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Stationary and Pulsed Magnetron Sputtering Technologies for Protective/Catalyst Layer Production for PEM Systems

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The results of stationary and pulsed magnetron sputtering (PMS) application for Pt deposition on titanium substrate for PEM (polymer electrolyte membrane) electrochemical devices are presented. The technology allows *in-situ* surface preparation (titanium oxide layer elimination) just before platinum deposition. Depending on the sputtering regime the coatings with various microstructure and electrochemical characteristics are produced. Operation regimes for the deposition of protective coatings preventing from saturation with hydrogen and surface oxidation/corrosion and also for the deposition of catalytically active layers are selected. The coatings were tested in sulfuric acid solutions (model conditions) and in PEM electrochemical cell (unitized regenerative fuel cell).

Keywords: Platinum coating; Pulsed magnetron sputtering; PEM electrochemical devices.

1. INTRODUCTION

Current collectors of PEM electrolyzers and reversible or unitized regenerative fuel cells; and also bipolar plates of PEM electrolyzers and fuel cells (with a solid polymer electrolyte) are usually produced from titanium which has good mechanical properties, electrical conductivity and high corrosion resistance. Titanium is harmless for environment and is not too expensive. However, these components of electrochemical devices are exposed to aggressive environment therefore they need additional protection from corrosion/oxidation. The different variants of titanium surface treatment and modification have been offered, for example, chemical or electrochemical gold plating on bipolar plates or carbon ion implantation [1, 2]. Platinum is a very perspective material for practical applications in spite of the price [3-5]. Platinum coating provides chemical resistance, high electrical conductivity, the necessary thermal conductivity and catalytic activity, which is rather important in the case of current collectors [4, 6]. It should also be noted that platinum coated titanium electrodes are used in some other processes such as cathodic protection, electrochemical waste water treatment [7-9]. Depending on the specific conditions coatings of different structure, compactness, thickness and porosity are required.

In this research the possibility of pulsed magnetron sputtering method application for the deposition of Pt coatings with different microstructure on titanium substrate is considered. Pulsed regime of coating deposition reduces substrate thermal loading (heating), substantially increases the discharge current density and ionization degree of the sputtered material. Parameters of pulsed sputtering regime influence on the coating microstructure and density. In our experiments bipolar power source was also used for pulsed bias voltage application to the titanium substrate. Pulsed negative bias voltage creates plasma sheath's environment near the substrate surface which accelerates the positive inert gas ions and enhances surface bombardment.

2. EXPERIMENTAL

2.1 Abbreviations frequently employed:

PMS refers to Pulsed Magnetron Sputtering, DC refers to Direct Current, TEM refers to Transmission Electron Microscopy, EDX refers to Energy-dispersive X-ray spectroscopy, CV refers to Cyclic Voltammogram, EAS refers to Electrochemically Active Surface area, PEM refers to Polymer Electrolyte Membrane or Proton Exchange Membrane.

2.2. Magnetron sputtering technology.

DC (direct current) magnetron system MIR-1 with the bipolar power source APEL-SB-5BP-1300 was used for the films and coatings deposition by sputtering. MIR-1 allows obtaining deposition on substrates of different forms and even on powder supports. The basic parameters of MIR-1: cylindrical horizontal working chamber, one DC planar magnetron, discharge current up to 5 A, discharge voltage 350-500 V. Usually Ar is used as working gas. The followings regimes of magnetron sputtering are used in this research:

DC magnetron sputtering. Bias voltage is not applied to the substrate. Magnetron current is 0.05 A, discharge voltage 410 V, inert gas - argon, Ar pressure – 9.3 x10^{-3} mbar.

DC magnetron sputtering with pulsed bias voltage (- 100 to - 400V), pulsed frequency 10 kHz, applied to the Ti substrate. Magnetron current is 0.05 A, discharge voltage 410 V, inert gas – argon, Ar pressure – 9.3 x10^{-3} mbar.

Mid-frequency pulsed DC sputtering (without bias voltage applied to the substrate). Pulsed frequency - 10 kHz. Magnetron current is 0.06-0.09 A, voltage - 328-400 V, inert gas – argon, Ar pressure – 9.3 x10^{-3} mbar. Negative pulse duration is 90 μs, positive pulse – 10 μs (small positive potential is applied to the target during the 'pulse-off' period for the neutralization of surface charges). Pulsed frequency - 100 kHz. Magnetron current is 0.10 A, voltage - 410 V, inert gas – argon, Ar pressure – 9.3 x10^{-3} mbar. Negative pulse duration is 7 μs, positive pulse – 3 μs (small positive potential is applied to the target during the ‘pulse-off’ period for the neutralization of surface charges).

2.3. Preliminary treatment of substrate surface

In-situ surface preparation consisted of 2 stages. First, preliminary heating up to 250^{o}C at Ar pressure of 2.7x10^{-4} mbar during 10 min was used to remove adsorbed molecules. Second, pulsed Ar^{+} ion treatment was used to remove surface titanium oxide layer by sputtering. Pulsed bias voltage of -600V (pulsed frequency 10 kHz) was applied to the substrate during 15 min at Ar pressure of 1.3x10^{-2} mbar.

2.4. Materials

For coatings deposition Pt target of 42 mm in diameter and of 1 mm thickness was used. Substrates 1x1 cm^2 were cut out from 0.1 mm titanium foil Russian trade mark VT1-0 (technical titanium with high mechanical properties and corrosion resistance). Chemical composition (wt %): Ti – basis, Si – 0.10, Fe – 0.25, O – 0.20, H – 0,010, N – 0.04, C– 0.07, other impurities – 0.030.

2.5. Microstructure and elemental composition

Pt coated titanium substrate microstructures were investigated by Transmission Electron Microscopy (TEM) using electronic microscope Titan 80-300 S/TEM (FEI, USA). Elemental composition was determined by the method of energy dispersion X-ray spectroscopy (EDS) with the help of EDAX EDS System (EDAX, USA) [10].

2.6. Electrochemical measurements

The electrochemical measurements were carried out in a three-electrode cell in 1M solution of sulfuric acid at the temperature of 25 ^{0}C. Platinum wire was used as a counter electrode, saturated silver-chloride electrode filled with saturated potassium chloride - as a reference electrode, thin titanium foil 1x1 cm with Pt layer deposited by magnetron sputtering – as a working electrode.

Polarization quasi-stationary curves (scan rate 0.1 mV/s) and potentiometric CV curves (scan rate 20 mV/s) were recorded on Solartron 1285 potentiostat (Solartron Analytical).

3. RESULTS AND DISCUSSION

3.1. Preparation of the titanium substrate surface prior to coating

Prior to platinum electrodeposition or electroless deposition titanium oxide layer elimination is necessary. This important but very difficult procedure usually involves several steps: sandblasting, etching in boiling acids, treatment in concentrated acids, ultrasonic cleaning (e.g. [11-13]). In contrast to it magnetron sputtering technology allows *in-situ* surface preparation in the same vacuum chamber just before platinum deposition. Surface preparation consists of preliminary heating up to 250°C at Ar pressure of 2.7×10^{-4} mbar during 10 min to remove adsorbed molecules followed by pulsed Ar^+ ion treatment to clean an oxide layer.

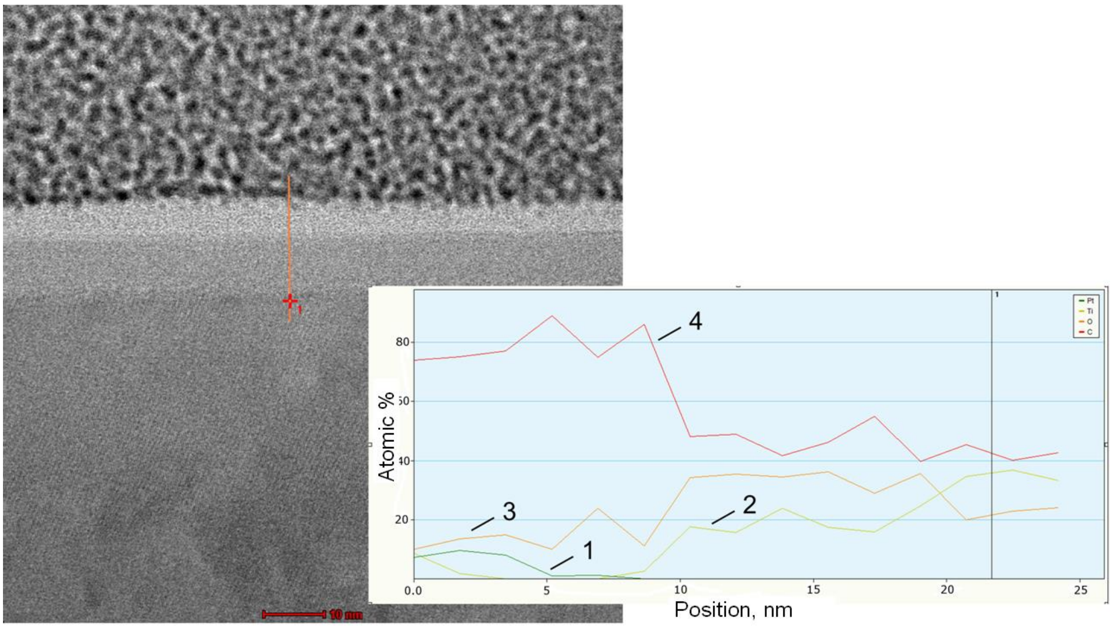

Figure 1. TEM image and EDX data for Ti substrate before cleaning. Ti oxide layer presents on the surface. *1* – Pt, *2* – Ti, *3* – O, *4* – C. Scale bar 10 nm. (Carbon is the component of the protective coating deposited according to EDX sample preparation method [10].)

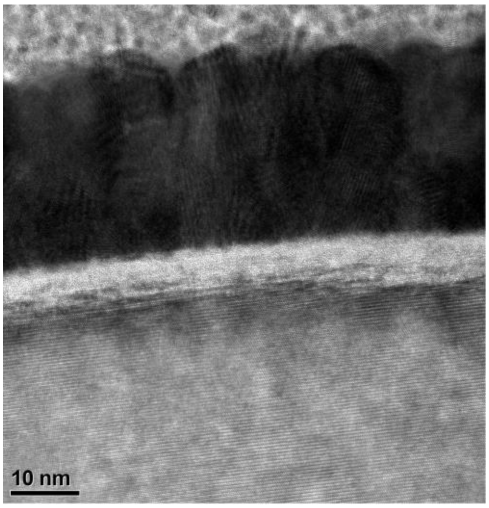

Figure 2. TEM image for Pt coated titanium substrate after heating up to 250°C at Ar pressure of 2.7×10^{-4} mbar during 10 min. Ti oxide layer presents between the substrate surface and Pt layer. Scale bar 10 nm.

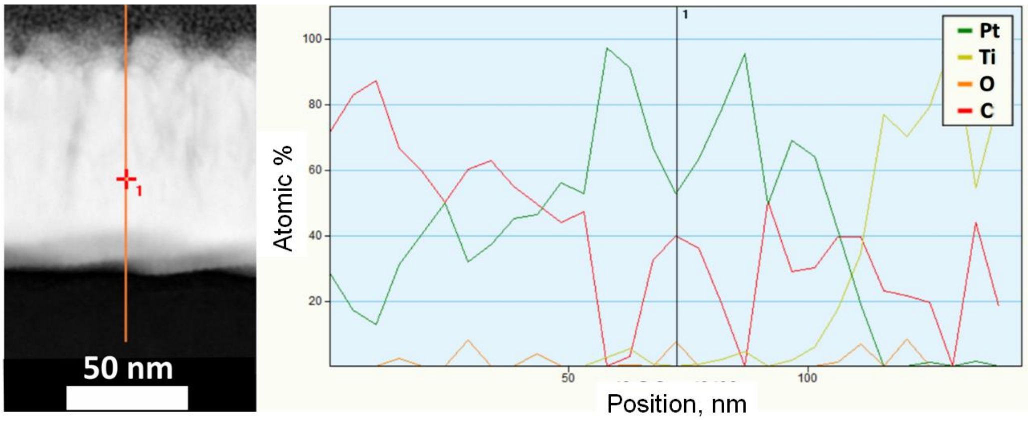

Figure 3. Sample 4: Pt layer deposited on Ti (VT1-0) foil (DC sputtering). Surface preparation: heating to 250°C, 10 min., Ar pressure of 2.7x10^{-4} mbar; pulsed Ar$^+$ ion treatment (bias voltage U = - 600V, pulsed frequency 10 kHz), 15 min, Ar pressure of 1.3x10^{-2} mbar. (Carbon is the component of the protective coating deposited according to EDX sample preparation method [10].)

Our experiments showed that effective oxide layer elimination occurred at pulsed bias voltage of - 600V or higher (pulsed frequency 10 kHz) applied to the substrate during 15 min at Ar pressure of 1.3x10^{-2} mbar. TEM images of initial Ti substrate, Ti substrate with Pt layer deposited after heating and Ti substrate with Pt layer deposited after heating and pulsed ion cleaning under conditions mentioned above are shown in Fig. 1-3. Titanium oxide layer can be seen in the first two cases. Elemental analysis data confirm its presence. Pulsed ion cleaning eliminated oxide layer (Fig.3). It can also be seen that Pt penetrated into the substrate to a depth of ~ 10 nm.

3.2. Deposition of Pt coatings with various microstructures

3.2.1. Operation regimes of sputtering.

For the deposition of Pt coatings with various microstructures the following operation regimes of magnetron sputtering were used:

1. Stationary DC magnetron sputtering (without bias voltage applied to the substrate);
2. Stationary DC magnetron sputtering with pulsed bias voltage of - 200V (pulsed frequency 10 kHz) applied to the Ti substrate;
3. Pulsed mid-frequency (10 kHz) DC sputtering (without bias voltage applied to the substrate);
4. Pulsed mid-frequency (100 kHz) DC sputtering (without bias voltage applied to the substrate).

Surface pretreatment (heating followed by pulsed ion cleaning as described above) has been carried out in all cases.

3.2.2. Stationary DC magnetron sputtering (without bias voltage applied to the substrate)

Microstructure and elemental composition of the samples produced in this base regime are presented in Fig. 3 and Fig.4. The coatings have non-uniform density: the lower part near the substrate surface (about half of the coating thickness) is more compact. The higher part consists of expanding columns which tops form rough surface. Roughness factor (defined as the ratio of electrochemically active surface area (EAS) to the geometric surface) is 4.8-6 (for details see section "Electrochemical measurements" below)

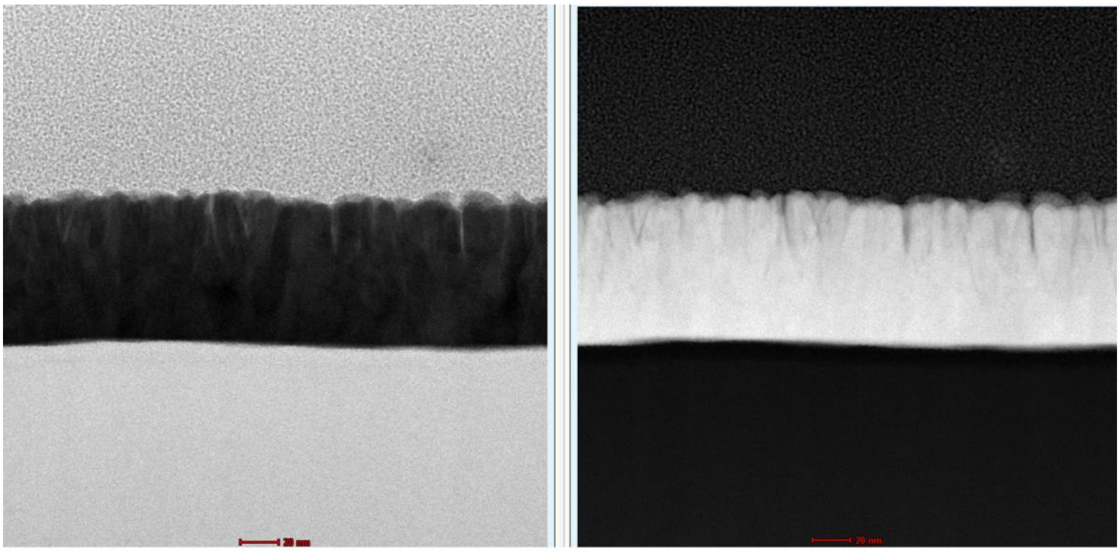

Figure 4. TEM image of Pt layer deposited on Ti (VT1-0) foil by DC sputtering. I =0.05 A, U=410 V. Ar pressure 9.3×10^{-3} mbar. T=10 min. Scale bar 20 nm.

3.2.3. Stationary DC magnetron sputtering with pulsed bias voltage applied to the Ti substrate

The application of pulsed negative bias voltage to a conductive substrate was first used in the early 90s of the last century for TiN deposition by cathodic arc evaporation [14]. As a result, the quality of the coating was improved (namely reduction of the macroparticles amount). Later pulsed negative bias voltage began to be used for coatings deposition by magnetron sputtering. This regime provided high adhesion, hardness, improved surface structure and morphology [e.g. 15, 16]. Pulsed negative bias voltage allows better control of surface roughness compared to DC bias. Application of pulsed negative bias voltage enhances plasma density and mobility. This is important to create more ions bombardments of the growing film and at the same time process temperature can be reduced.

Our preliminary experiments have shown that at pulsed bias voltage higher than -300V re-sputtering of the coating occurs leading to the loss of significant amount of deposited Pt. For pulsed bias voltage of -100 or -200V parameters of microstructure and electrochemical properties of the coatings had no appreciable distinctions. Below we present results obtained for -200V pulsed bias voltage applied to the Ti substrate.

The coating obtained in this regime is very dense near the substrate (Fig. 5). As the crystallites grow the compactness decreases to some extent. The roughness factor is rather low (1.53) and is close to that for Pt foil (1.4-1.8). This regime is preferable for protective dense coatings production.

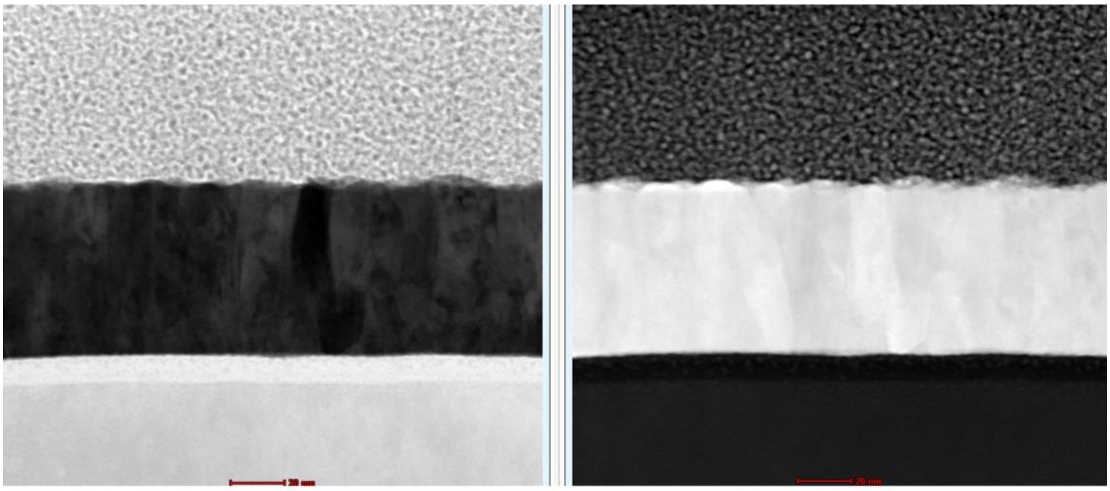

Figure 5. Sample 3. TEM image of Pt layer deposited on Ti (VT1-0) foil. Pulsed bias voltage U= -200V (pulsed frequency 10 kHz). I =0.05 A, U=410 V. Ar pressure 9.3x10^{-3} mbar. T=10 min. Scale bar 20 nm.

3.2.4. Pulsed mid-frequency (10 and 100 kHz) DC sputtering

During pulsed magnetron sputtering the target potential is periodically switched to a small positive potential thus providing the neutralization of surface charges. This is important for eliminating arcing problem. Both ions and electrons can follow the potential changes. Compared to continuous DC sputtering bipolar pulsed DC magnetron sputtering creates higher current density, more bombardments to the target and substrate surface. High quality defect-free dense films of small thickness can be obtained. The coatings obtained in this regime have improved electrical and mechanical properties.

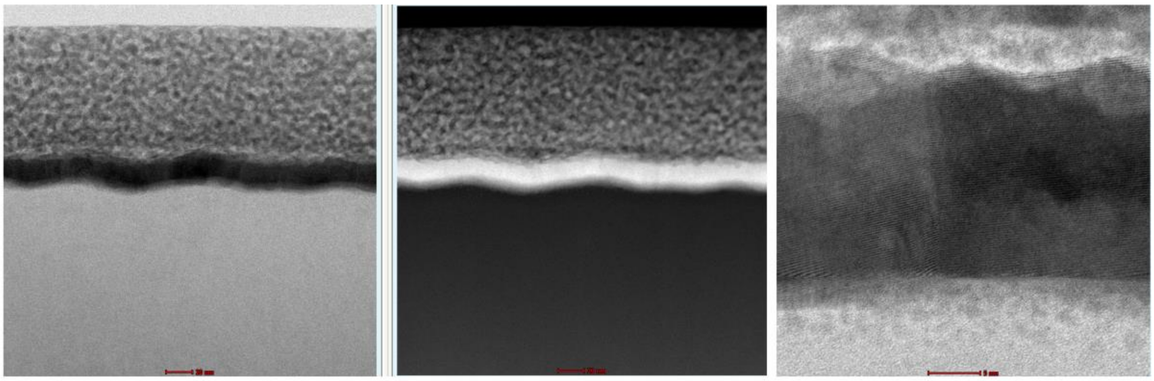

Figure 6. Sample 2. TEM image of Pt layer deposited on Ti (VT1-0) foil. Pulsed voltage U= -328V (10 kHz). I =0.06 A. Ar pressure 9.3x10^{-3} mbar. T=10 min. Scale bar: left and in the middle 20 nm, right – 5 nm.

It is necessary to note that processes during pulsed magnetron sputtering are much more complex than those at continuous (stationary) DC sputtering and even at RF (radio-frequency) sputtering [16-18].

Two samples with sharp distinctions in the thickness have been obtained in the regime of PMS 10 kHz. The 20 nm coating is very dense, textured, with the smooth surface (Fig. 6). Oriented growth of the film can be seen. It may be important for the development of a novel class of electrocatalysts based on the oriented thin metal films with highly ordered structure [19]. According to EDX data Pt penetrated into Ti substrate which improved adhesion. Roughness factor defined from electrochemical measurements is only 1.43 which is close to the value for Pt foil.

The structure of the sample 5 with a thick Pt layer is different (Fig. 7). At the initial stage of the deposition a compact quasi-homogeneous microstructure is formed. On reaching of the certain thickness it changes to a porous columnar structure. The roughness factor runs up to 6.9.

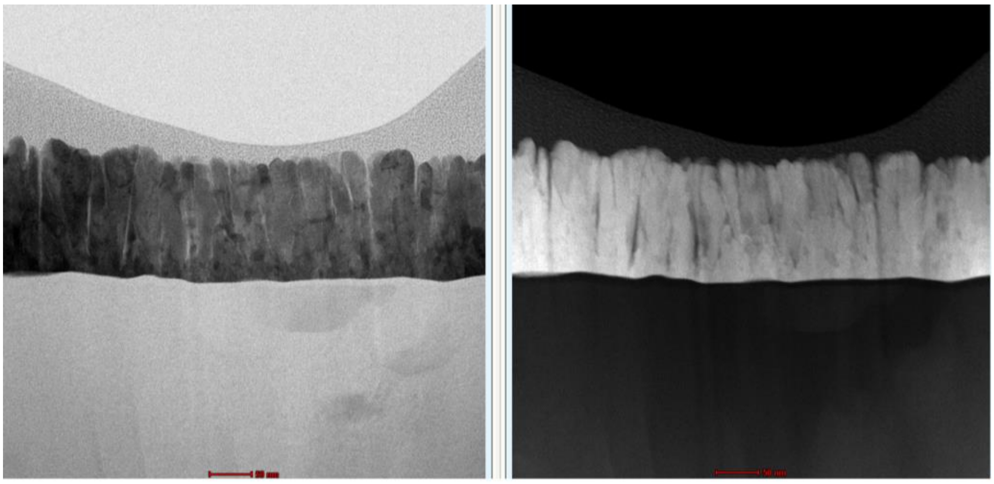

Figure 7. Sample 5. TEM image of Pt layer deposited on Ti (VT1-0) foil. Pulsed voltage U= -400V (10 kHz). I =0.09 A. Ar pressure 9.3×10^{-3} mbar. T=15 min. Scale bar 20 nm.

Sample 1 with a dense columnar coating was obtained in the regime of PMS 100 kHz (Fig. 8). The roughness factor runs up to 6.76 similar to that of the thick coating deposited in the regime of PMS 10 kHz (see Fig. 7).

The results show that the coatings deposited in the regime of PMS 10 or 100 kHz have a dense initial layer changing its structure to a columnar one with the developed surface.

Thus, it can be concluded that magnetron sputtering can be used for the deposition of Pt coatings with different microstructure on titanium substrate. All the coatings have high adhesion due to *in-situ* Ti surface preparation (oxide layer elimination) just before platinum deposition. The coatings obtained by DC magnetron sputtering with pulsed bias voltage applied to the Ti substrate are very dense near the substrate and can be used for protection. The coatings deposited using PMS regimes are also dense near the substrate surface but as the coating thickness of the layer grows the microstructure changes to a porous columnar one with the developed surface. It was shown that the microstructural features, density, porosity, surface area depend on parameters of pulsed sputtering regimes and film thickness. Coatings of this type can be used as catalytic/protective ones. We would like to stress that magnetron sputtering was successfully used for Pt-based electrocatalysts synthesis [20-24]. However the aim of these studies was to improve electrocatalytic performance due to the deposition of Pt nanoparticles but not Pt continuous layer as in the present work.

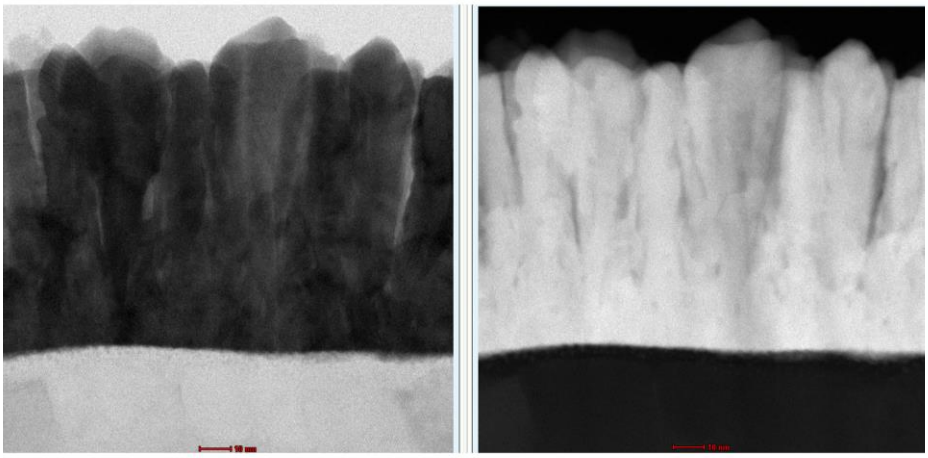

Figure 8. Sample 1. TEM image of Pt layer deposited on Ti (VT1-0) foil. Pulsed voltage U= -410V (100 kHz). I =0.10 A. Ar pressure $9.3x10^{-3}$ mbar. T=10 min. Scale bar 20 nm.

3.3. Electrochemical measurements

The cyclic voltammograms (CVs) for Pt coated Ti electrodes in the potential region -0.17-+1.2 V are presented in Fig. 9. Current was estimated for the visible (geometric) surface area of electrodes.

Data for the samples 4, 5, 1 obtained in the different regimes correspond to the typical voltammogram for polycrystalline Pt: in the hydrogen region distinct peaks of adsorption/desorption of weakly bound and strong bound hydrogen are present. This means that pure polycrystalline Pt practically entirely covers titanium substrate surface. Microstructures of these samples with coatings are shown in Fig. 3, 7, 8, correspondingly. Roughness factors are 4.8-6; 6.9 и 6.76. EAS values were estimated by the integration of hydrogen desorption peaks on the CVs using the technique described in detail in [25, 26]. It was taken into account that the electrical charge associated with hydrogen monolayer desorption is 0.21 mC/cm^2 [27]. Roughness factors were defined as the ratio of electrochemically active surface area of Pt and the electrode visible (geometric) surface [26].

Voltammograms for the sample with the coating deposited by DC sputtering with pulsed bias voltage of - 200V applied to the Ti substrate (curve 3) and for the sample with thin 20 nm coating obtained in the regime of PMS 10 kHz (curve 2) are different from CVs for the samples 4, 5 and 1 described above. No distinct peaks corresponding hydrogen adsorption/desorption on Pt could be seen. Microstructures of these samples with coatings are shown in Fig. 5 and 6, correspondingly.

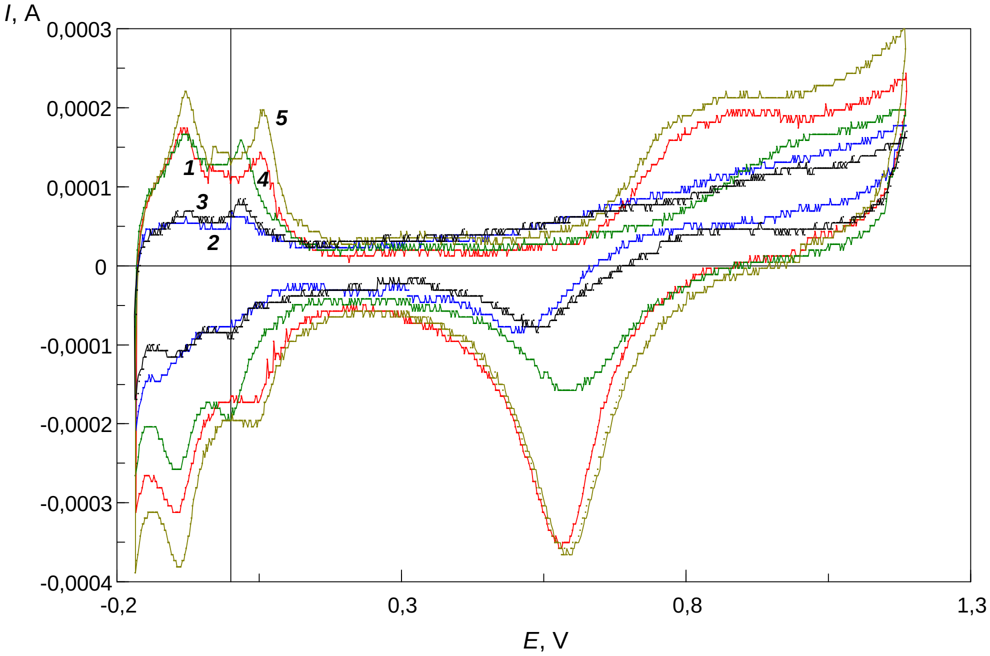

Figure 9. CV curves for Pt/Ti electrodes recorded in 1M solution of sulfuric acid in the potential region -0.17 V - + 1.2 V at the temperature of 25 ^{0}C (scan rate 20 mV/s). Curve 1 - Sample 1 with Pt coating obtained in the regime of PMS 100 kHz. Curve 2 - Sample 2 with 20 nm Pt coating obtained in the regime of PMS 10 kHz. Curve 3 - Sample 3 with Pt coating obtained in the DC regime with pulsed bias voltage of - 200V applied to the Ti substrate. Curve 4 - Sample 4 with Pt coating obtained in the DC regime without pulsed bias voltage. Curve 5 - Sample 5 with thick Pt coating obtained in the regime of PMS 10 kHz.

As was mentioned above for the sample 2 oriented growth of the film could be seen. Roughness factors are rather low (1.53 and 1.43, correspondingly) and are close to that for Pt foil (1.4-1.8). Therefore platinum films on these samples have the highest possible dense structure and the least developed surface (electrochemically active surface (EAS) is 1.8 and 2.6 m^2/g in spite of a very small coatings thickness). However for these samples the activity in the hydrogen evolution process at the potential $E \leq -0.23$ V was higher compared to those for other samples including Pt foil (Fig. 10). Most probably such “anomalous” activity is caused by structure peculiarities formed under high energy plasma. Among these peculiarities is the film texturing due to a high surface mobility of adsorbed atoms.

In the oxygen region (Fig. 11) sample 5 with thick Pt coating obtained in the regime of PMS 10 kHz (curve 5) and sample 1 with Pt coating obtained in the regime of PMS 100 kHz (curve 1) show the maximal activity which is in accordance with rather high surface roughness factors of these samples (~7). Microstructures of these samples with coatings are shown in Fig. 7 and 8, correspondingly. It is interesting that after potentiostatic measurements the surface roughness increased from 6.76 to 10.86 for sample 1 and from 6.9 to 11.0 for sample 5 and EAS reaches 6 m^2/g (for the sample 1). One can assume that quasi-stationary polarization in the anodic region of potentials increased electrode surface area by, for example, removal of impurities accumulated on a high-active Pt surface from the air during storage.

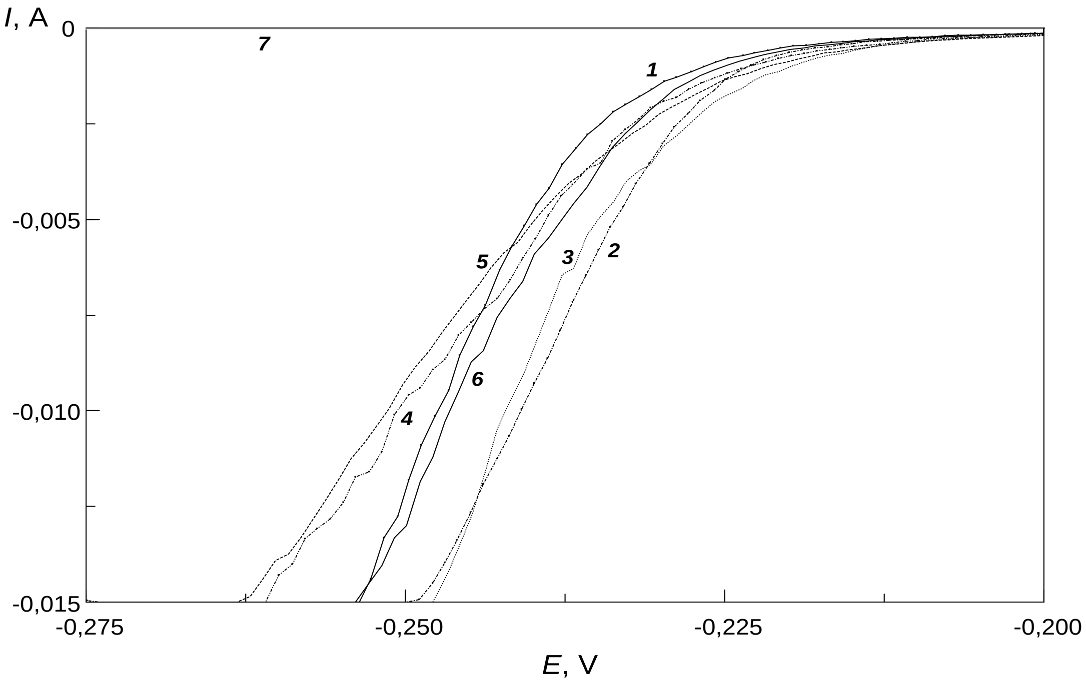

Figure 10. Quasi-stationary polarization curves for Pt/Ti electrodes recorded in water solution of 1M of sulfuric acid in the potential region from 0.6 V to – 0.35 V at the temperature of 25 ^{0}C (scan rate 0.1 mV/s). Curve 1 - Sample 1 with Pt coating obtained in the regime of PMS 100 kHz. Curve 2 - Sample 2 with 20 nm Pt coating obtained in the regime of PMS 10 kHz. Curve 3 - Sample 3 with Pt coating obtained in the DC regime with pulsed bias voltage of - 200V applied to the Ti substrate. Curve 4 - Sample 4 with Pt coating obtained in the DC regime without pulsed bias voltage. Curve 5 - Sample 5 with thick Pt coating obtained in the regime of PMS 10 kHz. Curves 6 for Pt foil and curve 7 for Ti foil are given for comparison.

Certainly a further optimization of technology and search for the minimum coatings thickness must increase EAS values. Sample 2 with thin 20 nm Pt coating obtained in the regime of PMS 10 kHz (curve 2) and sample 3 with Pt coating obtained in the DC regime with pulsed bias voltage of - 200V applied to the Ti substrate (curve 3) show lower activity in the oxygen evolution process. Absence of “anomalous” activity (as in the case of cathodic polarization) could be attributed to elimination of surface structure peculiarities due to surface oxide formation.

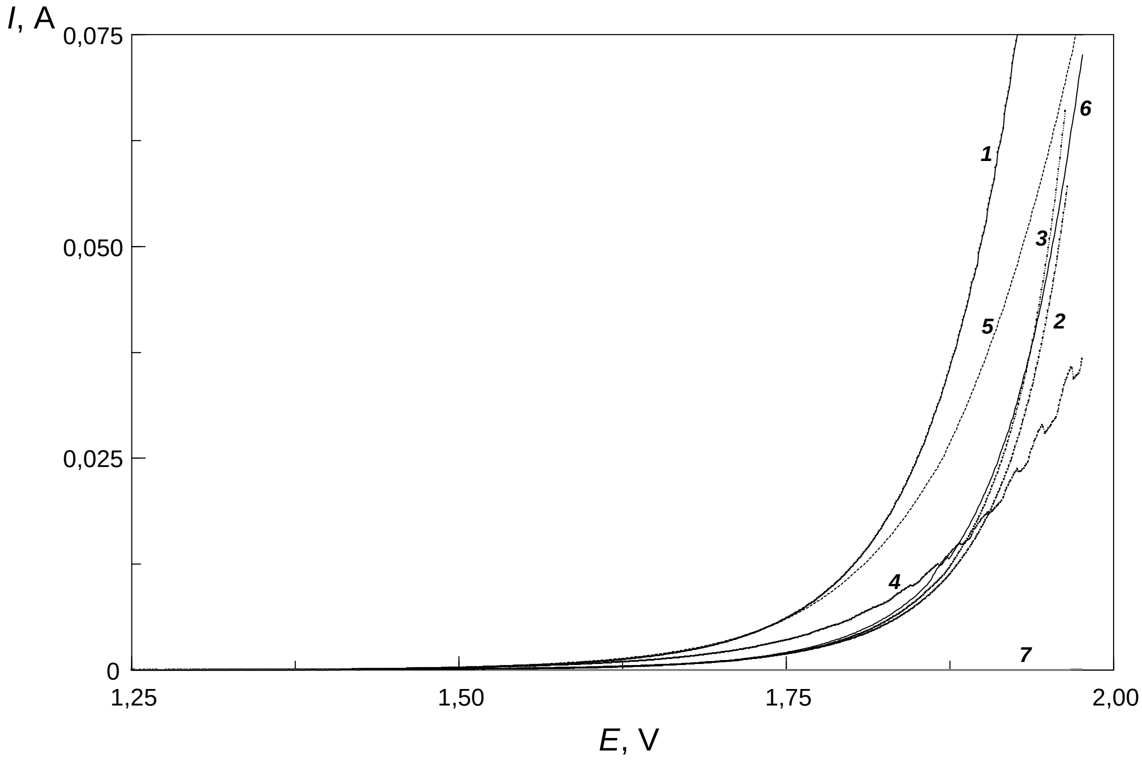

Figure 11. . Quasi-stationary polarization curves for Pt/Ti electrodes recorded in water solution of 1M of sulphuric acid in potential region 0.6 – 2 V at the temperature of 25 ^{0}C (scan rate 0.1 mV/s). Curve 1 - Sample 1 with Pt coating obtained in the regime of PMS 100 kHz. Curve 2 - Sample 2 with 20 nm Pt coating obtained in the regime of PMS 10 kHz. Curve 3 - Sample 3 with Pt coating obtained in the DC regime with pulsed bias voltage of - 200V applied to the Ti substrate. Curve 4 - Sample 4 with Pt coating obtained in the in the DC regime without pulsed bias voltage. Curve 5 - Sample 5 with thick Pt coating obtained in the regime of PMS 10 kHz. Curves 6 for Pt foil and curve 7 for Ti foil are given for comparison.

Sample 4 with Pt coating obtained in the DC regime without pulsed bias voltage (microstructure is shown in Fig. 3) has the roughness factor 4.8-6. Its behavior under conditions of anodic polarization differs from that of other samples (particularly, lower current at the potential $E \geq$ 1.8 V, Fig. 11). One can suppose that in this case a partial oxidation of titanium substrate occurred because of insufficient dense structure of Pt film.

The coatings mentioned above were also applied to the porous Ti plates (Russian trade mark PPTM-MP TU 14-1-1895-76 with chemical composition wt%, max: Ti – basis, Si – 0.10, Fe – 0.40, Ni – 0.40, H – 0.35, N – 0.08, C– 0.05, Ca – 0.08, Cl – 0.004; porosity — 30-45%). The structures of all the coatings were rather similar to the structures of Pt coatings deposited on nonporous Ti. Therefore the structures of Pt coatings were mainly determined by the sputtering regimes. These porous titanium samples with coatings were tested as current collectors in a unitized regenerative fuel cell described in detail in [28-31]. We should underline that most of investigations concerning unitized regenerative fuel cells are devoted to the powdered catalysts and not to the catalytic activity and stability of the current collectors.

All the samples demonstrated a good stability (with the exception of the sample with Pt coating obtained in the DC regime without pulsed bias voltage – in the same regime as the sample 4) for more than 300 hours. The samples obtained in the same regime as samples 1 and 5 additionally demonstrated some increase of the electrodes activity but only about 5 %. The detailed results will be published as a separate paper.

At the end of this section we want to mention once more that as is well known electrodeposition and chemical (electroless) Pt deposition can be used for the production of porous platinum electrodes [32] and also for corrosion protection of Ti electrodes [33, 34]. However these methods need toxic chemical reagents (e.g. acid solutions), regular control of reactant concentrations (especially at a large scale production) and do not permit to create interface Pt-Ti layer necessary for improved adhesion and corrosion protection. Magnetron sputtering technology is ecologically clean, has high productivity. Moreover it is rather universal and permits deposition of different types of coatings. DC magnetron sputtering with pulsed bias voltage applied to the Ti substrate is preferable for protective dense coatings production while PMS regimes provide more porous coatings with higher specific surface. As operation regimes can be easily changed during sputtering it is possible to deposit coatings with various properties according to the final goals. One can suppose that similar results can be obtained for Pt deposition on a wide range of metals. Therefore magnetron sputtering is a powerful tool for the future application in electrochemistry.

4. CONCLUSIONS

Results of pulsed magnetron sputtering application for functional Pt coatings deposition on titanium substrates are presented in this work.

Magnetron sputtering technology allows effective *in-situ* surface preparation just before platinum deposition – preliminary heating to remove adsorbed molecules followed by pulsed Ar^+ ion treatment to clean titanium oxide layer. Optimal parameters of ion treatment have been selected: pulsed bias voltage of - 600V (pulsed frequency 10 kHz, negative pulse duration 90 µs, small positive pulse duration 10 µs) should be applied to the substrate during 15 min at Ar pressure of 1.3×10^{-2} mbar.

Depending on the deposition conditions coatings with various microstructure and electrochemical characteristics were produced. Operation regimes for the deposition of protective and catalytically active coatings were selected. To produce dense coatings protecting from saturation with hydrogen and surface oxidation it is expedient to use DC magnetron sputtering with pulsed bias voltage of - 200V (pulsed frequency 10 kHz) applied to the Ti substrate. Thin films (20nm) deposited in the regime of PMS (pulsed frequency 10 kHz) and having maximal density and smooth surface could mainly be used as protective coatings. However in spite of minimal surface area these electrodes showed “anomalous” activity in the hydrogen evolution process. Such surface activity may be connected with microstructure peculiarities but it remains unclear till now.

In the oxygen region thick Pt coatings obtained in the regime of PMS 10 kHz and 100 kHz and having the most developed surface showed maximal activity. It should be noted that roughness factors of these samples increased from ~7 to ~ 11 after potentiostatic measurements. Microstructure of these coatings is dense near the substrate surface but on reaching of certain thickness it changes to porous columnar structure with high surface area. Therefore, such coatings can be used not only as catalytically active but also as protective ones both for oxygen and hydrogen processes. Preliminary tests of such coatings on porous Ti in PEM unitized regenerative fuel cell confirmed this conclusion.

The results of our research show that depending on the deposition conditions different types of coatings can be obtained. Moreover changing the regime of sputtering during **one stage** process may be very efficient for the production of coatings with combined properties for different applications.

It is also worth to note that the possibility of thin Pt films oriented growth has been demonstrated in the regime of magnetron pulse sputtering with the frequency of 10 kHz. It is important for the development of a novel class of electrocatalysts based on highly oriented thin films [19].

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