Comparison of continual and molecular modeling of gas flow for diamond deposition

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Abstract. For the purpose of simulation of diamond-growth processes, the comparison of reacting gas flows modelled in a heated cylindrical channel has been performed by two different approaches: DSMC method and solution of Navier-Stokes equations. The impact of the channel length on the degree of hydrogen and methane dissociation in the gas mixture has been analyzed. The obtained data were compared with the experimental data.

1. Introduction

The Hot-Wire Chemical Vapor Deposition (HWCVD) technique is widely used for the diamond synthesis [1-3]. This technique is based on the use of hydrogen and carbon-bearing gas mixtures, activated by the hot-metal surfaces. The interaction of gases with hot metal causes different precursors formation, which can be deposited on the relatively cold substrate surface. Several last years the significant progress in the gas-jet synthesis of diamonds by technique based on the thermal activation of the hydrogen/methane mixture flow through the heated tungsten channel was attained [3-6].

Since the CVD is the multifactor governed process [1-3], the optimization of experiments and analysis requires gas-dynamic and kinetic simulations. Diamond and carbon structures formation is controlled by the content of the carbon-bearing molecules delivered to the surface and their velocity distribution functions. In [6-12], the direct simulation Monte Carlo (DSMC) method [13] was employed to study the characteristics of the flow with heterogeneous reactions in a cylindrical channel. In [6, 10-12], the 1D approach was applied for analysis of methane decomposition due to gas-phase reactions.

In this paper two approaches are employed for reacting gas flow simulation: the DSMC method and the method based on solving of the Navier-Stokes (NS) equations. Gas-dynamic flow parameters obtained within both methods are compared. The channel length impact on the methane degradation and diamond deposition is studied by solving the NS equations.

2. Problem statement

The considered problem statement was chosen to approximate the experimental setup [4-6]. The H₂/CH₄ mixture is delivered through a cylindrical channel (Fig. 1). The channel consists of two parts: cold input section (cylindrical domain 1) and hot section (cylindrical domain 2). The length of the input section h is 0.01 m in all computations, whereas the length of the hot section L is varied. The
wall temperature of hot section is set 2400 K, the inlet gas temperature and temperature of cold domain are 300K, and substrate temperature is 1200 K. The flow rates of H2 and CH4 are 1500 sccm and 15 sccm, respectively. The mixture expands from the channel into the chamber with a fixed pressure (cylindrical domain 3). At distance $L_{\text{sub}} = 0.01$ m from the channel exit, a substrate is located, onto which carbon is deposited. The substrate diameter is 0.016 m. The channel length $L$ is varied from 0.011 m to 0.033 m, the channel diameter is set 0.003 m. Two approaches for the reacting gas mixture axisymmetric flow description were employed: the DSMC method and method based on the NS equations.

![Figure 1. Scheme of the gas-jet CVD reactor.](image)

The DSMC consists in modeling the particles movement and collisions with each other and boundaries. The employed DSMC algorithm takes into account both homogeneous and heterogeneous chemical reactions (see [11] for details). For mixture composition analysis the 1D approach based on the solving the set of chemical kinetics equations is used [11]. The 11-component mixture is considered: H2, H, CH4, CH3, CH2, CH2(s), CH, C, C2H2, C3, C2H. Thirteen pairs (forward and backward) of the gas-phase chemical reactions are taken into account. The main source of chemical transformations in the mixture is decomposition of molecular hydrogen on the hot surfaces. On the remaining surfaces, only hydrogen recombination is considered (see [11] for details).

One of the disadvantages of the DSMC method is its significant time consumption when applied for rather high pressure conditions: calculations for 20 Torr requires about 30 days on a processor of the i7-5820k Haswell-E type. Correct consideration of the aforementioned set of chemical reactions also encounters difficulties due to significant difference (of several orders of magnitude) of different species concentrations.

The splitting the velocities and temperatures of the light and heavy components have been observed within the DSMC simulations, however impact of those effects on the chemical species concentrations is almost invisible. That makes it possible to employ the continuous media approach, using NS equations with the same set of the gas-phase and surface reactions. Thermodynamic functions were calculated via JANNAF coefficients. Maxwell-Stefan equations were solved for the diffusion matrix calculation. No thermal diffusion was taken into account. On the inlet the flux and temperature have been set, while on the outlet the pressure was fixed.

Large-scale vortex structures have been observed in the domain near the outlet. Those vortexes cause the reverse flow delivering different species (mostly $H_2$ and $CH_4$) to the near-substrate zone. Since the vortex scale was larger than the calculation domain, the latter was varied till its further enlargement did not affect the mixture in the near-substrate zone 3 (max sizes: 28 mm × 24 mm). It was concluded that reverse flows may not be taken into account as the factors affecting the growth process.

3. Results and discussion

At the first stage, for comparison of the mentioned above approaches several calculations under close conditions have been performed. The results of calculations of expansion into space with a background gas pressure of 2 Torr without volumetric chemical reactions are presented in Fig. 2. It is
visible that though the flow is rarefied with essential non-equilibrium and simulation methods differing in their nature, the results are close to each other.

\[ \text{Figure 2. Gas-dynamic parameters distribution along the axis: a – pressure, b – number density, c – temperature, d – velocity along the axis direction.} \]

At the second stage, the calculations of flows with gas-phase reactions on the basis of the NS equations for the cylinder of the different length and pressure of 2 and 20 Torr have been performed. Distributions of the gas-dynamic parameters along the symmetry axis for the cylinders of three lengths are presented in Fig. 3. The results of calculations without reactions are also presented. It can be seen that the gas is heated rapidly after entering the hot zone, and is slowly cooled after expanding into the filled space of the chamber. The sharp temperature drop occurs in a compressed layer near the substrate. Gas accelerates during its motion through the channel. After entering the chamber, the gas flow transforms. This leads to the decreasing in Vx. Another reason of that decrease consists in deceleration of gas on the background gas as well as on the compressed layer. It should be noted that the gas-phase reactions had a slight effect on the gas flow.
Atomic hydrogen plays the important role in the diamond synthesis from the gas phase. On the one hand, it stimulates the diamond synthesis directly on the surface, and on the other hand, it initiates fragmentation of methane due to gas-phase chemical reactions. As mentioned in [10], one of those fragments, methyl is the main component in the diamond deposition within the gas-jet synthesis method. Figure 4 presents the axis distributions of the hydrogen dissociation degree $\alpha = \frac{n_H}{(2n_H^2 + n_H)}$ and methyl number density for 20 Torr.

The data on average number densities of the main species on the substrate at 2 Torr and 20 Torr are presented in Fig. 5. The simulations with simple deposition model (the probability of deposition of all carbon radical species excluding CH3 is set 0.05, for CH3 it is 0.005) were performed. Modern studies of the surface chemistry of the diamond deposition [14,15,16] does not allow us to create the adequate
model of that process adjusted for using in gas-dynamic simulations. Therefore, special attention will be drawn for its study in our further research.

Figure 6 shows the profiles of the deposition rate of some main species along the substrate for different channel lengths. The experimental data from [6] are also presented. From a comparison of experimental data and simulation data it can be seen that not only parameters of surface deposition reactions but also the coefficients of gas-phase reactions and recombination/dissociation of hydrogen need to fit to these conditions. Future studies will be carried out in this direction.

![Figure 5](image1.png)

**Figure 5.** Average number density of components above substrate for 2 (left) and 20 Torr (right).

![Figure 6](image2.png)

**Figure 6.** The deposition of C, C3, CH3 and CH2 radicals on substrate, “diamond” is experimental data from [6].
Conclusions

Comparison of the flow gas-dynamic parameters obtained by the continuous media (NS equation solving) and by molecular simulations (DSMC method) has been performed. Analysis of the results has shown that even for the cases when the flow is rather rarefied and characterized by essential non-equilibrium and though simulation methods are different in their nature, results are close to each other. Simulations based on the NS equation solving have shown that the channel length weakly impacts the final hydrogen dissociation degree, while methane decomposition strongly depends on it. Impact of gas-phase reactions on flow parameters is shown to be small. Thus, it is shown that the solution of the NS equation can be used to fit the parameters of chemical processes in gas-jet deposition of diamonds.

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