Formation of Nanosized Electrocatalytic Coatings on Carbon Substrates with Application of Catalytic Metals Ion Beam Deposition from Pulsed Arc-Discharge Plasma

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Abstract – Ion beam assisted deposition (IBAD) of catalytic metals onto carbon substrates is implemented out of neutral fraction of vapor and ionized plasma of pulsed electric arc. The deposition of a metal and the mixing of a precipitable layer with substrate surface atoms by accelerating ions of the same metal were carried out from a neutral vapor fraction and the vacuum arc discharge plasma respectively of a pulsed electric arc ion source. Structure, composition and electrocatalytic activity of the coatings were examined. The coatings had amorphous atomic structure, almost repeat the structure of a substrate, and their thickness obtained ∼100 nm. The coatings consist of the deposited metal, the substrate material and oxygen. The content of deposited metal atoms in the coatings is ∼10^{16} \text{ cm}^{-2}. The electrocatalytic activity of carbon-based electrodes with the coatings in the electrochemical hydrogen evolution reaction obtained the activity of a platinum electrode.

1. Introduction

Ion-beam surface modification of engineering and functional materials provides the introduction of a controlled amount of any alloying impurity into their near-surface layers on the nanosize atomic scale under non-equilibrium conditions. Ion-beam modification of the materials whose service properties are mainly controlled by the surface composition is of particular interest. These materials include catalysts for chemical reactions, in particular, electrocatalysts, namely, electrodes for electrochemical devices.

A catalytic reaction is based on an electronic mechanism: the electron exchange between reacting molecules occurs through a catalyst with the participation of catalyst electrons. The properties of deposited heterogeneous catalysts are controlled by the electronic structure of active centers on the surface that form during preparation. The active centers of electron exchange as often as not related to catalytic-metal particles. Therefore, the nature of the deposited catalytic metal is very important [1]. The catalytic properties of the surface irradiated by an ion beam are more frequent determined due to specific ion alloying effects induced by the nature of the implanted impurity and the target material [2].

The purpose of this work is to form coatings by ion-beam-assisted deposition of a catalytic metal onto carbon substrates and to study their composition and electrocatalytic activity in the electrochemical hydrogen evolution reaction.

2. Experimental

Ion beam assisted deposition (IBAD) of palladium, iridium, platinum and other transition metals onto carbon substrates is implemented out of neutral fraction of vapor and ionized plasma of pulsed electric arc. The substrates were made of a graphite MG-1 (MG) and glassy carbon GC-2000 (GC) (NIIGrphite, Russia). The deposition of a metal and the mixing of a precipitable layer with substrate surface atoms by accelerating ions of the same metal were carried out in an experimental setup from a neutral vapor fraction and the vacuum arc discharge plasma respectively of a pulsed electric arc ion source with electromagnetic or electromechanical actuator. That is, the IBAD process was performed under the condition of self-radiation. The discharge pulse frequency was 50 Hz; assisting ions were accelerated at a voltage in the range 10–20 kV, the average ion current density was 4–5 μA·cm², and a vacuum of 10^{−2} Pa was maintained in the working chamber.

The structure and composition of the deposited coatings was investigated using the electron diffraction, RBS, SEM, EPMA, and XPS methods. The RBS spectra of 4He ions accelerated to an energy \( E_0 = 1.5 \text{ MeV} \) in an AN-2500 accelerator were recorded at the normal incidence of a beam of analyzing particles onto the sample surface, and the scattering angle of 4He ions was 170°. The energy resolution of the spectrometer with a surface-barrier silicon detector was 18 keV. The RBS spectra were processed according to a standard technique and using simulation with the RUMP software package [3]. The EPMA examination of the structure and composition of the coatings and microscopic analysis were performed with a JEOL JSM-5610LV scanning electron microscope. The energy of the ions scanning over the sample surface and exciting the characteristic X-ray radiation of the atoms

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entering into the composition of the layer to be analyzed was 20 keV. XPS investigations were carried with use ES-2401 spectrometer.

The electrocatalytic properties of ion assisted deposited coatings on carbon substrates have been analyzed using electrochemical polarization measurements in the 1 M H₂SO₄ solution using a standard three-electrode electrochemical cell, a PI-50-1 potentiostat, and a PR-8 programmer.

3. Results and discussion

According the RBS data (Figs. 1 and 2) the coatings consist of the deposited metal, the substrate material and as well as impurity oxygen.

![Fig. 1. RBS spectra (experiment and simulation) of ⁴He ions scattered from a GC surface with a coating formed by platinum IBAD](image)

![Fig. 2. RBS spectra of ⁴He ions scattered from a GC surface with a coating formed by Pd, Ir/IBAD](image)

![Fig. 3. Electron-microscopic micrograph of a coating formed by IBAD of iridium on GC (a), and the EPMA distributions of carbon (b) and iridium (c) over the coating surface](image)

The concentration of deposited metal atoms in the depth distribution maximum equals about a few at. %, thickness of the catalytic layers – ~100 nm, contents of metal atoms in the layer – ~10¹⁶ cm⁻².

Investigations with use of the reflection electron diffraction (EG-100M) detected amorphous atomic structure of coatings. The microstructure of the coatings in fact does not differ from the structure of the carbon substrate (Fig. 3, a). Atoms of the elements comprising the coatings are in fact evenly distributed on the surface (Figs. 3, b and c). Inclusions of the deposited metals of about several micrometers occur on the surface which is conditioned by metal drops deposition from the electric arc source (Fig. 3).

The deposited metal atoms, as well as atoms of carbon and oxygen in the under investigation coatings, available in a few valence states. Thus, according XPS investigations platinum atoms in coating formed onto GC surface available in three different valence states (Fig. 4, a). A relationship between atom amounts in different valence states change subject to impurity depth (cf. Figs. 4, a and b). These experimental data evidenced by interaction between atoms of IBAD formed catalytic layers components, which result in change of an atom electron structure.
The results of measurement of electrocatalytic activity of the under investigation coatings presented in Figs. 5 and 6 in a cathode polarization curves form.

In the capacity of the electrode activity in hydrogen evolution reaction extent represent the current density \( j \) of an electrochemical process at a defined value of the potential \( U \) of electrode.

The electrocatalytic activity of the electrodes with coatings is comparable to that of platinum electrode; meanwhile carbon substrate shows no activity in hydrogen evolution reaction.

Significant dependence of coating properties on nature of deposited metals was found. Properties of coatings differ from those of pure metals due to interaction between deposited metal and carbon matrix. Interaction between two different deposited metals is observed, too.

4. Conclusions

We developed method of the catalytic coatings formation by ion-beam-assisted deposition of metals from the plasma of a pulsed arc discharge under conditions where deposited-metal ions are used as deposition-assisting ions, and studied the structure, composition, and electrocatalytic properties of the coatings formed on carbon substrates.

The coatings characterized by amorphous atomic structure, and consist of the deposited metal, the substrate material and oxygen; their thickness reaches...
~100 nm. The atoms of the elements entering into the coating composition are uniformly distributed over the surface. Moreover, metal droplets several microns in diameter are deposited from the arc discharge of a source; they cover less than 1% of the surface area. The content of platinum metal atoms in the coatings is \( \sim 2.6 \times 10^{16} \text{ cm}^{-2} \), or less than 0.02 mg/cm\(^2\). The atoms of the coatings components also characterized by compound electron structure.

We investigated the electrocatalytic activity of the coatings in the electrochemical process of hydrogen evolution. Activity of the electrodes with coatings is comparable to that of platinum electrode.

References