The Use of Mathematical Modelling Methods in the Creation of Composite Materials Based on Carbon Fibre Materials

Valery Varentsov 1, Valentina Kuzina 2, Alexander Koshev 2, Valentina Varentsova 1

1 Institute of Solid State Chemistry and Mechanochemistry of the Siberian Branch of the Russian Academy of Sciences, Novosibirsk, Russia
2 Penza State University of Architecture and Construction, Penza, Russia

kuzina@pguas.ru

Abstract. The report provides data on the electrochemical modification of carbon-graphite fibers as the basis for the creation of composite materials. The results of studies of the electrodeposition of metals on pre-electrochemically modified carbon fiber materials (CFM) in order to obtain composite materials based on them are presented. The use of CFM for the creation of composite materials is associated with the possibility of deposition of metals, alloys or their compounds on the surface of their constituent fibers. Electrochemical treatment in aqueous solutions of electrolytes is a promising method for modifying the surface properties of carbon materials, including in order to improve their adhesive properties. Preliminary electrochemical modification of carbon fiber materials in indifferent solutions of electrolytes made it possible to obtain composite and nanocomposite materials with good adhesion of the electrodeposited metal to the surface of the fibers of carbon materials. When metals are deposited on carbon fiber materials, it is necessary to solve the problem of applying a uniform metal deposit or with a certain profile in the thickness of the material. In this case, it is effective to use methods of mathematical modeling of metal deposition processes in a flowing three-dimensional electrode. Depending on the selected modes of deposition of metal sediment on the CFM, some electrochemical parameters of the process and system may be dependent on both the time of the process and the thickness coordinate of the electrode. This is especially true for the value of the resistivity of the solid phase of the system, that is, carbon-graphite fibrous material. Other electrochemical parameters, such as the specific electrode surface, the exchange current and the transfer coefficient of the electrochemical reaction, the porosity of the material, etc., can also change during the electrodeposition of the metal on the CFM. It is proposed to take into account the change in the characteristic properties of modified carbon fiber materials in the mathematical modeling of the processes of electrodeposition of metals on carbon fiber materials in order to determine the technological parameters to improve the efficiency of the properties of composite materials. In order to implement mathematical models used in the calculation of electrochemical processes in the volume and on the surface of carbon fiber materials, a set of programs based on modern computational methods and programming languages has been developed.

1. Introduction
Composite materials based on carbon fiber materials (CFM) are widely used in construction, aviation, medical, chemical and other industrial sectors [1, 2]. The use of CFMs to create composite materials is associated with the possibility of deposition of metals, alloys or their compounds on the surface of
their constituent fibers. One of the promising methods for this is electrochemical, which allows mathematical modeling of the process and allows you to control the current and hydrodynamic modes of electrolysis, the composition of the electrolyte, and the design of the electrode system [3–8].

For adhesion of metals or their connection with a surface material (SM), it was usually subjected to preliminary treatment with surfactants, high-temperature oxidation in a gaseous medium, oxidation in hot solutions of concentrated acids of various oxidizing agents: K$_2$S$_2$O$_8$, K$_2$Cr$_2$O$_7$, etc. [1, 2].

A promising method for modifying the surface properties of carbon materials, including with the aim of improving their adhesion properties, is electrochemical treatment in aqueous solutions of electrolytes [5, 6, 8]. Unlike chemical methods, electrochemical treatment is carried out in non-aggressive solutions with low concentrations of reagents; the process can be controlled by changing the electrolysis conditions and the composition of the solution.

2. Algorithm Description

When depositing metals on a CFM, it is necessary to solve the problem of applying a uniform deposit of metal or with a certain profile along the thickness of the material. In this case, it is effective to use methods of mathematical modeling of metal deposition processes in a three-dimensional flow electrode (TDFE) [6, 9]. The theoretical laws of migration and convection of charged particles in most electrochemical systems are described by systems of partial differential equations [6]:

\[
\frac{\partial C_i}{\partial t} = -\nabla \cdot \left( z_i u_i FC_i \nabla E + C_i v \right),
\]

(1)

where $z_i$, $C_i$, $u_i$ are, respectively, the charge, concentration and mobility of the $i$-th electroactive component in a pseudo-homogeneous medium; $\nabla E$ is the gradient of the electric field potential; $v$ is the vector of the rate of convective transfer of the solution; $F$ – Faraday number, $\nabla \bullet$ is the vector divergence.

The transformation of system (1) for the one-dimensional case, which is often realized in the considered electrochemical systems, in accordance with the existing rules and well-known models adopted in electrochemical kinetics [6], ultimately leads to the following system of differential and algebraic equations:

\[
zF \frac{\partial C}{\partial t} = -\frac{\partial E}{\partial t} - \frac{\partial E}{\partial x} \left( \frac{\rho_r \rho_G}{\rho_r + \rho_G} \right) + \frac{\rho_r \rho_G}{\rho_r + \rho_G} S_T j_S; \quad \nabla \cdot \left( zF \frac{\partial C}{\partial x} \right) = -S_T j_S; \quad (2)
\]

\[
j_S(x) = j_0 \frac{\exp(\alpha zF(E - \phi_R)/R_T) - \exp((\alpha - 1) zF(E - \phi_R)/R_T)}{1 + j_0 \exp(\alpha zF(E - \phi_R)/R_T)/zFK_m C}; \quad (3)
\]

\[
C(0,t) = C_0; \quad C(x,0) = C_0; \quad \frac{\partial E}{\partial x}(0,t) = \rho_r j(t); \quad \frac{\partial E}{\partial x}(L,t) = \rho_G j(t); \quad E(x,0) = \phi_R. \quad (4)
\]

Here $j(t)$ is the overall current density at time $t$; $C_0$ is the metal concentration at the electrode inlet; $\rho_r$ is the resistivity of the solid phase; $\rho_G$ is the resistivity of the liquid phase; $j_0$, $\alpha$, $\phi_R$ are, respectively, the exchange current density, the transfer coefficient and the equilibrium potential of the electrochemical reaction; $R$ is the universal gas constant; $T$ is the absolute temperature of the process; $S_T$ is the specific reaction surface of the CFM, referred to the mass; $j$ is the local total current density; $K_m$ is the coefficient of mass transfer.
Depending on the selected modes of deposition of a metal deposit on the CFM, some electrochemical parameters of the process and system can be dependent both on the process time and on the coordinate along the electrode thickness. This especially concerns the value of $\rho_T$ – the resistivity of the solid phase of the system, that is, the carbon-graphite fibrous material. In the process of metal electrodeposition on the CFM, other electrochemical parameters can also change, such as specific electrode surface, exchange current and transfer coefficient of the electrochemical reaction, material porosity, etc. Methods for calculating the listed dynamic parameters have been developed by us and published, for example, in monograph [6]. The described theoretical assumptions are confirmed by experimental studies.

3. The results of experiments
Experimental studies concerning the modification of CFMs were carried out on woven, non-woven and combined carbon materials differing in electrical conductivity, reaction surface, and porosity [3, 4, 6, 8]. Electrochemical modification of carbon materials was carried out in solutions of various electrolytes by anodic polarization or sequentially cathodic-anodic polarization, or their various combinations. As a result of electrochemical treatment, the number of surface oxygen-containing groups, which determine the hydrophilic properties of the material, increases (Table 1). Preliminary electrode treatment of carbon materials in solutions of acid, alkali or indifferent salt [5, 6, 8] significantly affects the adhesion of the deposit to the CM surface, the possibility of subsequent effective metal deposition.

| Original ANM | I$^a$ | II$^a$ |
|--------------|-------|-------|
| Element      | Weight, % | Element | Weight, % | Element | Weight, % |
| C            | 89,80   | C      | 87,96   | C       | 78,40   |
| O            | 8,99    | O      | 10,28   | O       | 19,11   |
| Na           | 0,40    | Na     | 0,26    | Na      | 0,35    |
| Si           | 0,36    | S      | 0,69    | S       | 1,70    |
|              | 0,45    | Si     | 0,81    | Si      | 0,44    |

$^a$ I – overall current density: 700 A/m$^2$, cathodic polarization – 20, anodic – 10 minutes; II – overall current density: 500 A/m$^2$, cathodic polarization – 10, anodic – 30 minutes.

The experience in the development of technological processes for the electric extraction of noble and non-ferrous metals from industrial solutions on a CFM [3 – 9] has shown that the deposition of metals on preliminarily electrochemically treated materials makes it possible to calculate the optimal modes of electrodeposition, which makes it possible to obtain uniformly distributed metal deposits throughout the electrode thickness, improve the structure, morphology and composition of sediments, and hence the properties of the composite material (Figure 1) [5, 6, 8].

In order to implement mathematical models used in calculating electrochemical processes in the volume and on the surface of the CFM, a complex of programs has been developed based on modern computational methods and programming languages.

Figure 2 shows the calculated by the mathematical model (1) – (4) and experimental data of the study of the processes of joint electrodeposition of silver from thiourea sulfate solution of the composition: H$_2$SO$_4$ – 0.5 mol/l, thiourea – 50 g/l, silver – 76 mg/l (Figure 2, a); and silver – 141 mg/l (Figure 2, b). The studies were carried out with a frontal (from the side of the counter electrode) supply of a solution to the electrode. In the first case, the electrode was composed of 12 layers of CFM and 6 layers in the second. CFM characteristics (VVP-66-95): specific surface area – 255 cm$^2$/cm$^3$, ...
specific electrical conductivity – 0.03 Cm/cm, porosity – 0.95 [4, 5]. The specific conductivity of the solution is 0.1 Cm/cm, the electrolysis time is 60 minutes.

![Micrographs of copper deposits on the original (a) and electrochemically modified (b) CFM](image)

**Figure 1.** Micrographs of copper deposits on the original (a) and electrochemically modified (b) CFM

![Distribution of the silver deposit over the electrode thickness](image)

**Figure 2.** Distribution of the silver deposit over the electrode thickness: $d$ – the ratio of the metal mass to the CFM mass; 1 – experiment; 2 – calculation; $n$ – layer number; $T$ is the back of the electrode.

- a) electrode thickness – 1 cm; current density – 0.2 A/ m$^2$; solution flow rate – 0.56 cm/s;
- b) electrode thickness – 2 cm, current density – 0.7 A/ m$^2$; solution flow rate – 0.56 cm/s

The experimental and calculated dependences presented in Figure 2, as well as the consistency of the calculated distributions of electrochemical functions of the classical electrochemical theory, allow us to conclude about the effectiveness of using the mathematical models and calculation algorithms described above in this article and in our other works [6 – 7, 9, etc.] to carry out numerical studies of the processes of electrodeposition of metals in the creation of composite materials with a certain morphology and distribution of the metal deposit on the surface of CFM fibers and the extraction of metals from solutions of processing mineral and technogenic raw materials, from industrial wastewater to flowing three-dimensional electrodes.

Nanosized metal particles can be electrolytically deposited on the surface of CFM fibers or completely "cover" the fiber surface with sediment of various thicknesses (Figure 3).

Composite catalytic materials based on CFM with deposits of platinum, silver or an alloy of platinum with silver turned out to be not only more effective in the catalytic process of oxidation of
aliphatic alcohols and aldehydes, as well as complex mineral-organic condensates in aqueous solutions, oxidation of Ce (III) in a sulfuric acid solution [5, 6, 9], but they are also more convenient when used in various designs of electrochemical reactors than activated carbon.

![Figure 3. Micrographs of platinum deposits on the CFM](image)

4. Conclusions
It is advisable to study the processes of metal electrodeposition on electrochemically modified carbon fibrous materials both by experimental methods and by methods of mathematical modeling. The software package developed on the basis of modern computational methods allows performing numerical experiments to calculate the distribution of the electrochemical process in electrolyzers with CFM in order to optimize the electrodeposition processes.

Preliminary electrochemical modification of carbon fibrous materials in indifferent electrolyte solutions made it possible to obtain composite and nanocomposite materials with good adhesion of electrodeposited metal to the surface of carbon fibers.

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