Influence of the conditions of methane decomposition on gas-jet synthesis of diamond structures

A A Emelyanov, M Yu Plotnikov and I B Yudin*
Kutateladze Institute of Thermophysics SB RAS 630090, Novosibirsk, Russia

*E-mail: yudinib@gmail.com

Abstract. The present work is devoted to a numerical and experimental investigation of the effect of methane decomposition conditions on the growth of diamond structures during gas-jet deposition. The results of experiments on the diamond gas-jet synthesis from methane and hydrogen mixture flows are presented. The direct simulation Monte Carlo method in cylindrical geometry for numerical analysis of these experiments was applied. A one-dimensional approach based on the solution of equilibrium chemical kinetics equations was used to analyze gas-phase methane decomposition. The conducted researches have shown that at decrease in time of decomposition of methane in absence of high temperatures of the fed mixture it is possible to receive higher rates of growth of diamond structures. The obtained results can be useful for optimization of gas-dynamic sources of activated gas diamond synthesis.

1. Introduction
The method of gas-phase deposition using thermal activation (Hot Wire Chemical Vapor Deposition (HWCVD)) of precursor gases is widely used for the synthesis of diamond structures [1, 2]. This method is based on the using of mixtures of hydrogen with hydrocarbons activated on hot metal surfaces and interacting with a relatively cold substrate. Gas-jet modification of the method has been actively developed in recent years [2-6]. Under the given conditions on the substrate, the deposition rate of diamond structures is determined by the ratio of concentrations of atomic hydrogen and fragments of the original carbonaceous gases (in our case, methane), colliding with the substrate surface. The numerical study [7] showed that it is possible to choose methane decomposition conditions to provide optimal conditions for gas-jet synthesis of diamond structures.

The presented work is devoted to the numerical and experimental investigation of the influence of methane decomposition conditions on the growth of diamond structures.

2. Experimental technique
The hydrogen channel 1 with a diameter of 0.013 m and the tube 5 with a diameter of 0.003 m are made of two-layer tungsten foil with a thickness of 30 µm (figure 1). Inside the hydrogen channel a cylindrical spiral 2 is accommodated coaxially. Spiral 2 is made of tungsten wire with a diameter of 0.001 m. The length of the hot part of the activator $L$ in experiments was established 0.011, 0.022 and 0.033 m, the distance to the substrate was $L_{sub} = 0.01$ m. The coil with a winding diameter of 0.008 m has a different number of turns depending on the length of the hot part of the activator. Heat shield 6 with a diameter of 0.017 m is made of two-layer molybdenum foil. The length of the supply part of the
tube 4 was 0.03 m, its temperature in the absence of cooling reached 1300 K, while on cooling the temperature was about 300 K. Substrate 3 has a diameter of 0.03 mm. The H₂ + CH₄ mixture is fed to the tube 5, and only hydrogen is injected into channel 1. Temperatures of tubes 1, 4, 6 and molybdenum substrate 3 were measured by tungsten-rhenium thermocouples. Experiments on diamond synthesis were carried out on reactors with channels of length \( L = 0.011, 0.022 \) and 0.033 m. The temperature of the reactor channel 5 was set equal to 2400 K at a distance of 0.005 m from the outlet of the channel by selecting the heating power of the spiral.

Separate supply of hydrogen and methane to the substrate allows to protect the spiral from the direct ingress of carbon to the spiral. However, when reflected from the substrate and due to diffusion, methane decomposition products may enter the hydrogen channel and cause carbonization of the spiral. The carbonization changes the spiral catalytic properties [8], which can affect the rate of deposition of diamond structures. Control of the degree of the spiral carbonization was carried out through the measurement of its electrical resistance. It was found that the change in the electrical resistance of the spiral during the experiment by no more than 20% provides good repeatability of the deposition rate and morphology of the resulting diamond coating. Further experiments satisfying this criterion were used for the analysis.

The experiments were performed under the following conditions of methane decomposition: temperature of the inlet tube 4 was 300 K; the temperature of the tube 5 was 2400 K; the time of synthesis was 3 hours; the pressure in the deposition chamber was 20 Torr; hydrogen flow rate in both channels was 1500 sccm, the methane flow rate was 8 sccm.

3. Computation methods
The algorithm of the direct simulation Monte Carlo (DSMC) method [9] is adapted for calculating flows in cylindrical channels and behind them (see figure 1). The majorant frequency scheme [10] is used in the computations. A gas mixture (1%) CH₄/H₂ with an initial temperature of \( T_s \) is injected into a cylindrical channel with diameter \( d = 0.003 \text{ m} \) and length \( h + L \) (figure 2). The channel consists of two parts: input section (cylindrical domain 1) and output section (cylindrical domain 2). The length of the input section \( h \) is 0.01 m in all computations, whereas the length of the output section \( L \) is varied. The wall temperature is \( T_{ws} \) in the input section and 2400 K in the output one. The mixture expands...
from the channel into the vacuum chamber (cylindrical domain 3). At the distance $L_{\text{sub}} = 0.01 \, \text{m}$ from the channel exit, there is a substrate onto which diamond is deposited. The diameter of the substrate is $0.015 \, \text{m}$. The substrate temperature is taken to be $1300 \, \text{K}$. The flow rate of hydrogen is $1500 \, \text{sccm}$. The pressure in the chamber is $20 \, \text{Torr}$. Three values of the channel length $L$ ($0.011$, $0.022$, and $0.033 \, \text{m}$) and two initial temperatures of $T_i$ ($300$ and $1500 \, \text{K}$) are used in the computations.

The calculations were performed for the mixture of the $\text{H}_2$, $\text{H}$ and $\text{CH}_4$. Interparticle collisions are considered with the use of the variable soft sphere (VSS) model [9]. Particle/surface interaction is described by the specular-diffusion reflection model typical for rarefied gas dynamics [9]. Dissociation (recombination) of hydrogen is described with a coefficient $\alpha_d$ ($\alpha_r$), which means that a molecule dissociates with a probability $\alpha_d$ (in this case, atoms leave the surface with complete accommodation of momentum and energy), and a molecule is simply reflected from the surface with a probability $(1 - \alpha_d)$. The situation is similar for the coefficient $\alpha_r$: atoms recombine with a probability $\alpha_r$ (in this case, the resultant molecule leaves the surface with complete accommodation of momentum and energy) and atoms are reflected from the surface with a probability $(1 - \alpha_r)$. In the presented work we used the following coefficients of dissociation and recombination: $0.09$ and $0.2$ for the surface of tube, $0$ and $0.75$ for the substrate. DSMC algorithm parameters were chosen according to recommendations of [11,12].

Obtaining more detailed information about the concentrations of particles approaching the substrate requires data on the degree of methane decomposition into fragments. In this case, it is possible to use a one-dimensional approach [7] 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 when solving the equations of equilibrium chemical kinetics: $\text{H}_2$, $\text{H}$, $\text{CH}_4$, $\text{CH}_3$, $\text{CH}_2$, $\text{CH}_5(S)$, $\text{CH}$, $\text{C}$, $\text{C}_2\text{H}_2$, $\text{C}_3$, and $\text{C}_2\text{H}$. The computations are performed for 13 forward and backward chemical reactions.

4. Results of experiments and calculations

Gas-phase formation of diamond structures on the substrate occurs from fragments of decomposition of methane with the active participation of atomic hydrogen. Methyl [2, 13, 14] is considered as the main fragment for the construction of the diamond, although the possible contribution of other fragments (carbon and acetylene) is not excluded. The role of heterogeneous reactions in the decomposition of methane to methyl is small [15]. Therefore, decomposition of methane into fragments occurs through gas-phase reactions involving atomic hydrogen. In the gas-jet deposition under consideration, the decomposition rate of methane is influenced by the mixture temperature, the amount of atomic hydrogen and the time required for methane molecules to pass the distance from the feed point to the substrate. In particular, the decomposition rate of methane depends on the residence time of methane molecules in the hot part of the activator.

In the absence of high-temperature decomposition of methane, diamonds with facets up to $60 \, \mu \text{m}$ were obtained [4]. In this case, the channel with the spiral $L = 0.022 \, \text{m}$ fed only hydrogen and the gas mixture $\text{H}_2 + \text{CH}_4$ was fed through the side of the tungsten tube with a diameter of $3 \, \text{mm}$ at an angle to the reactor axis of $45 \, \text{degrees}$ into the space between the spiral and the substrate. The side tube temperature at a distance of $5 \, \text{mm}$ from the outlet of channel was $1300 \, \text{K}$. Other parameters of the synthesis were identical to that used in the present work (the synthesis time was $4 \, \text{hours}$; the pressure in the deposition chamber was $20 \, \text{Torr}$; hydrogen flow rate in both channels were $1500 \, \text{sccm}$, the methane flow rate was $8 \, \text{sccm}$). In experiments using axisymmetric activator, the size of the faces of synthesized diamonds did not exceed $30 \, \mu \text{m}$. From calculations by the DSMC method, it follows that under the chosen hydrogen flow of $1500 \, \text{sccm}$ in the conditions of the experiment, the degree of dissociation of hydrogen at the outlet of the channel depends little on its length. At the same time, decomposition of methane significantly depends on the tube length and temperature. These facts stimulated a more detailed numerical and experimental study of the effect of the feed mixture temperature and the length of the channel on the deposition of diamond structures.
The principal difference between the presented study and the previous one [3-6] was the possibility of feeding a cold mixture. In the synthesis with the use of hot supply tube (1300 K) methane is preheated to 1300 K before entering the high temperature channel. The micrographs of diamond coatings obtained under different conditions are presented on figure 3.

When using a cold feed ($T = 300$ K), the maximum deposition rate ($7 \mu m/h$) is obtained at the length of the hot tube $L = 0.022$ m. On the basis of DSMC calculations it can be assumed that the degree of hydrogen dissociation at the outlet of the hydrogen channel weakly depends on the channel length. Since the distance to the substrate is the same in all experiments, in this case there is an optimal time of methane presence in the high-temperature zone. Reducing and increasing the time of exposure to high temperatures leads to a decrease in the rate of crystal growth. In the synthesis with the use of hot supply tube the mixture is preheated up to 1300 K before entering the high temperature channel. The growth rate of the crystal in this case is slightly reduced in relation to the synthesis with cold feed ($L = 0.022$ m). Lateral supply of methane allows synthesis in the absence of high-temperature effects on the decomposition of methane, which leads to acceleration of crystal synthesis up to $15 \mu m/h$ [4]. However, the side flow does not provide good repeatability of the results and complicates the numerical analysis.

For a more detailed study of the influence of individual processes on the rate of decomposition of methane we have performed numerical simulation of the mixture flow through a cylindrical channel. Variants with cold and hot supply of the mixture to the channel of different lengths were considered. Figure 4 shows the axial density distribution of the mixture components for $L = 0.033$ m (a) and the axial distribution of the degree of dissociation of hydrogen for three tube lengths (b).

![Figure 3. Microphotographs of diamond coatings obtained under different conditions: a-c – cold feed of methane, d – hot feed of methane. a) $L = 0.011$ m (2 $\mu$m/h); b) $L = 0.022$ m (7 $\mu$m/h); c) $L = 0.033$ m (5 $\mu$m/h); d) $L = 22$ mm (6 $\mu$m/h)]
The presented data indicate the beginning of hydrogen dissociation at the entrance to the hot part of the channel. The degree of dissociation reaches a maximum value and does not change until the end of the channel. The degree of dissociation at the output of the channel is close for all three lengths of the channel. The temperature of the mixture in the range under consideration has a weak effect on the degree of dissociation of hydrogen.

Figure 5a shows the composition of the mixture obtained by a one-dimensional approach. The process of methane decomposition begins when the mixture enters the hot channel. A rapid increase in the concentration of methyl is observed at the beginning of the hot channel. Further along the channel, methyl begins to be processed into other carbon-containing components. Specific flux $nV$ for five components of the mixture at the outlet of the channel is given in figure 5b. These data show that with increasing the length of the hot channel the flux of atomic hydrogen changes little, and the flux of methane decreases rapidly due to its decomposition. The flux of methyl initially increases and then decreases. Accordingly, the fluxes of carbon and acetylene increase. The temperature of the supplied mixture has a slight effect on the mixture composition (a slight increase in the decomposition rate of methane and methyl at hot supply of the mixture is observed). The numerical data for the decomposition of methane are in qualitative agreement with the experimental data for the rate of growth of diamond coatings.
5. Conclusions
The present work is devoted to a numerical and experimental investigation of the effect of methane decomposition conditions on the growth of diamond structures during gas-jet deposition. The direct simulation Monte Carlo method in cylindrical geometry for numerical analysis of these experiments was applied. A one-dimensional approach based on the solution of equilibrium chemical kinetics equations was used to analyze gas-phase methane decomposition. Experiments were carried out to study the effect of the length of the methane channel and the temperature of the mixture on the synthesis. The conducted researches have shown that with decreasing time of methane decomposition in absence of high temperatures of the fed mixture it is possible to receive higher rates of growth of diamond structures. The obtained results can be useful for optimization of gas-dynamic sources of activated gas diamond synthesis.

References
[1] Spytsin B V, Alekseenko A A 2007 Protection of Metalls 43 5456–5474
[2] Rebrov A K 2017 Phys. Usp. 60 2179–186
[3] Emel’yanov A A, Rebrov A K, Yudin I B 2016 Tech. Phys. 61 (12) 1821-1824
[4] Rebrov A, Emelyanov A, Kosolobov S and Yudin I 2015 Phys. Status Solidi C 12 (7) 931–933
[5] Rebrov A, Andreev M, Bieiadovskii T, Kubrak K 2017 Surf. Coat. Techn. 325 210–218
[6] Rebrov A K, Emel’yanov A A, Plotnikov M Yu and Yudin I B 2017 J. Appl. Mech. Tech. Phys. 58(5) 881–888
[7] Rebrov A, Plotnikov M, Mankelevich Yu and Yudin I 2018 Phys. Fluids 30 016106
[8] Winters H F, Seki H, Rye R R and Coltrin M E 1994 J.Appl. Phys. 76 1228–1243
[9] Bird G A 1994 Molecular Gas Dynamics and the Direct Simulation of Gas Flows (Oxford: Clarendon Press)
[10] Ivanov M S, Rogasinsky S V 1988 Russ. J. Numer. Anal. Math. Model. 3(6) 453–465
[11] Morozov A A, Plotnikov M Yu, Rebrov A K, Yudin I B 2016 AIP Conference Proceedings (30th Intern. Symp. on Rarefied Gas Dynamics, University of Victoria, Victoria BC, Canada) 1786 050015
[12] Plotnikov M Yu, Shkarupa E V 2012 Comput. Fluids 58 102–111
[13] Celii F G and Butler J E 1992 J. Appl. Phys. 71(6) 2877–2883
[14] Khmel’ntskii R A 2015 Phys. Usp. 58 134–149
[15] Plotnikov M Yu and Shkarupa E V 2017 J. Appl. Mech. Tech. Phys. 58(3) 402–409