Influence of catalyst material on growth rate and morphology of fluoropolymer coating deposited by Hot Wire CVD

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Abstract. The effect of various activator materials on the structure and properties of fluoropolymer coatings was studied using hexafluoropropylene oxide as the precursor gas. Nichrome, nickel and tungsten wires were used as catalysts. Coatings were obtained on various materials: stainless steel, copper, glass and silicon with different structures that can be used for practical applications.

1. Introduction

Fluoropolymers are characterized by high chemical, radiation and corrosion resistance due to the presence of a large number of fluorine atoms in their structure. Fluoropolymer materials have low coefficients of friction, low water absorption and gas permeability, good dielectric characteristics and high electrical strength. Fluoropolymer is resistant to all acids, petroleum products, and alkalis in the temperature range from -269°C to + 260°C, so it was called "plastic platinum". It is affected only by melts of alkali metals, solutions of alkali metals in ammonia, trifluoride chlorine and elemental fluorine at high temperatures.

In accordance with the structure of the fluoropolymer molecule \((\text{C}_2\text{F}_4)_n\), the molecular weight is 500,000 - 2,000,000 atomic units, which corresponds to the value \(n = 5000 - 20000\). Properties of fluoropolymer in the bulk form are: melting point of 327°C, decomposition temperature of 415°C, and density of 2.2 g/cm³ (20°C).

Thin fluoropolymer deposited films protect metals from corrosion, provide superhydrophobic properties of various surfaces, are used in medical implants, protect functional layers in organic light-emitting diodes, improve the efficiency of field-effect transistors, etc. [1, 2].

The growth of thin films involves the appearance nucleation centers and other growth processes on the substrate. Nucleation is extremely important for the creation of microstructure of the resulting films and hence for the properties of the coatings produced. The initial nucleation process is especially important for the growth of thin films, the thickness of which lies in the nanometer range. The Hot Wire Chemical Vapor Deposition (HWCVD) or Hot Filament CVD (HFCVD) method is also known as catalytic CVD. Catalytic chemical vapor deposition (Cat-CVD) [2-6] includes activation of the precursor gas flow on hot wire catalysts at low gas pressure from 10 to 1000 Pa. The determining influence of the temperature and the activator material on the structure and properties of the resulting coatings was established in [5]. This effect is conditioned by the dependence of the structure of the
obtained coatings on the rate of formation of active components on the surface of the activator material. In paper [7] the method is proposed for cleaning the surface of a Ni activator from compounds of the formed carbon and maintaining the catalytic properties at a constant quality. The structure of the coating determines their properties [8].

2. Methods of production and diagnostics
A scheme of the HW CVD method for depositing a fluoropolymer film and using hexafluoropropylene oxide (C₃F₆O) as a precursor is shown in figure 1. At the same time, reactions of decomposition of precursor gas molecules and formation of active components occur on the surface of the activator, forming a polymer coating on the substrate.

In our research the influence of various activator materials on the structure and properties of fluoropolymer coatings was studied using hexafluoropropylene oxide as the precursor gas. Nichrome, nickel and tungsten wires were used. Coatings may be obtained on various materials: stainless steel, copper, glass and silicon with different structures that can be used for practical applications. The morphology of the surface of the obtained coatings and the deposition rate were determined by the scanning electron microscopy (SEM) using the JEOL JSM6700F electron microscope.

3. Results and discussion
A study of the morphology of fluoropolymer coatings obtained using tungsten activator show that the coatings have a uniform granular structure, which practically does not depend on the temperature of the activator. The grain size is about 10 nm (figure 2). The deposition of the fluoropolymer begins at an activator temperature of about 850°C. The growth rate of fluoropolymer coatings depends on the activator temperature and varies from 0.5 nm/min (at 900°C) to 1 nm/min (at 1100°C). Experimental studies have shown that the tungsten activator is more fragile and less convenient for its manufacture and operation than activators from nichrome and nickel.

![Figure 1. Scheme of the HW CVD method](image-url)
Figure 2. Morphology of the fluoropolymer film deposited on the silicon surface at different temperatures of the tungsten activator: (a) 900°C, (b) 980°C, (c) 1000°C and (d) 1100°C. The insets show photographs of a drop of water on the coatings obtained and the measured apparent contact angles (CA).

Figure 3. Morphology of the fluoropolymer film deposited on the silicon surface at different temperatures of the nickel activator: (a) 510°C, (b) 700°C, (c) 740°C and (d) 800°C. The insets show photographs of a drop of water on the coatings obtained and the measured apparent contact angles (CA).
The morphology of the fluoropolymer coatings obtained using a nickel wire activator differs significantly from those obtained with a tungsten activator. It was found that the deposition process begins at the temperature of nickel activator of 500°C. The coating has a homogeneous structure with 50 nm globules located at a distance of 1 μm from each other (figure 3). The structure of the coating changes with an increase in the activator temperature up to 700°C. It becomes porous, with pore sizes of about 30 nm. A further increase in temperature leads to the intergrowth of the pores and the formation of cracks and dendritic-like structures. Cracks have a length of 500 nm and a width of 50 nm. The size of the dendrites is about 300 - 400 nm. A further increase in the temperature of the activator leads to the expansion of cracks and the fusion of dendrites into the arrays. The length and width of the cracks increase up to several micrometers and hundreds of nm, respectively. The diameter of the arrays of dendrites is about 1.5 - 2 μm. The structure of coatings obtained using the nichrome activator largely coincides with that described for the nickel activator [8]. The growth rate of fluoropolymer coatings depends on the temperature of the activator and varies from 6.5 (at 500°C) to 80 nm/min (at 800°C) using a Ni activator. These values are lower than the deposition of coatings with a nichrome activator (4 μm/min at 800°C), but higher than depositing coatings with tungsten (0.5 nm/min at 900°C).

The properties of the obtained fluoropolymer coatings were characterized, in particular, by measurements of apparent contact angles (CA) with water, determined on the DSA-100 KRUSS.

4. Summary
Optimal parameters (temperature of the filament) of the activator materials under study for obtaining fluoropolymer coatings with a given structure have been determined. It has been found that the structure of fluoropolymer coatings deposited by the HW CVD method directly depends on the number of activated radicals in the precursor gas stream reaching the deposition surface. The most suitable activator materials for various applications of the HW CVD method have been recommended. The apparent contact angles for obtained fluoropolymer coatings under different deposition regimes have been determined.

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