Temperature distribution of gas flows in a grid area activated by chemical vapor deposition

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Abstract. The scheme of gas temperature measurements in flows of rarefied precursor gases by HW CVD was elaborated. The gas flow temperature of air, argon and hexafluoropropylene oxide was measured at different mass flow rates. The presence of a large well-heated area in gas flows forward the activator was discovered. Asymmetric heating of the gas flow in areas above and under an activator was observed. Cooling of gas flows by increase in the precursor gas mass flow rate was confirmed. The parameters, optimal for the formation of the area with uniform temperature flows above the surface of substrate holder, were determined.

1. Introduction
The HW CVD method is widely used to produce thin coatings from variety of materials [1-5]. Special interest is the production of fluoropolymer coatings due to their unique properties. However, previously discovered effects of the precursor gas flow rate (OGFP, Hexafluoropropylene oxide - C₃F₆O) on the deposition of fluoropolymer coatings [6] stimulated the more detailed consideration of a gas activation process. Estimations have shown that one of possible reasons affecting a growth rate of the coating may be a decrease in temperature of precursor gas flows moving from the activator to the deposition surface. As a result, the number of active radicals reaching the deposition surface decreases. This leads to a significant decrease in the growth rate of the fluoropolymer coating.

The main aim of the presented work was to confirm this assumption by direct measurements of gas flow temperatures by introducing thermocouples directly into the gas flow, just to measure the temperature distribution under the conditions of HW CVD deposition.

2. Experimental details

2.1. Experimental setup
An experimental setup was created on the basis of the vacuum setup for deposition of fluoropolymer coatings. The scheme of the device is presented in Figure 1. The substrate is located at a distance of 40 mm from the activator filaments. Two nets (2 and 4) with three thermocouples each were placed above and below the activator filament at equal distances R from filaments. Such scheme made it possible to exclude the contribution of radiation from activator filaments to the thermocouple indications. In addition, the formation of fluoropolymer coatings is the exothermic polymerization process. In order to estimate and exclude this contribution of heat to the temperature measured, air and inert gas argon were used in the experiments with the gas precursor OGFP (C₃F₆O).
2.2. Measurement parameters
Thermocouple nets were installed at the same specified distance $R$ from the top and bottom of the activator filament. The vacuum chamber was pumped to the pressure of 0.13 Pa. The voltage was applied to the nichrome thread of the activator and the filament was heated to the operating temperature of 680°C. This process was carried out for 15 minutes. This time was enough for uniform heating of all elements of the activator and stabilization of thermoelectric parameters. Then, investigated gas with temperature 20°C and a predetermined flow rate and the pressure 67 Pa was injected into the vacuum chamber. Readings were recorded after temperature stabilization, and then the gas flow into the vacuum chamber was stopped. Next the chamber was pumped out to 0.13 Pa. After each experiment, the chamber was thoroughly washed with alcohol.

Five series of experiments were conducted with different distance $R$ between the thermocouple nets and activator filaments: 0; 10; 20; 30 and 40 mm. In each series of experiments, the flow temperature was measured at a predetermined flow rate: 0; 15; 30; 60; 90, 120 and 150 sccm for each of investigated gases.

3. Result and discussion
Figure 2 shows flow temperatures of different gases depending on their flow rates. At the pressure of 0.13 Pa and heated net of the activator the difference between the thermocouple readings was not more than 10°C or 1.5% of the activator filament temperature.

When the pressure of the gas in the chamber becomes work (67 Pa), thermocouples register a substantial rise in temperature. This indicates that the temperature of the gas flow is measured directly. In this case, convective heat transfer dominates over radiation which was before. Figure 2 shows the dependence of temperature of gases on the flow rate. Differences of temperatures for different gases at measuring points are 10 - 30°C (1.5 – 4.5% of the activator filament temperature). We suggest it is due to differences in the thermal conductivity of gases. In this case, the OGFP has a higher temperature than air and argon. The polymerization process on the thermocouple surface is extremely difficult to measure in this case, since the gas temperature increase is comparable with the measurement errors.
The analysis of obtained experimental data showed that the region of gas heating in the flow is widely distributed not only down the gas flow (activator-substrate holder), but also up (Shower-activator), Fig. 3. This is typical of all types of investigated gases. Also, the asymmetry of the gas flow heating relative to the activator was established. For example, at the distance of 10 mm in the OGFP flow above and under the activator the temperature is 385°C, but at a distance of 30 mm temperature of the gas after the activator is 85°C lower than that of the incoming flow. This is due to the fact that the substrate holder (cooled by water) lowers the temperature of the coming flow. In measurements without the substrate holder the temperature of the gas above and under the activator is aligned.

The decrease of gas temperature in the flow is weakly dependent on the gas flow rate at used parameters. At a distance of 10 mm from the activator, the gas temperature decreases from 400°C to 340°C with increase the flow rate from 15 sccm to 150 sccm. This is partially consistent with the data presented in [6], but to decrease the fluoropolymer coating growth rate by 10 times, as shown in this work, it is necessary to reduce the gas flow temperature by several hundred degrees. This is not observed. We believe that in order to explain the results, we should consider the length of the area of flow in which the temperature of the gas remains above a certain value. Thus, a greater number of radicals forming the coating are kept in the gas flow. Figure 3 shows the influence of the area for different gas flow rates where the gas temperature is above 300°C. By increasing the flow rate from 15 to 150 sccm, this area is reduced by 1.5 times from 38 to 25 mm. Thus, the size of this area is reduced, consequently, the amount of radicals reaching the deposition surface is reduced too.

The obtained data show that the minimum decrease in gas temperature occurs at gas flow rates about zero. However, in this case, the process of fluoropolymer coating growth will stop due to the lack of active radicals on the substrate surface. For this reason, the gas flow rate, optimal to achieve a high coating growth rate, is 15 sccm. In this case, conditions in the flow allow us to save a high number of active radicals when they move from the activator to the deposition surface.

Figure 2. Temperature dependence of investigated gases on their flow rate at R = 30 mm.
Summary

It is shown that the gas heating area in the flow extends not only down the gas flow (activator-substrate holder), but also up (Shower-activator).

The asymmetry of the gas flow heating is established. This is due to the influence of the investigated gas cooled by substrate holder on the coming flow.

The data on the temperature decrease in the activated gas flow into the area of the deposition surface with an increase in the precursor gas flow rate are obtained. The parameters, optimal for the formation of the area with uniform temperature flows above the surface of substrate holder, were determined. It allows us to save a high number of active radicals, when they move from the activator to the deposition surface, and obtain the uniform fluoropolymer coating.

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