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Formation of catalytic and corrosion protective layers with use of ion beam assisted deposition of metals from vacuum arc discharge plasma

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Abstract. This paper presents a brief overview of our studies on the modification of materials using ion beam assisted deposition (IBAD) of metals from vacuum arc discharge plasma in order to form catalytically active and corrosion-resistant layers on the surface. Deposition of metals on different materials with simultaneous mixing of the deposited layer with the substrate surface by accelerated ions of the deposited metal was carried out in an experimental setup with a pulsed electric arc ion source. Catalytic and corrosion properties of the materials with the obtained layers were studied using electrochemical voltammetric measurements. The microstructure and composition of the resulting layers were studied using the SEM, EDX, WD-XRF, XPS, EBSD, and RBS methods.

1. Introduction

Ion-plasma technologies provide the possibility of modifying the surface of structural and functional materials in order to improve the performance characteristics of products made of them without changing the bulk properties of the material. Of particular interest is the ion-plasma modification of materials, the properties of which, in particular, catalytic [1–3] and corrosion-resistant [4, 5], are primarily determined by the composition of the surface.

The purpose of this article is to present a brief overview of our research on the formation of catalytic also corrosion protective layers on the surface of functional materials using ion beam assisted deposition of active or alloying metals from vacuum arc discharge plasma, which is generated in metal vapour.

2. Experiment

During the formation of the studied layers, deposition of metals on various materials with simultaneous mixing of the deposited layer with the substrate surface by accelerated ions of the deposited metal was carried out on an experimental setup with a pulsed electric arc ion source. Evaporation of the deposited metal and ionization of its atoms occur in a low-voltage vacuum arc discharge between two electrodes made of the deposited metal at their periodic contact. The contact of the electrodes is carried out as a result of the reciprocating motion of one of them under the action of an electromechanical drive. The metal deposition substrate is under a high negative potential, which accelerates metal ions from the arc discharge plasma. The acceleration of the assisting ions was carried



out in various experiments with a voltage of 5 or 10 kV. The frequency of the discharge pulses was 50 Hz; pressure in work chamber $\sim 10^{-2}$ Pa.

The composition of the layers were studied by energy dispersive X-ray microanalysis (EDX) with scanning electron microscopy (SEM) using a JSM-5610LV scanning electron microscope with an EDX JED-2201 (JEOL) spectrometer, as well as with a LEO 1455 VP microscope (Zeiss) equipped with an AZtec Energy Advanced X-Max80 (Oxford Instruments) spectrometer, wave dispersive X-ray fluorescence analysis (WD-XRF) using a PANalytical Axios spectrometer (Netherlands), X-ray photoelectron spectroscopy (XPS, ES2401 spectrometer), electron backscatter diffraction (EBSD) using an HKL Channel 5 Premium EBSD system and the LEO 1455 VP microscope, and Rutherford backscattering spectrometry (RBS) of ^4He ions accelerated in various experiments to the energy 1.0 – 1.5 MeV using an AN-2500 accelerator complex (High Voltage Engineering Europe).

Catalytic and corrosion properties of the materials with the obtained layers were studied using electrochemical voltammetric measurements [6, 7] in various solutions with use of conventional three-electrode electrochemical cell and IPC-Pro M potentiostat.

3. Results and discussion

Catalytic surface layers were prepared by IBAD of platinum as basic active metal and one of metals (Ir, Sn, Ce, Gd, Dy, Ho, Yb) as an activating additive. The choice of metals introduced into the formed layers was determined by the peculiarities of the mechanism of the catalyzed electrochemical reaction [8–10]. Valve metals (Al, Ti and Ta) [11-13] and carbon materials (glassy carbon, Toray Carbon Fiber Paper TGP-H-060 T and AVCarb[®] Carbon Fiber Paper P50) [14–16], as well as a Nafion[™] N115 membrane [17], were used as substrates in the studies. Carbon fiber catalyst carriers and Nafion membrane are used as material of diffusion layers and electrolyte of membrane electrode assemblies for electrolyzers and low-temperature fuel cells with polymer membrane electrolyte, which requires the presence of catalytic layers.

It has been established that the morphology of materials surface remains practically unchanged during the formation of layers. According to EBSD data [13, 14], the prepared layers are characterized by an amorphous atomic structure.

When studying the composition of the layers by the EDX, WD-XRF, XPS, and RBS methods, it was established that they contain atoms of deposited metals and substrate components, as well as technological impurities of carbon and oxygen. Against the background of an almost uniform distribution of elements over the surface of the layer, drops of deposited metals are observed, falling from the arc discharge of the source. The distribution of elements over the surface of the carbon fiber catalyst carriers is not uniform due to the heterogeneity of the substrate itself (figure 1). In the X-ray fluorescence spectra of the studied samples, lines of characteristic radiation of atoms of deposited metals (figure 2), elements that make up the corresponding substrate, as well as carbon and oxygen are observed.

The layers formed on the surface of all materials were studied in detail by the RBS method. The spectra of Rutherford backscattering of ^4He ions on the nuclei of the atoms of the elements included in the analyzed layer were measured at normal incidence of the analyzing radiation and a scattering angle of 170° . In the IBAD process of metals in the applied mode, ion mixing takes place and multicomponent layers are formed, including the deposited metals, components of the corresponding substrate, and technological impurities. According to the RBS data (figures 3–5), the thickness of the prepared layers is $\sim 50\text{--}80$ nm, and the content of deposited metal atoms in the formed layers is $\sim n \times 10^{16} \text{ cm}^{-2}$. The concentration of deposited metal in the maximum distribution located near the surface is several atomic percent.

Interaction between the atoms that are part of the layers is possible. The XPS study of the layer formed during the IBAD of platinum on glassy carbon showed that the metal, carbon and oxygen atoms in the layer are in several different valence states [14]. Thus, the following states of platinum in

the composition of the layer have been identified: platinum in the metallic state; platinum with adsorbed oxygen; platinum in the composition of PtO oxide and in a higher oxidation state.

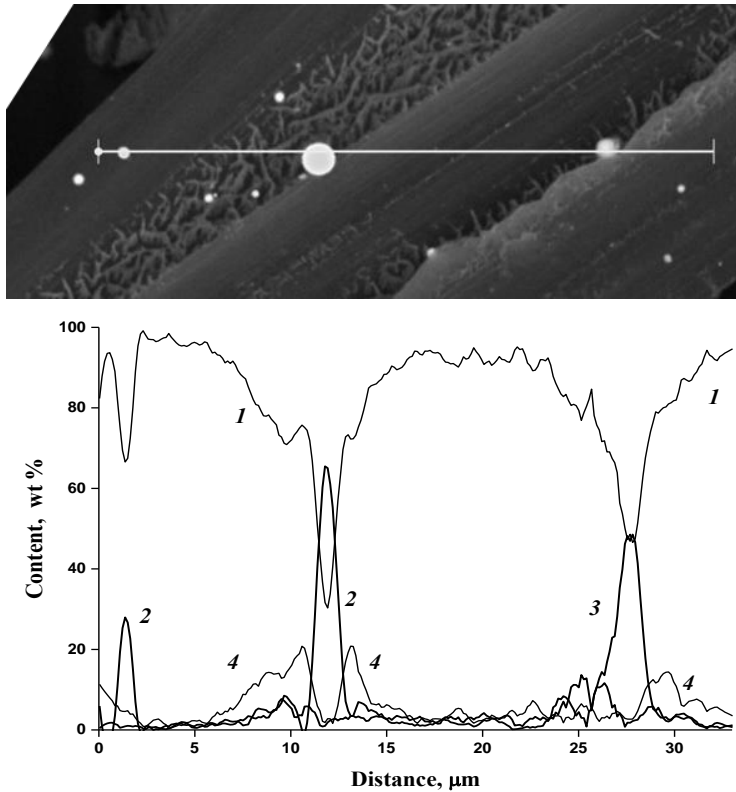


Figure 1. SEM image of the electrocatalyst surface on a Toray Carbon Fiber Paper TGP-H-060 T carrier with layer prepared by Gd and Pt IBAD; distribution of carbon (1), platinum (2), gadolinium (3) and fluorine (4) according the scanning line (according EDX microanalysis) [16].

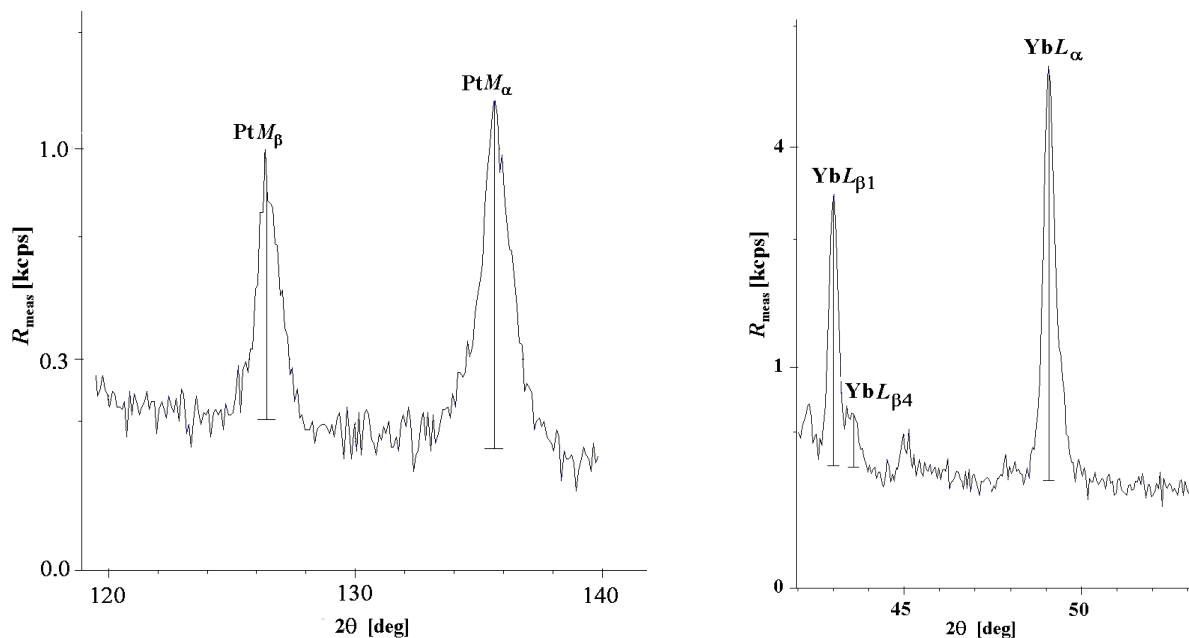


Figure 2. Fragments of the WD-XRF spectrum of the electrocatalyst prepared by platinum and ytterbium IBAD onto Toray Carbon Fiber Paper TGP-H-060 T catalyst carrier [15].

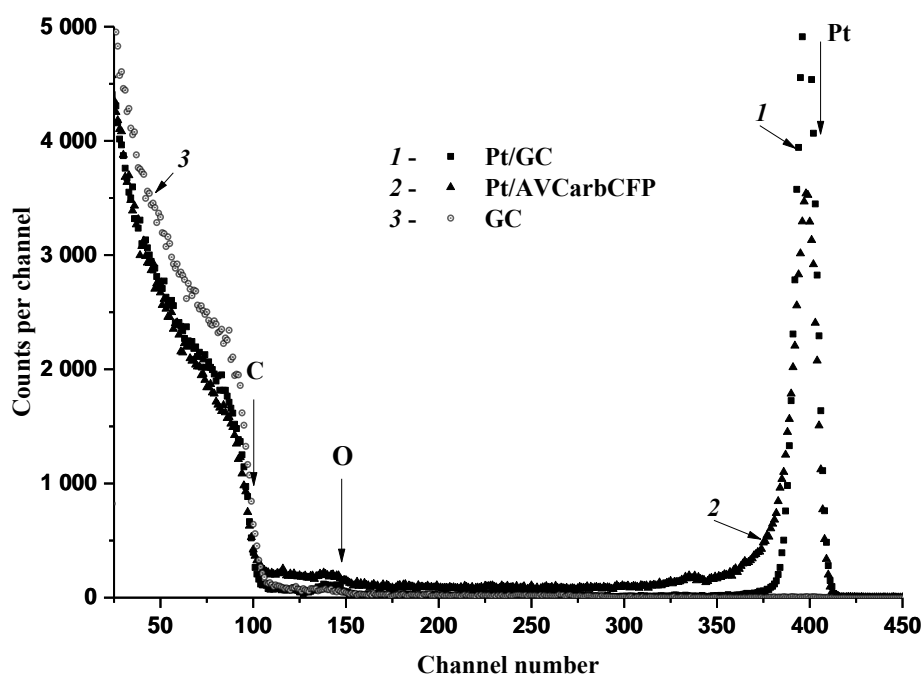


Figure 3. RBS spectra of ^4He ions scattered both on the glassy carbon (GC) and AVCarb[®] Carbon Fiber Paper P50 carrier surfaces with catalytic layers formed by the IBAD of platinum, (1) – Pt/GC and (2) – Pt/AVCarbCFP respectively, and on initial GC (3) [14].

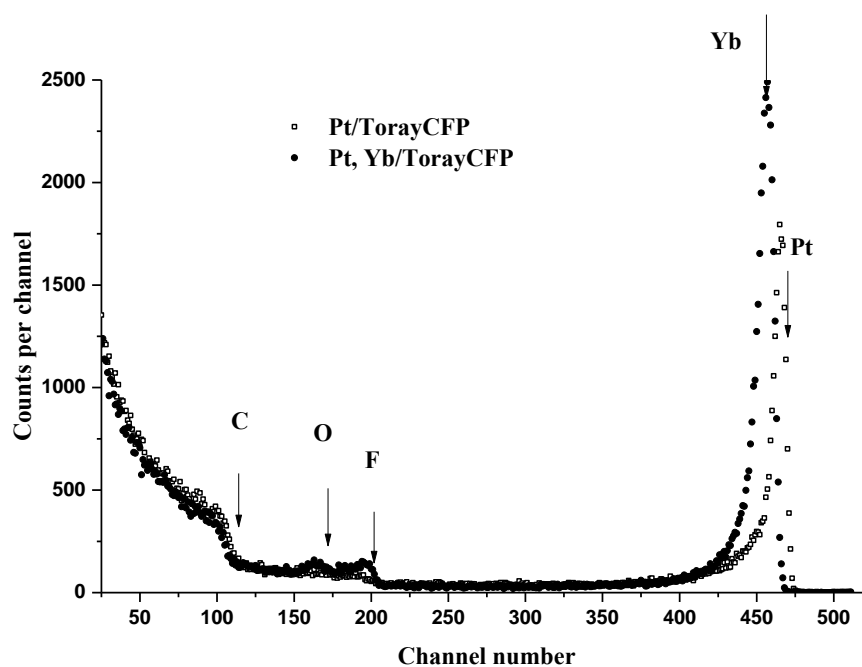


Figure 4. RBS spectra of ^4He ions scattered on the electrocatalysts prepared by platinum (Pt/TorayCFP) platinum and ytterbium (Pt, Yb/TorayCFP) IBAD onto Toray Carbon Fiber Paper TGP-H-060 T catalyst carrier [15].

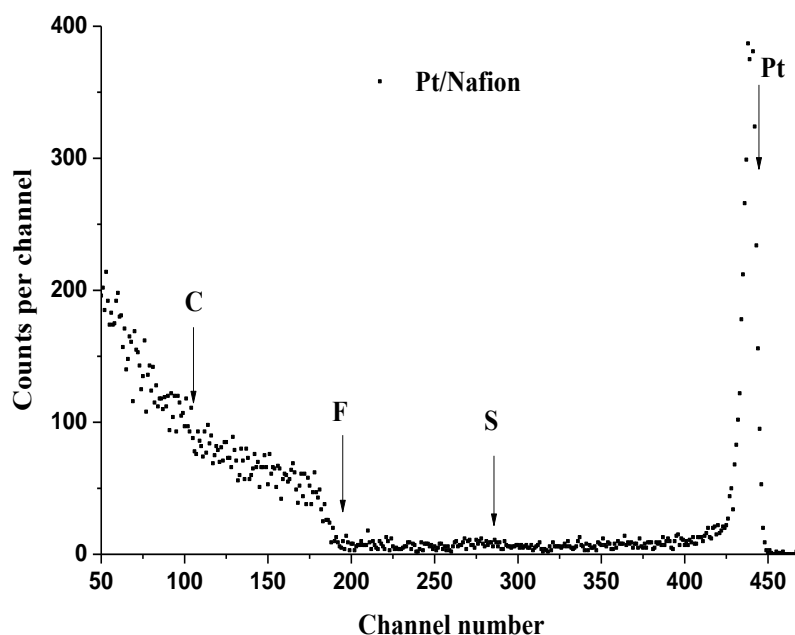


Figure 5. RBS spectrum of ^4He ions scattered on the surface polymer membrane electrolyte NafionTM N115 with layer prepared by platinum IBAD [17].

A catalytic property of samples with prepared layers was studied in electrochemical reactions of the hydrogen evolution and oxidation of methanol and ethanol, which determine the principle of action of low-temperature fuel cells. The activity of electrocatalysts in the hydrogen evolution was studied by the method of cathodic polarization in solution 1 M H_2SO_4 , in oxidation processes of ethanol and methanol – by cyclic voltammetry [6, 7] in solutions of alcohols in sulfuric acid (1 M $\text{C}_2\text{H}_5\text{OH}$ + 0.5 M H_2SO_4 and 1 M CH_3OH + 0.5 M H_2SO_4).

The studied samples are active in each of these processes. The activity determined by the value of the current density in voltammetric measurements depends on the composition of the layer, i.e. on the type of deposited metals during its formation.

Let us consider in more detail the results of the study [16] of the activity of the obtained electrocatalysts based on AVCarb[®] Carbon Fiber Paper P50 and Toray Carbon Fiber Paper TGP-H-060 T carriers in the ethanol oxidation reaction, which are presented in figures 6 and 7 in the form of cyclic voltammograms.

The process of the electrochemical oxidation of both ethanol and methanol is multistage, complex, and has not been thoroughly studied in detail yet. It includes the following main stages: the electrochemical adsorption of alcohol molecules, their decomposition by successive dehydrogenation in the adsorbed state, the formation of adsorbed carbon-monoxide molecules CO_{ads} , and their subsequent removal upon interaction with chemisorbed water molecules or OH_{ads} groups [8, 9].

The electrochemical oxidation of alcohol in a sulfuric acid solution is displayed on cyclic voltammograms in the form of specific current peaks when the electrode potential changes in both the anode and cathode directions [18]. Such peaks are clearly manifested in the cyclic voltammograms (figures 6, 7) of all studied samples of electrocatalysts, which indicates their activity in the ethanol oxidation process. When the potential changes in the anode direction, there is a current peak on the voltammogram due to the process of multistage oxidation of ethanol. This is followed by a decrease in current due to blocking of the electrocatalyst surface by electrochemical adsorption products. With the subsequent sweep of the potential in the cathode direction, a fairly intense current peak appears on the voltammogram with a maximum at a potential value of about 400 mV, which is due to the resumption of the ethanol oxidation process on the reduced catalyst surface [9, 18].

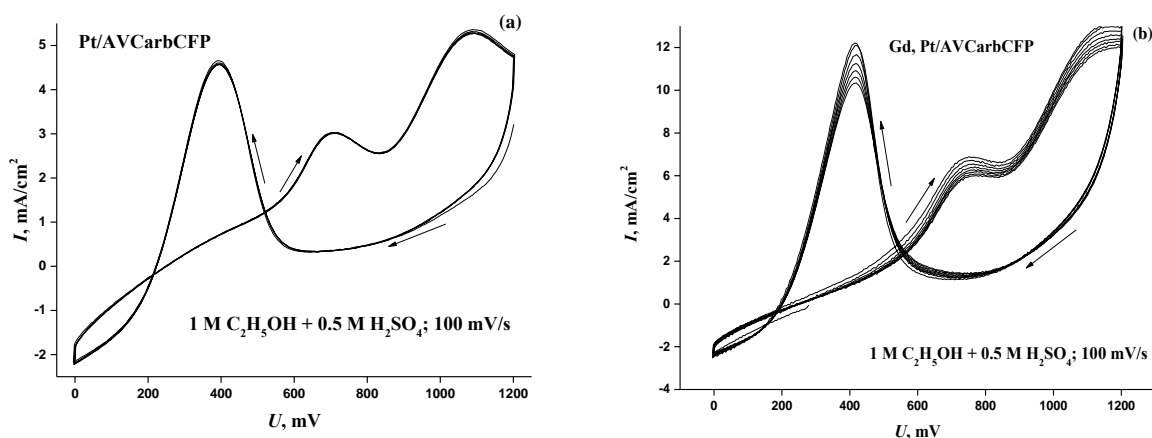


Figure 6. Cyclic voltammograms of the electrocatalyst prepared by platinum (a), gadolinium and platinum (b) IBAD on AVCarb[®] Carbon Fiber Paper P50 carrier in ethanol contained solution 1 M C₂H₅OH + 0.5 M H₂SO₄ [16].

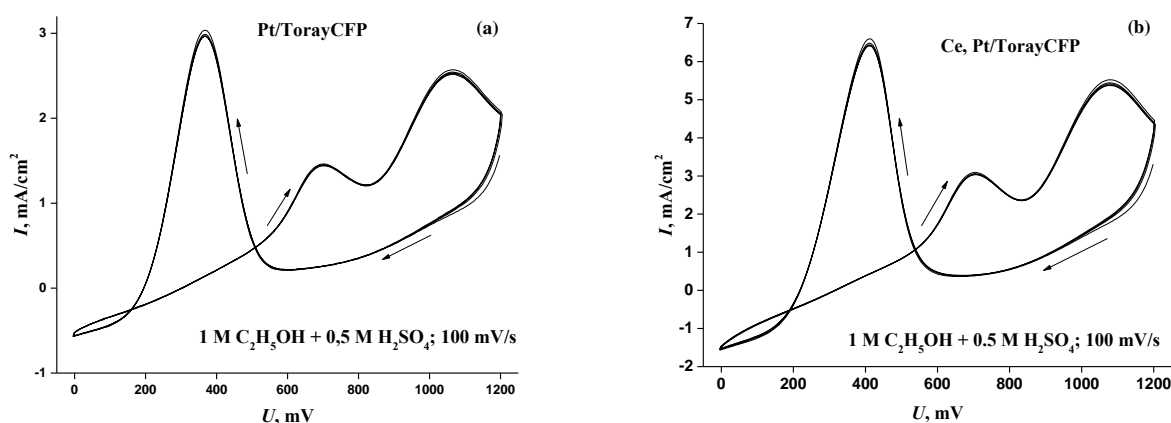


Figure 7. Cyclic voltammograms of the electrocatalyst prepared by platinum (a), cerium and platinum (b) IBAD on Toray Carbon Fiber Paper TGP-H-060 T carrier in ethanol contained solution 1 M C₂H₅OH + 0.5 M H₂SO₄ [16].

Electrocatalysts based on carbon fiber carriers obtained by IBAD of platinum and one of the rare earth metals have a higher activity in the oxidation of more complex ethanol molecules C₂H₅OH compared to methanol CH₃OH, for which it is necessary to ensure the break of the C–C chemical bond. The introduction of a rare-earth metal in addition to platinum as an activating additive into the formed layers contributes to a significant increase in the activity of electrocatalysts in the ethanol oxidation reaction [16].

Corrosion protective layers were formed by IBAD of alloying metals: Cr, Sn onto stainless-steel [19]; Zn, Cd and Al – onto carbon steel and stainless-steel [20]; Zn, Cd, Zr and Cr – onto pure aluminium and aluminium alloy [21]. Corrosion properties of samples with IBAD produced layers were tested with use of electrochemical polarization method [22]. According to the data of polarization measurements, the values of the corrosion potential and corrosion current density of the studied materials are determined.

The layers formed by the deposition of metals in the IBAD mode on the surface of steels are characterized by a similar composition as the catalytic layers. The layers obtained on aluminium and aluminium alloy are localized mainly in the area of the surface oxide film [21] (figure 8).

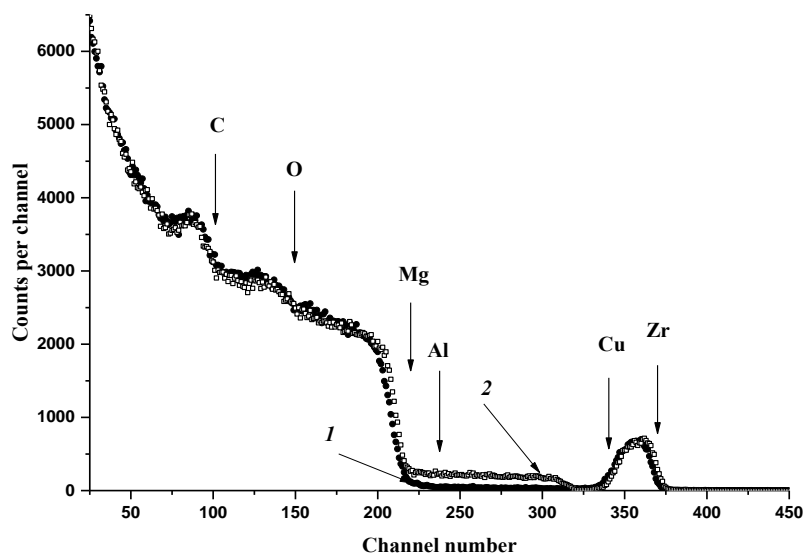


Figure 8. RBS spectra of ^4He ions scattered on the surface pure aluminium grade A7 (1) and aluminium alloy D16 (2) with layers prepared by zirconium IBAD [21].

In [19] the possibility of obtaining chromium-containing protective layers on the surface of current collectors of fuel cells made of 12X18H9T stainless steel using vacuum-plasma methods, including in the IBAD process, was investigated. A significant (by more than two orders of magnitude) increase in the corrosion resistance of steel in $1\text{M H}_2\text{SO}_4 + 2 \cdot 10^{-6}\text{M HF}$ solution occurs after IBAD of chromium and tin.

Studies carried out in [20] showed the possibility of using IBAD of metals (zinc, cadmium, aluminium) when forming layers on the surface of carbon and stainless steels that weaken the intensity of corrosion of aluminium and aluminium alloy in contact with steel parts.

4. Conclusions

We have developed a method for the formation of catalytic and corrosion protective layers by the deposition of metals from the plasma of a vacuum electric arc discharge, which is characterized by simplicity and reproducibility of results. In this case, the metal is introduced into the formed layer under nonequilibrium conditions of treatment with accelerated ions of the deposited metal. Nanosized multicomponent layers were obtained containing atoms of the deposited metals and substrate components, as well as oxygen and carbon impurities.

In particular, during the deposition of platinum and one of the rare earth metals (Ce, Gd, Dy, Yb, Ho) as an activating additive, catalytically active surfaces of electrocatalysts based on special carbon carriers AVCarb[®] Carbon Fiber Paper P50 and Toray Carbon Fiber Paper TGP-H-060 T were obtained, designed for the manufacture of diffusion layers of membrane electrode assemblies of fuel cells direct oxidation of ethanol and methanol with a polymer membrane electrolyte.

The active-surface formation during the deposition of the two metals (platinum and activating additive) was performed in vacuum in two steps, which favorably compares with traditional multi-stage methods of preparing supported catalysts based on carrier impregnation with solutions of compounds of each deposited metal, their reduction to the metallic state, repeated washing to remove impurities, and drying.

The relevance of research in terms of ion-plasma formation of corrosion-resistant layers is due to the need to overcome the disadvantages of electroplating technologies for the formation of protective coatings, such as environmental hazards, multi-stage, complexity of process control, etc. The expediency of using IBAD of metals in the formation on the surface of steels and aluminium alloys of

layers that weaken the intensity of corrosion of products made of these materials is shown. In comparison with the electroplating deposition of protective metal coatings, vacuum IBAD is characterized by simplicity of substrate surface preparation, single-stage, environmental safety and cost-effectiveness.

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