The currentless synthesis of tantalum and niobium carbide coatings on the carbon fibers and their electrocatalytic activity for the hydrogen peroxide decomposition reaction

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Abstract. Coatings of tantalum and niobium carbides on the carbon fibers Carbopon-B-22 were obtained by the currentless transfer in the molten salts. The kinetics of the electrocatalytic reaction of the hydrogen peroxide decomposition on the surface of TaC/C and NbC/C composite materials was studied. The order of reactions was established, the rate constants were determined, and the activation energies of the hydrogen peroxide decomposition were calculated. It was established that the electrocatalytic activity of the NbC/C composition is higher than TaC/C.

1. Introduction
The requirement of the aerospace industry for construction materials with a high level of thermomechanical properties has influenced an increasing number of studies on the creation of ceramic composites reinforced with carbon fibers. For example, carbon fibers are used in the panels of the nose fairings of space shuttles, on the blades of gas turbine engines, etc. Refractory metal carbides reinforcing carbon fibers can improve the performance characteristics of fibers due to its high melting point, heat resistance and high microhardness [1–4]. Use of refractory metal carbides deposited on carbon fiber is of great interest as catalytic and electrocatalytic systems.

The purpose of this study was to obtain coatings of tantalum and niobium carbides on carbon fibers, as well as to study their electrocatalytic properties for the reaction of the hydrogen peroxide decomposition.

2. Experimental
For coating tantalum or niobium carbides, the currentless transfer of electronegative metal (Ta, Nb) onto a more electropositive substrate (carbon fiber) through a molten salt containing tantalum or niobium compounds was used [1–4]. The molten salt of an equimolar mixture NaCl-KCl, containing 30 wt.% potassium heptafluorotantalate K₂TaF₇ or heptafluoroniobate K₂NbF₇ in an equilibrium with the metal tantalum or niobium in the form of powder or chips on the bottom of the crucible was used as a melt for currentless transfer process of tantalum or niobium to carbon fiber brand Carbopon-B-22.

A glassy carbon crucible (brand SU-2000) with a mixture of salts was placed into a retort from thick-walled stainless steel cup with special technological holes. The cell was evacuated with stepwise heating and then filled with purified and dried argon, after the electrolyte was melted. The synthesis was carried out at a temperature of 1123 K.
3. Results and discussion

The mechanism of the currentless transfer process can be explained by the formation of refractory metal complexes in an intermediate oxidation state and the subsequent disproportionation reaction on the substrate, or participation in the transfer of refractory metal complexes of reduced forms by alkali metal cations [5]. However, due to the large difference in the standard electrode potentials of refractory and alkali metals, the probability of the process proceeding by the second mechanism is extremely small. The formation of refractory metal complexes in an intermediate oxidation state occurs when the metal interacts with its own salt [2–3]:

\[ n\text{Me}^{m+} + (m-n)\text{Me} \rightarrow m\text{Me}^{n+}, \]  

(1)

where \( m>n \).

The tantalum or niobium complexes in an intermediate oxidation state diffuse through the melt and disproportionate on the surface of the substrate:

\[ m\text{Me}^{n+} + (m-n)C \rightarrow (m-n)\text{MeC} + n\text{Me}^{m+} \]  

(2)

The Gibbs energy of the carbide formation \( \Delta G_{\text{MeC}} \) is the driving force of reaction (2). The complexes of the refractory metal with the highest oxidation state, which appear in the melt as a result of reaction (2), diffuse to the surface of the metal, where complexes of an intermediate oxidation state metal are formed again as a result of the interaction. Thus, the transfer of metal to the surface of the substrate is closed into a cycle, and the resulting reaction, taking into account processes (1) and (2), can be written:

\[ \text{Me} + C \rightarrow \text{MeC} \]  

(3)

![Figure 1. SEM of carbon fibers (brand Carbopon-B-22) with tantalum (a) and niobium (b) carbide coatings obtained by the currentless transfer of a refractory metal in the NaCl-KCl-K\(_2\)MeF\(_7\) (30 wt.%) – Me melt. The synthesis temperature is 1123 K. The synthesis time of tantalum carbide is 24 hours, niobium carbide is 6 hours.](image)

During the synthesis of tantalum and niobium carbides, no splicing of carbon fibers with each other was observed, and the coating repeated the relief of the original carbon fiber, the coatings were uniform both in the cross section and the length of the entire fiber. The thickness of the coatings of TaC and NbC was about 50–250 nm, depending on the synthesis time (figure 1).

To study the kinetics of the electrocatalytic decomposition of hydrogen peroxide on the surface of tantalum and niobium carbides coatings on the carbon fibers, the measuring of the volume released gas (oxygen) was used. The original carbon fibers of the brand Carbopon-B-22 were used as a cathode, carbon fibers with a coating of TaC or NbC were used as the anode. Anodic polarization of the samples was carried out at a voltage of 30 V. To compare the results of electrocatalytic activity of carbide coatings on carbon fibers, the reaction of the hydrogen peroxide decomposition was also studied on a copper and platinum electrodes.
In this work, we used integral methods for determining the order of the reaction for the hydrogen peroxide decomposition including the substitution method and the graphic one. Since the graph of the function of changing the reaction product volume (oxygen) versus time $\Delta V(t)$ on TaC/C, NbC/C, platinum and copper electrodes is linear, the reaction of the hydrogen peroxide decomposition has a zero order and is characterized by the kinetic equation: $\nu = k$ (figure 2).

Figure 2. Kinetic dependences for the different reaction’s order of the electrocatalytic decomposition of hydrogen peroxide, obtained on NbC/C electrode at a temperature of 303 K.

The reaction rate constants were determined by the tangent of the straight line in the corresponding coordinates. The activation energies of the process were calculated based on the experimental data obtained at different temperatures.

Figure 3 shows the kinetic dependences of the reaction of the hydrogen peroxide decomposition at a temperature of 303 K on different electrodes. From these dependences it follows that the reaction rate increases in the next row TaC $<$ Pt $<$ Cu $<$ NbC. It was established that this series is maintained at other temperatures.

Using the values of the rate constants of the reaction of the hydrogen peroxide decomposition at different temperatures, the values of the activation energy on platinum, TaC/C, copper and NbC/C electrodes were calculated using the Arrhenius equation, which amounted to 82.24; 74.76; 48.24 and 37.07 kJ/mol, respectively.

It was established that the reaction rate is constant in time, does not depend on the concentration of reactants, and the rate of diffusion of reactants to the surface is less than the rate of their chemical transformation. The electrocatalytic reaction of the hydrogen peroxide decomposition is irreversible.

4. Conclusions

Tantalum and niobium carbides coatings on the carbon fibers were obtained by the currentless transfer in the molten salts. The electrocatalytic properties of these compositions in the reaction of the hydrogen peroxide decomposition were studied and the kinetic parameters of the reaction were
determined. It has been established that the composite material “niobium carbide coating - carbon fiber” has a greater electrocatalytic activity in the reaction of the hydrogen peroxide decomposition than copper, platinum and TaC/C.

**Figure 3.** Kinetic dependences of the electrocatalytic decomposition of the hydrogen peroxide, obtained on different electrodes at a temperature of 303 K.

**References**

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