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INFLUENCE OF PRECURSOR GAS FLOW RATE ON FLUOROPOLYMER COATING GROWTH RATE DURING HOT WIRE CHEMICAL VAPOR DEPOSITION

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Abstract: The formation of a fluoropolymer coating by chemical deposition has been studied experimentally. It has been found that increasing the flow rate of the precursor gas leads to a decrease in the growth rate of the coating. Deposition conditions were analyzed, and the gas-dynamic parameters of the process were estimated. The estimates are consistent with experimental data.

Keywords: fluoropolymer, thin films, HWCVD, gas-dynamic flow regime, catalyst.

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INTRODUCTION

Fluoropolymer coatings are highly hydrophobic, chemically inert, biocompatible, and heat-resistant, and have good dielectric and antifriction properties [1, 2]. High hydrophobicity of thin fluoropolymer coatings can be used to intensify heat transfer during phase transformations [3–5]. Vapor phase chemical deposition of polymers makes it possible to produce coatings of complex shape and obtain their new properties by fabricating nanoscale structures [6, 7].

Deposition of fluoropolymers requires activation of the precursor gas, which can be carried out on the heated surface of thin metal wires. In the English-language literature, this method is called hot wire chemical vapor deposition (HWCVD). The HWCVD method can be used to obtain ultra-thin layers of insoluble polymers such as polytetrafluoroethylene. The temperature of the substrate remains close to room temperature, which contributes to the adsorption of film-forming materials [6–11]. Using IR spectroscopy, Rogachev et al. [9] have found that the structure of the layers formed depends significantly on the rate of their growth. Yasuoka et al. [10] have shown that the temperature and material of the activator have a major influence on the structure and properties of the obtained coatings. The dependences of the deposition rate on the temperature of the activator and substrate and on the pressure in the deposition chamber have been studied in detail by Safonov et al. [7].

This paper is devoted to the study of the previously observed increase in the growth rate of a fluoropolymer coating with decreasing mass flow rate of the precursor gas G in the case of HWCVD at constant pressure.

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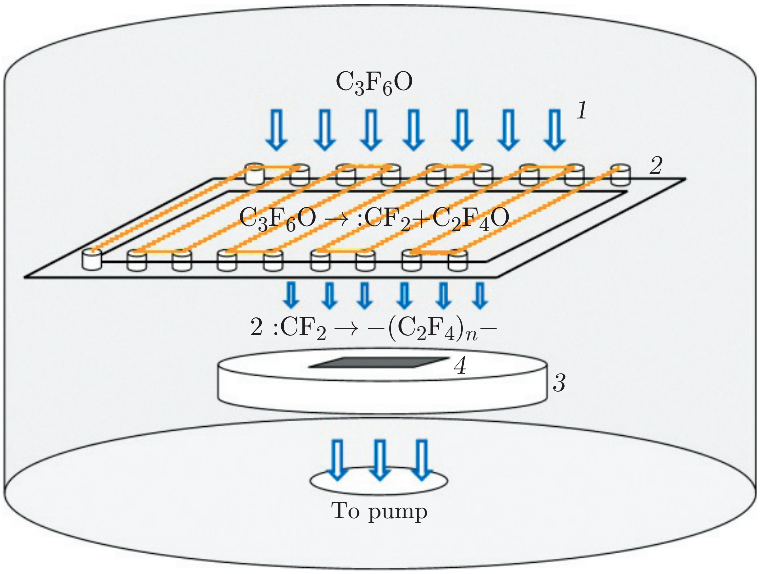

Fig. 1. Diagram of the working section of HWCVD: (*1*) precursor gas flow; (*2*) grid of hot wires of the activator; (*3*) target; (*4*) substrate.

EXPERIMENTS AND EQUIPMENT

A series of experiments has been performed to determine the dependence of the growth rate of the thickness of the fluoropolymer coating on the flow rate of the precursor gas (C_3F_6O) for fixed main parameters: the temperature of the activator and the substrate, the geometric dimensions of the working area, the pressure of the precursor gas in the deposition chamber, and the deposition time. A diagram of the working site is presented in Fig. 1. The structure and thickness of the coatings obtained were determined by scanning electron microscopy using a JEOL JSM6700F instrument.

Consider the processes occurring during activation of the precursor and its polymerization on the substrate. Activation of precursor molecules occurs on the surface of the grid wires mainly due to the catalytic decomposition of the molecule [10] and, to a much lesser degree, due to the interaction of the IR photons emitted by the wires with precursor gas molecules [12, 13].

During deposition of fluoropolymers by HWCVD using hexafluoropropylene oxide (C_3F_6O) as the precursor gas, the following main reactions occur on the activator and substrate:

$$C_3F_6O \xrightarrow{\text{activation}} :CF_2 + C_2F_4O; \tag{1}$$

$$2\ :CF_2 + (-CF_2 - CF_2-)_n \xrightarrow{\text{polymerization}} (-CF_2 - CF_2-)_{n+1}; \tag{2}$$

$$2\ :CF_2 \xrightarrow{\text{recombination}} C_2F_4. \tag{3}$$

Active radicals $:CF_2$ form a polymer on the substrate surface [see (2)] or recombine [see (3)] upon collisions in the gas and lose their ability to polymerize. The above main reactions determine the main characteristics of the deposition of the fluoropolymer, primarily, the growth rate of the film [8, 10].

RESEARCH RESULTS AND DISCUSSION

The dependence of the growth rate of the thickness of the fluoropolymer coating on the main parameters of the deposition process, taking into account the deactivation of the components upon collisions in the gas and the properties of the obtained coatings have been studied previously [7, 14]. Further studies have shown that at constant deposition parameters (the temperature of the activator and the substrate, the pressure of the precursor gas in the

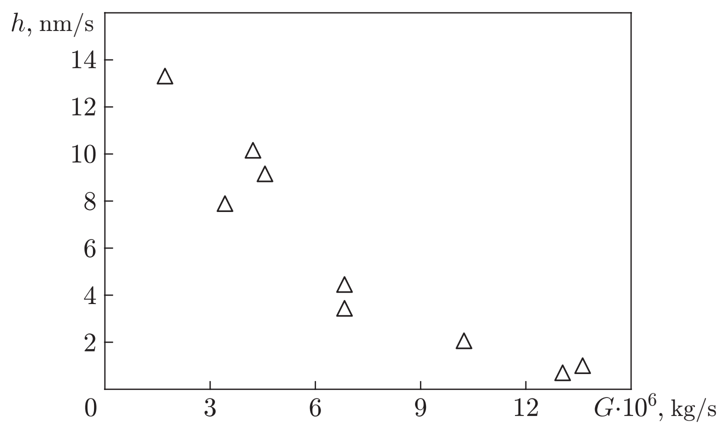

Fig. 2. Growth rate of the fluoropolymer coating h versus flow rate of the precursor gas G at $P \approx 67$ Pa (continual regime).

chamber and the geometric dimensions of the working section, the thickness of the deposited coating per unit time increases with decreasing flow rate of the precursor gas in the chamber at a chamber pressure $P \geqslant 66.7$ Pa. The obtained dependence of the rate of deposition of the fluoropolymer h on the flow rate of the precursor gas (C_3F_6O) G is shown in Fig. 2.

Despite the fact that with increasing flow rate of the precursor gas supplied into the chamber, one would expect an increase in the thickness of the coating h, the results of repeated experiments on deposition show that at a pressure $P \approx 67$ Pa, the growth rate of the thickness of the fluoropolymer coating decreases with increasing flow rate G. The assumption of a decrease in activator temperature due to cooling by the moving gas was not confirmed. The temperature of the activating grid was maintained constant regardless of the gas flow rate. Changes in the properties of the activating surface were also eliminated by replacing the working areas of the activator and by conducting tests. Similar dependences were obtained in [12], where they are explained by the formation of vortices in the chamber, which allows repeated activation of precursor gas molecules at low velocities of the directional flow.

Estimates of the gas-dynamic parameters of the process obtained in this work show that the Rayleigh number (Ra) calculated from the characteristic size of the chamber is $\text{Ra} \approx 100$. This suggests the presence of only very weak convective flows.

The gas flow velocities in the chamber are several centimeters per second, the Reynolds number (Re) determined from the characteristic size of the chamber is $\text{Re} \approx 50$, and from the diameter of the activator wire, $\text{Re} < 0.1$, which corresponds to laminar flow. Measurements of the deposition rate h were carried out with the introduction of obstacles into the flow to eliminate the symmetry of the gas flow in the chamber and the initiation of vortex formation. The measurements did not reveal significant changes in the dependence presented in Fig. 2. Thus, the existence of vortices in the chamber in the regimes of gas motion used and their influence on the dependence of h on G is in doubt.

Consider other possible reasons for the decrease in the deposition rate h with increasing flow rate G.

On the activator surface, there is heating of the gas flow. We estimate the gas temperature at different flow rates. In accordance with the well-known Newton–Richmann dependence, the heat flux from the activator to the gas q is given by

$$q = \alpha(t_a - t_g)S,$$

where t_a and t_g are the surface temperatures of the activator and the gas, respectively, S is the activator surface area, and α is the heat transfer coefficient. The values of t_a, t_g, and S are constant. The heat-transfer coefficient α is determined from the dependence of the Nusselt number (Nu) on the Reynolds number calculated from the diameter of the activator wire. For $\text{Re} = 0.1$–4.0 in the case of transverse flow around the cylinder [15], the Nusselt number is

$$\text{Nu} = 0.99\text{Pr}^{0.35}\,\text{Re}^{0.305}\,. \tag{4}$$

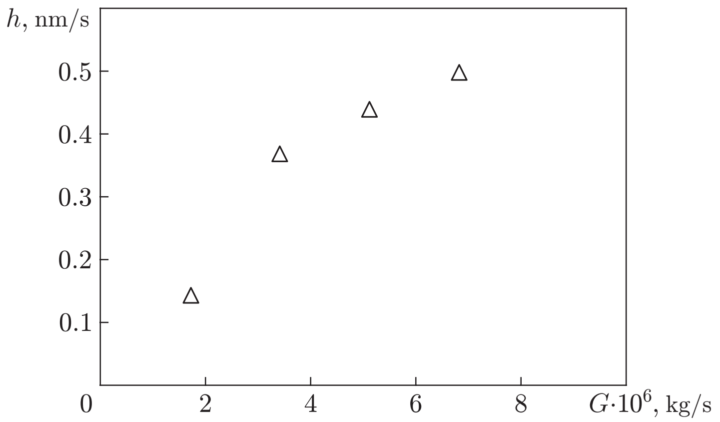

Fig. 3. Growth rate of the fluoropolymer coating h versus precursor gas flow rate G for $P = 6.7$ Pa (free molecular regime).

We note that for this flow regime, the Knudsen number (Kn) determined from the flow parameters and the diameter of the activator wire is less than 0.1. In this case, the flow past the wires is close to continual flow, which allows us to use formula (4). Consequently, the Nusselt number, the heat-transfer coefficient α, and the heat flux from the activator to the gas q increase with increasing gas flow rate and, hence the velocity u (according to the law $u^{0.305}$). At the same time, the gas flow rate $G \sim u$ and, hence, the change in the gas temperature $\Delta t \sim q/G \sim u^{0.305}/u = u^{-0.695}$; i.e., the temperature of the gas decreases with an increase in its velocity (flow rate). Thus, with increasing flow rate, the temperature at which the activated gas reaches the substrate decreases. The dependence of the rate of the polymerization reaction on the temperature of the activated gas is described by the Arrhenius equation

$$k = A\,\mathrm{e}^{-E_a/(RT)},$$

where k is the reaction rate constant, A is a coefficient, E_a is the activation energy, R is the universal gas constant, and T [K] is the gas temperature.

Consequently, the rate of polymerization decreases with increasing gas flow rate C_3F_6O due to a decrease in gas temperature provided the maintenance of the flow regime for which the above estimates are valid.

In addition, a decrease in the temperature of the gas in the flow leads to a shift of the equilibrium in the radical recombination reaction (3) in accordance with the Le Chatelier principle toward a decrease in the number of active radicals.

Thus, increasing the flow rate in the continual flow regime at velocities corresponding to Reynolds numbers $\mathrm{Re} \leqslant 1$ leads to a decrease in the gas temperature, resulting in an exponential decrease in the rate of polymerization and the shift of the equilibrium of reaction (3) toward a decrease in the number of active radicals.

At a low pressure in the chamber ($P = 6.7$ Pa), the dependence of the deposition rate h on the gas flow rate changes (Fig. 3). An increase of h due to an increase in the flow rate G is observed for values of h much smaller than those shown in Fig. 2. For these flow parameters, the Knudsen number determined from the diameter of the activator wire, $\mathrm{Kn} \approx 3$, which corresponds to the free-molecular flow around the wires. In this case, the number of molecules that reached the activator and passed through it, is proportional to the flow velocity u. In this regime, the average gas temperature in the flow does not change with increasing flow rate since the ratio of the number of molecules reaching the hot wire to the number of molecules passing through the wire is determined only by the geometry of the working section and remains constant. Consequently, in the free-molecular flow regime the gas at different flow rates is heated to the same temperature. An increase of h is due only to an increase in the number of activated molecules with increasing flow rate. The recombination conditions of active molecules during gas motion to the surface are also unchanged. Hence, the polymerization rate does not change with a change in the gas flow rate, and the amount of activated molecules increases in proportion to the flow rate. In this case, the values of h at $P = 6.7$ Pa are much smaller than those at $P = 67$ Pa ($\mathrm{Kn} \approx 0.3$) (see Fig. 2), which corresponds to the balance between the number of molecules reaching the activator and the number of molecules forming the film.

CONCLUSIONS

It has been shown that increasing the flow rate of the precursor gas decreases the growth rate of the thickness of the fluoropolymer coating. Factors responsible for this phenomenon were established and the dependence of the coating growth rate on the gas flow rate were experimentally determined.

A simple model was proposed for the investigated phenomenon occurring during the deposition process under the conditions considered. The processes leading to a decrease in the rate of polymerization in the continual flow regime were determined. The transition from continual to free molecular flow leads to a significant change in the nature of the dependence of the deposition rate on the flow rate of the precursor gas.

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