydrogen is sufficient to form a large amount of methyl. However, the decrease in the amount of atomic hydrogen leads to a decrease in further fragmentation of methyl, which results in a decrease in the amount of carbon and acetylene.

3 Conclusions

In this study, the algorithm of DSMC method was used to study the hydrogen and methane mixture in a cylindrical channel. The effect of heterogeneous reactions on flows has been analyzed. A one-dimensional approach based on the solution of equilibrium chemical kinetics equations was used to analyze gas-phase methane decomposition. The obtained results may be useful for optimizing gas-dynamic sources of activated gas by diamond synthesis. They are related to problems of heat transfer by non-equilibrium flows in channels.

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