Effect of pressure on the hydrogen dissociation degree in a hot tube

A A Morozov, M Y Plotnikov, A K Rebrov and I B Yudin
Kutateladze Institute of Thermophysics SB RAS, Novosibirsk, Russia
E-mail: morozov@itp.nsc.ru

Abstract. The effect of pressure decrease on the degree of dissociation of hydrogen flowing inside a hot tube was studied. The experimental data were analysed using the previously developed thermal model of the reactor. The heat exchange of gas with the tube wall was estimated based on the direct Monte Carlo simulation. It was shown that decreasing the pressure from 20 mm Hg down to 1 mm Hg leads to a slight increase in the degree of hydrogen dissociation, from 11% up to 13%.

1. Introduction
Atomic hydrogen plays an important role in many technological processes. One of the methods for its generation is the decomposition of molecular hydrogen on hot metal surfaces. Flows through thin tubes are used for the dissociation of hydrogen, as well as oxygen, nitrogen, and other gases [1]. A distinctive feature of this approach for hydrogen is the use of heterogeneous processes in multiple collisions of molecules with the hot tube surface [2-4]. Developing new approaches to determine the probability of hydrogen dissociation for experimental conditions and obtaining new experimental data on the hydrogen dissociation degree remain relevant today. One of the common approaches used to assess the probability of dissociation on the surface is the analysis of heat balance. In particular, it is the analysis of the heat balance of a heated wire placed in an atmosphere of hydrogen [5-8].

The presented work is a development of the combined numerical-experimental approach [9], based on the analysis of the heat balance of a heated tube when hydrogen flows through it. This approach was stimulated by the gas-jet synthesis of diamond structures developed in recent years, when gas flow through a heated tube was used for the gas activation [2,10,11]. The calculated heat balance allowed us to estimate the degree of dissociation of hydrogen at the outlet of the tube for the pressure of 20 mm Hg in the deposition chamber, which is typical for experimental studies on the hot tube deposition of diamond-like films.

In the present paper, we consider the effect of pressure decrease in the deposition chamber on the degree of dissociation of hydrogen flowing in a hot tube. It was suggested that with decreasing pressure while maintaining the gas flow rate through the tube, the degree of hydrogen dissociation can increase, which can lead to an increase in the deposition rate of the films.

2. Statement of the problem
In this paper, we deal with a simplified model of the reactor consisting of one current-carrying tube [9]. A tube with a diameter of 6 mm and a length of 155 mm is considered. Figure 1 shows a schematic representation of the experimental reactor. The tube consists of two parts: a 110 mm long molybdenum tube and 38 mm long tungsten foil tube. A tube of tungsten foil is obtained by rolling a
plate with a length of 55 mm and a width of 21 mm, for part of the foil tube with a length of 10 mm to overlap the molybdenum tube. In order to achieve good electrical contact between the wires and the tungsten foil, a 7 mm molybdenum cylinder is inserted from the open edge into the foil tube. The entire tube is mounted in a chamber with a diameter of 340 mm. The thickness of the tungsten foil is 3.25 μm, and the wall thickness of the molybdenum tube is 0.5 mm. The tube is heated by current to high temperatures (2200 °C for 130 A). The current flows to the tungsten foil tube from one side through the molybdenum tube and from the other side through two molybdenum wires. The resistance of the central part of the foil tube with a length of 18 mm is measured. The temperature of the tube at different points is measured by the pyrometer.

Figure 1. Schematic illustration of the experimental set-up.

3. Model
The analysis of the degree of hydrogen dissociation is carried out on the basis of a previously developed thermal model of the hot tube [9]. In the framework of the model for a hot current-carrying tube, the non-stationary heat conduction equation is solved taking into account the radiation of the tube, heating of the gas flowing and surrounding the tube, and its dissociation:

\[ cgS \frac{\partial T_w(x,t)}{\partial t} = \frac{I^2 \rho}{S} + \lambda S \frac{\partial^2 T_w(x)}{\partial x^2} - 2\pi R\varepsilon, \sigma(T_w^4 - T_{w0}^4) - \alpha_{out} \cdot 2\pi R\varepsilon \sigma(T_w^4 - T_{w0}^4) - \alpha \cdot 2\pi R(T_w - T_{w0}) - H_{emis}(T_w) - C_{gas}G \frac{dT_{gas}}{dx} - E_{dis} \cdot 2\pi R \frac{P_{tubef} + P_{atm}}{\sqrt{2kT_w\pi m}} h_{dis}(T_w), \]

where \( c \) is the specific heat of the metal; \( g \) is the metal density; \( T_w(x,t) \) is the tube wall temperature; \( S = \pi \Delta (2R + \Delta) \) is the tube cross-section; \( \Delta \) is the tube wall thickness; \( R = 3 \) mm is the tube radius; \( I \) is the current strength; \( \rho \) is the resistivity; \( \alpha \) is the coefficient of thermal conductivity of the metal;

\[ \varepsilon_r = \left( \frac{1}{\varepsilon} + \frac{R}{R_{Cu}} \left( \frac{1}{\varepsilon_{Cu}} - 1 \right) \right)^{-1} \]

is the reduced emissivity for calculating radiation from the outer surface of the tube [12]; \( \varepsilon \) is the tube emissivity; \( \varepsilon_{Cu} = 0.4 \) is the copper emissivity; \( R_{Cu} = 170 \) mm is the radius of the chamber; \( \sigma \) is the Stefan-Boltzmann constant; and \( T_{w0} = 27 \) °C is the temperature of the chamber surface;

\[ \alpha_{out}(x) = \frac{1}{2} \left( \frac{2 + x^2}{\sqrt{4 + x^2}} - x \right) \]

is the probability for the emitted photon to escape through the end opening (in the left part of figure 1) when it is emitted from the inner surface of the tube; \( a = h \cdot Nu_D / D \) is the heat transfer coefficient; \( h \) is
the coefficient of thermal conductivity of the gas; $N_{ud}$ is the Nusselt number ($N_{ud} = 0.6$ for the background pressure $p_c = 1$ mm Hg and 0.8 for 20 mm Hg);

$$H_{emis}(T_w) = \int_0^{x_{gas}} \alpha_{emis} \left( \frac{x'-x}{R} \right) \cdot \sigma \left( \varepsilon(T_w(x))T_w(x) + \varepsilon(T_w'(x'))T_w'(x') \right)^2 \pi Rdx'$$

(4)

is the heat flux caused by radiation between the tube sections with different temperatures;

$$\alpha_{emis}(y) = \frac{1}{2} \left( 1 - \frac{y(6 + y^2)}{4 + y^2} \right)$$

(5)

is the fraction of photons absorbed on the inner surface of a cylinder of unit length at a distance $x'$ from the emission point $x$; $C_{gas}$ is the gas heat capacity; $G = 1500$ sccm is the gas flow rate;

$$T_{gas}(x) = T_w(x) + (T_w - T_{gas}) \exp \left( \frac{x - L_{tube}}{L} \right)$$

(6)

is the temperature distribution of the flowing gas along the tube; $L_{tube} = 155$ mm is the tube length; $L$ is the length of relaxation of the gas temperature to the wall temperature, which is defined as the distance over which the temperature difference $(T_w - T_{gas})$ decreases by the factor $e$; $E_{dis} = 4.5$ eV is the dissociation energy of hydrogen; and $p_{tube}$ is the pressure inside the tube;

$$h_{dis} = A_{dis} \exp \left( - \frac{E_{cat}}{kT_w} \right)$$

(7)

is the probability of effective dissociation when a molecule collides with the surface; $E_{cat} = 2$ eV is the activation energy on the catalytic surface; $A_{dis}$ is the pressure-dependent constant that is chosen to best describe the experimental dependence $R = R(I)$. For the considered pressures 1 and 20 mm Hg, the values $A_{dis} = 500$ and 25 were chosen, respectively. Accordingly, for the highest possible observed temperatures of 2000 °C, we obtain the effective dissociation probability $h_{dis} \approx 0.02$ and 0.001. Such a large difference can be explained, on the one hand, by the fact that for higher pressure the particles experience more collisions during the passage through the tube and can recombine on the wall, and on the other hand, by the increase of the occupancy of the activation centers on the tube wall [8]. The properties of substances used for calculations can be found in [9].

4. DSMC calculations

The free unknown parameter in the model is the relaxation length $L$, which is related with both the accommodation coefficient and the pressure of the gas flowing inside the tube. To determine this parameter, the gas flow in the tube is calculated by the direct simulation Monte Carlo (DSMC) method [13]. The gas flow rate is set the same, at 1500 sccm, but with different background pressures: 1 and 20 mm Hg. The calculation takes into account two rotational degrees of freedom with the relaxation collision number $Z = 300$. The accommodation coefficient of hydrogen with the wall is set equal to 0.02 for both the translational and rotational degrees of freedom. The energy of molecules colliding with the wall is equal to $(2 + j/2)kT$, where $j$ is the number of internal degrees of freedom [13]. Since for hydrogen $j = 2$, in the proposed model (1) the gas heat capacity is taken as $C_{gas} = 3R_{gas}$, where $R_{gas}$ is the universal gas constant.

Figure 2 shows the distribution of energy flow from the tube wall to the flowing gas. For a pressure of 1 mm Hg, the gas velocity inside the tube is approximately 10 times higher than for a pressure of 20 mm Hg. As a result, the flowing gas does not have time to warm up to the temperature of the tube, and the heat flux from the tube to the gas is much less than for 20 mm Hg. Based on a comparison with the results of the DSMC calculations, the parameter values $L = 120$ and 12 mm are set for a pressure of 1 and 20 mm Hg, respectively.
Figure 2. Distribution of energy flux from the tube to flowing hydrogen for the current of 100 A: DSMC calculation and the model for the distance $L = 12$ mm and 120 mm.

Figure 3. The temperature profile of the tube wall $T_w$ and the gas flowing inside the tube $T_{gas}$ for the current of 100 A: experimental measurements, DSMC calculations, and the model for the distance $L = 12$ mm and 120 mm.

5. Results and discussion

Figure 3 shows the tube temperature profiles calculated in the framework of the model in comparison with pyrometer measurements. One can see quite good agreement in the tube wall temperature $T_w$ between the model and experiment. The temperature difference near the exit from the tube (for $x = 0$) can be attributed to the presence of a massive hot substrate opposite the tube outlet in the experiment. The temperature of the gas flowing inside the tube $T_{gas}$ is shown in figure 3 as well. The gas temperature in the DSMC calculation is determined as the average temperature of the gas over the tube cross section. It should be noted that the gas temperatures from the DSMC calculation and the model are in good agreement with each other. One can see that for 20 mm Hg, the gas warms up much more than for 1 mm Hg. It is interesting that for 20 mm Hg the gas near the tube outlet (at $x = 5$ mm) does not have time to cool, and its temperature becomes higher than the wall temperature ($T_{gas} \approx 1500$ C, while $T_w \approx 1300$ C).

Figure 4 shows the dependence of the resistance of the central part of the tube and the degree of dissociation of the hydrogen flowing out of the tube $\alpha$ on the current strength for a pressure of 1 and 20 mm Hg. It is seen that for lower pressure the resistance of the tube is much larger, which is associated with less heating of the flowing gas. In this case, the degree of dissociation of the flowing gas increases slightly, from 11% for 20 mm Hg up to 13% for 1 mm Hg.
Figure 4. The resistance of the central part of the tube $R$ and the degree of hydrogen dissociation $\alpha$ depending on the current strength: experimental measurements in comparison with the calculation for 1 and 20 mm Hg.

Conclusion
Effect of pressure in the deposition chamber on the degree of dissociation of hydrogen flowing inside a hot tube has been studied. The analysis of experimental data has been carried out on the basis of the previously developed thermal model of the reactor and has been accompanied by gas-dynamic calculations by the DSMC method. It is shown that decreasing the pressure from 20 to 1 mm Hg leads to a slight increase in the degree of hydrogen dissociation, from 11% up to 13%.

Acknowledgments
The authors thank T.T. B’yadovskiy and K.V. Kubrak for their help in processing the experimental data. The experimental part of the study was performed under financial support of RFBR (grant N 19-08-00533), while theoretical part of the study was carried out under financial support of state contract with IT SB RAS (AAAAA17-117030110017-0).

References
[1] Lukas C B 2014 Atomic and Molecular Beams. Production and Collimation (CRC Press)
[2] Rebroyok A K 2017 Diamond & Related Materials 72 20–5
[3] Rebroyok A K and Yudin I B 2016 Doklady Physics 61(5) 223–6
[4] Plotnikov M Yu and Shkarupa E V 2016 Vacuum 129 31–7
[5] Langmuir I and Mackay G M J 1914 J. Am. Chem. Soc. 36 1708–22
[6] Gat G and Angus J C 1993 J. Appl. Phys. 74(10) 5981–9
[7] Zheng W and Gallagher A 2006 Surf. Sci. 600 2207–13
[8] Mankelevich Yu A, Ashfold M N R and Umemoto H 2014 J. Phys. D: Appl. Phys. 47 025503
[9] Morozov A A, B’yadovskiy T T, Kubrak K V, Plotnikov M Yu, Yudin I B 2019 Interfacial Phenomena and Heat Transfer 7(2) 139–49
[10] Rebroyok A K, Emelyanov A A and Yudin I B 2015 Thin Solid Films 575 113–6
[11] Rebroyok A K, Andreev M N, B’yadovskiy T T, Kubrak K V and Yudin I B 2016 Rev. Sci. Instrum. 87 103902
[12] Mikheev M A and Mikheeva I M 1977 Fundamentals of Heat Transfer (Moscow: Energiya) (in Russian)
[13] Bird G A 1994 Molecular Gas Dynamics and the Direct Simulation Monte Carlo Method (Oxford: Clarendon Press)