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Alexander Velichenko¹, Valentina Knysh¹, Olesia Shmychkova¹, Tatiana Luk'yanenko¹,
Svitlana Pukas², Pavlo Demchenko², Vasyl Kordan², Roman Gladyshevskii²

Comprehensive study on physicochemical properties of materials based on titanium suboxides

¹Department of Physical Chemistry, Ukrainian State University of Chemical Technology, Dnipro, Ukraine,

o_shmychkova@ukr.net

²Department of Inorganic Chemistry, Ivan Franko National University of Lviv, Lviv, Ukraine,

svitlana.pukas@lnu.edu.ua

This study focuses on the surface structures and microstructural changes of titanium dioxide nanotubes, when electrochemically coated with platinum and/or palladium. Ti samples anodized in a fluorine-containing electrolyte exhibit self-organized nanotubes of varying diameters with open pores. Annealing at 773 K led to compaction of the porous layer, the formation of cracks, and the appearance of corrugation in the nanotubes. The deposition of platinum produced a transition from a nanotubular surface structure to a microcrystalline structure consisting of rutile crystallites. The palladium-coated samples showed fused blocks characteristic of titanium suboxides. The tubular structure was preserved, even after crystallization. SEM images revealed a comb-like pattern in coatings with varying metal content. XRPD analysis confirmed the presence of anatase and elemental titanium. PdO was detected on the surface of the thermally treated samples. For samples co-treated with Pd and Pt, mutual diffusion of the two metals took place during the heat treatment. The findings reveal surface characteristics, metal deposition effects, and phase composition of titania nanotubes, providing valuable insights for further research.

Keywords: nanotubes, titanium dioxide, platinum group metals, morphology, physico-chemical properties.

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Introduction

Titania nanotubes have attracted considerable attention owing to their use in photocatalysis, treatment of energy storage wastewater, bioanalytical sensors [1-3], motivated by their high surface area and unique structure. They are employed in applications such as water purification, air purification, self-cleaning surfaces, and solar cells [4]. TiO₂ nanotubes are used in energy storage devices, particularly in lithium-ion batteries and supercapacitors, because of their high electrochemical stability and fast ion diffusion properties [5-7]. Their unique structure and biocompatibility make them promising candidates for controlled release systems (drug delivery) [8]. TiO₂ nanotubes can act as catalysts, or catalyst supports, in various catalytic reactions, including oxidation, hydrogenation, and dehydrogenation processes

[9]. Their unique properties and versatility make them a subject of ongoing research and development in numerous fields.

In the present work we investigate physico-chemical properties of electrochemically obtained titania nanotubes coated with a layer of platinum and/or palladium. These systems, where the matrix is made from nonstoichiometric titanium oxides and platinum, is an electron donor and can be promising for use as anode materials [10]. On the one hand, titanium suboxide materials deposited from fluoride-containing electrolytes represent a considerable interest due to their high electrochemical stability and better mechanical properties, in comparison with coatings obtained by hydrothermal synthesis or thermal decomposition of titanium hydroxide. On the other hand, despite a large number of publications [11-13], several issues on surface effects need to be clarified before

drawing final conclusions concerning optimal conditions for deposition, and the correlation between type of deposit and physico-chemical properties.

I. Experimental

All chemicals were reagent grade. Suboxides of titanium were used as a matrix for creating coatings. In contrast to analogues described in the literature [14, 15], the investigated coatings were obtained through a two-step electrochemical synthesis. At the first stage, TiO₂ nanotubes were formed by two-fold anodic polarization of metallic titanium. At the second stage, these nanotubes were partially reduced through cathodic polarization, resulting in the formation of titanium suboxides of different compositions. The original TiO₂ nanotubes were prepared by anodizing Ti foil in ethylene glycol with 0.3 wt.% ammonium fluoride and 2 vol.% water at a constant potential for 3 h (1st anodization), followed by anodizing in ethylene glycol with 5 wt.% H₃PO₄ (2nd anodization). The reduction was conducted in 1 M HClO₄ for 1 h (electrochemical reduction). This approach enabled the creation of a porous surface on the matrix, suitable for subsequent electrodeposition of catalytic layers of platinum and/or palladium. Nitrite electrolyte was used for the deposition of Pt and phosphate electrolyte for the deposition by Pd [16]. The amount of platinum and palladium on the template surface varied from 0.25 to 1.0 mg/cm². Subsequent heat treatment under variable partial oxygen pressures allowed for the formation of composites with different compositions. The high concentration of cation vacancies and oxygen ion deficiency in the matrix significantly increased the mobility of the platinum/palladium atoms during the heat treatment, resulting in nearly metallic electrical conductivity. It should be noted that heat treatments at temperatures above 700 °C led to complete sublimation of palladium from the surface [16]. In addition, at high processing temperatures under air, the formation of titanium nitrides cannot be excluded. These will form titanium oxide during the anodic polarization [10], which is undesirable in this work.

The prepared electrocatalysts were observed by SEM microscopy, and the surface compositions were determined by means of energy-dispersive X-ray spectroscopy (EDXS; scanning electron microscope TESCAN Vega3 LMU, equipped with an energy dispersion X-ray analyzer Oxford Instruments Aztec ONE with a detector X-Max^N20). XRPD data were collected in the reflection mode on a STOE Stadi P diffractometer with the following setup: Cu K α_1 -radiation, curved Ge (1 1 1) monochromator on the primary beam, $2\theta/\omega$ -scan, angular range for data collection 24.000-116.625 ° 2θ with an increment of 0.015°, linear position-sensitive detector with a step of 0.480 ° 2θ , 100-200 s per step, $U = 40$ kV, $I = 35$ mA, $T = 20$ °C. Preliminary data processing and X-ray qualitative phase analysis were performed using the STOE WinXPOW and PowderCell [17] program packages. The crystal structures of the phases were refined by the Rietveld method [18] with the program FullProf.2k [19], applying a pseudo-Voigt profile function and isotropic approximation for the atomic displacement

parameters. Microstructural parameters (size of coherently diffracting domains accepted as average apparent crystallite size D , and average maximum strain ε) were identified by isotropic line broadening analysis [20] using simplified integral breadth methods for the (2 0 0) reflection of the face-centered cubic structure of Pt and/or Pd.

II. Results and discussion

Fig. 1a shows that after anodizing, the surfaces of the Ti samples contained self-organized nanotubes with open pores and effective diameters from 40 to 70 nm, in agreement with the results obtained in [21]. As evidenced by the figure, the coating exhibits variations in pore sizes across different domains, which can be attributed to the peculiarities of the mechanism of oxide film dissolution during titanium anodization. A comb-like pattern is observed for the entire array of nanotubes. Changes in the mesoscopic structure of the surface of the investigated nanotubes upon annealing in air at 500 °C (Fig. 1a) are evidenced, firstly, in a certain compaction of the defective porous layer and the formation of cracks within it, and secondly, in the appearance of corrugation in the nanotubes, consisting of smaller nanoscale formations.

After the deposition of a platinum layer and annealing in air, a transition from the nanotubular mesoscopic surface structure to a microcrystalline structure was observed. The microcrystalline structure consists of a collection of randomly arranged particles with linear dimensions of 1-3 μm (Figs. 1b, c), and the characteristic shape of rutile crystallites [22]. The coating exhibits a well-developed surface, and due to diffusion and sintering, platinum is distributed across the surface. Fused platinum islands can be seen on the surface.

SEM images of samples covered with a layer of palladium show visible fused blocks (Fig. 1d), which is characteristic of the surface morphology of titanium suboxides [23]. The surface is mostly formed by micro-scaled and to a lesser extent by submicron aggregates.

For samples containing a small amount of metal, it has been established that the tubular structure of the oxide is preserved despite crystallization. This can be clearly seen for the samples coated with 0.25 mg/cm² of metal (Figs. 1e, f).

In Figs. 1g, h, SEM images of titanium dioxide nanotubes coated with sequentially deposited layers of platinum and palladium of varying concentrations are presented. It is noteworthy that the comb-like pattern of the coatings is preserved up to a metal content of 1 mg/cm². As the metal content increases, the surface growth of the matrix becomes more prominent.

The distribution of elements on the surface of the samples was determined from characteristic X-ray emission spectra using an energy-dispersive detector (EDXS). The obtained data are presented in Table 1. This method makes it possible to estimate the composition of the surface to a depth of several micrometers. A high content of elemental titanium indicates that the coating is thin. In addition, titanium can act as an additional electron donor. As can be seen from the table, the composition of the resulting coating most likely differs from TiO₂, which

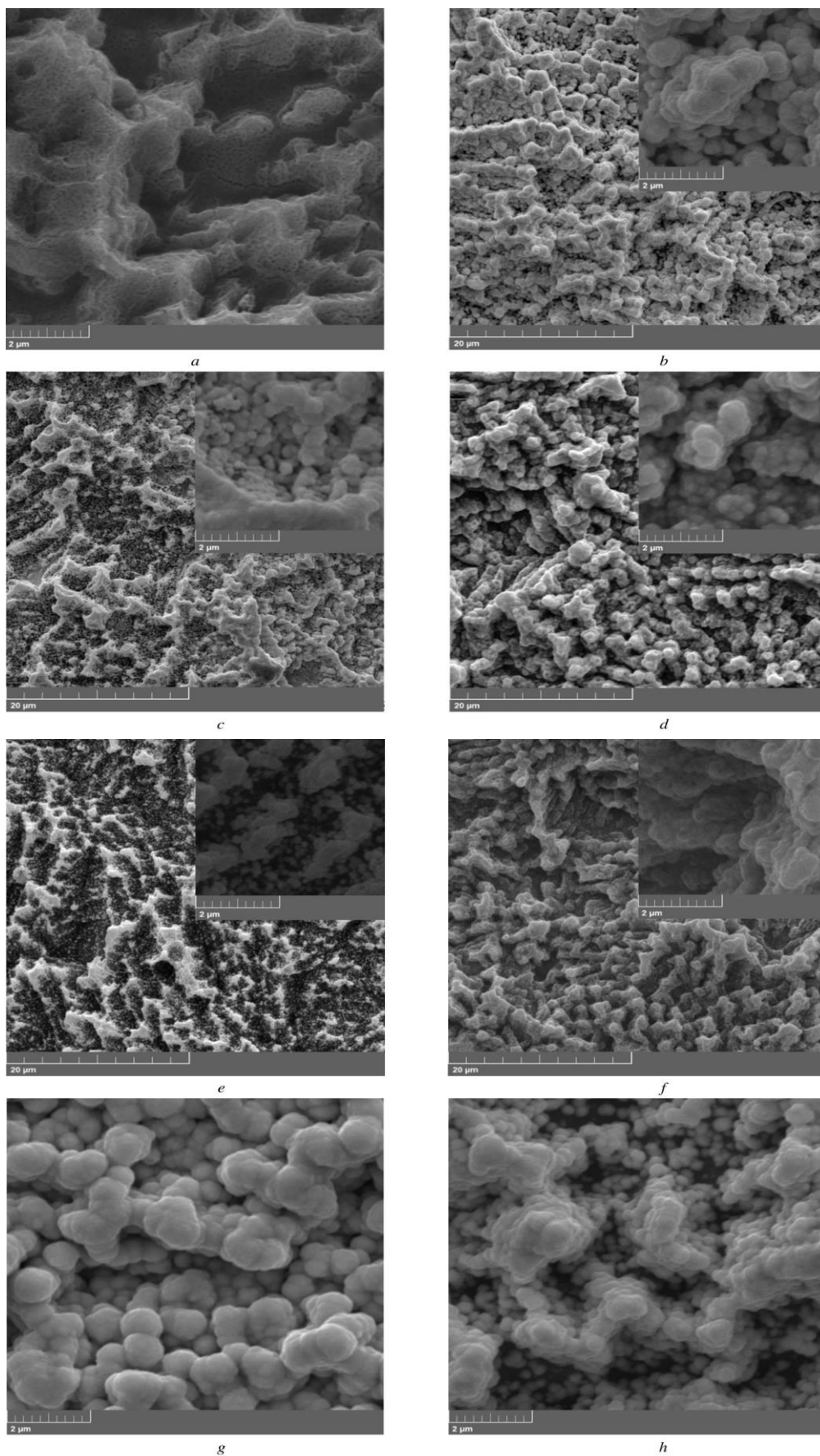


Fig. 1. SEM micrographs of surfaces of TiO₂ nanotubes coatings obtained electrochemically. Pristine nanotubes (a); with electrodeposited layers containing 1 mg/cm² Pt (b), 0.5 mg/cm² Pt (c), 0.5 mg/cm² Pd (d), 0.25 mg/cm² Pt (e), with 0.25 mg/cm² Pd (f), with subsequently electrodeposited layers containing 0.5 mg/cm² Pt and 0.5 mg/cm² Pd (g), 0.25 mg/cm² Pt and 0.25 mg/cm² Pd (h).

Table 1.

Coating	Chemical composition of the surface of the TiO ₂ based samples			
	Elemental analysis, at.%			
	Ti	O	Pt	Pd
0.5 mg/cm ² Pt	30.7	4.3	64.6	–
0.5 mg/cm ² Pd	29.1	13.0	–	56.4
0.25 mg/cm ² Pt	51.3	18.9	29.8	–
0.25 mg/cm ² Pd	47.1	21.0	–	31.9
0.5 mg Pt, 0.5 mg/cm ² Pd	5.6	4.4	53.5	36.4
0.25 mg Pt, 0.25 mg/cm ² Pd	34.6	9.3	26.5	22.2
1.0 mg/cm ² Pt	10.2	4.3	85.5	–

facilitates the electrochemical deposition of the metal (Pt and/or Pd). In the case of stoichiometric titanium dioxide, the oxide surface is strongly hydrated (blocked by hydroxides) and the metal does not adhere to it.

According to the EDXS data, in the case of a platinum coating with a content of 1 mg/cm², the surface of the nanotubes is covered with platinum at a level of 90-95 %. Oxygen was detected on the thermally treated surface of the platinum coating, indicating the formation of surface oxide layers, with an approximate oxygen content of 4 at.%. However, X-ray diffraction did not reveal the presence of platinum oxide phases on the surface, most likely due to their small thickness and insufficient material for analysis. It should be noted that the peaks on the XRPD diagram of the thermally treated samples are narrower than those of the untreated coating (Fig. 2), indicating an increase in the crystallinity and crystallite size of the coating [24, 25]. This can also suggest a decrease of surface hydroxylation due to water entrapment during the electrolytic deposition of the coatings. Similar effects are particularly pronounced in the case of coatings made from metal oxides obtained by electrodeposition, such as manganese dioxide and lead dioxide [26]. Recrystallization of the Pt coating probably occurs during the thermal treatment, reducing the defects in the crystalline lattice, and is accompanied by the loss of so-called crystallization water. Even metallic electroplated coatings may contain a small amount of hydrated phases in the form of hydroxides and oxides, especially if their deposition is accompanied by hydrogen evolution in the cathode compartment. Some of the palladium on the surface is in the form of oxide. Indirect evidence of this is the change in the color of the coating from blue to gray during the reduction process (palladium oxide is reduced to metal).

Powder XRD patterns showed mixed crystalline phases of titanium suboxides, and a broad nanocrystalline face-centered cubic phase from the metal particles. The primary particle size of the metal phase was of the order of 3-4 nm, as estimated from the Scherrer linewidth equation. All of this indicates that the as-prepared catalyst is a heterogeneous mixture of metal and template. Diffractograms of the investigated samples covered with a layer of palladium are shown in Fig. 3.

From the XRD analysis it was found that the phase composition of the nanotubes thermally treated at 500 °C corresponds to anatase (Fig. 4) and elemental titanium.

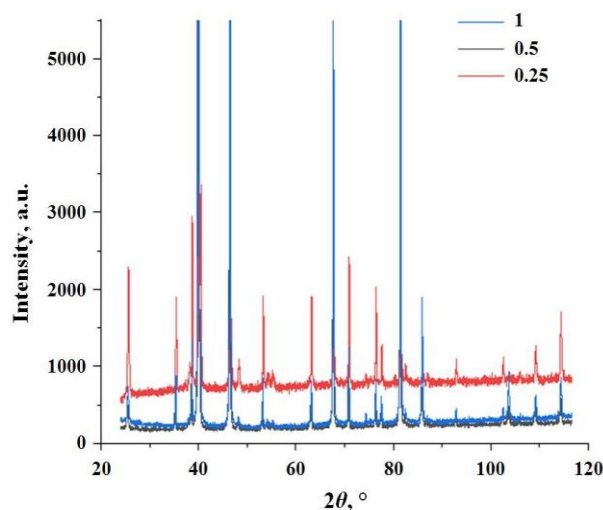


Fig. 2. X-ray diffractograms of the surfaces of electrochemically fabricated TiO₂ nanotubes with an electrodeposited Pt layer. The legend shows the content of noble metal (mg/cm²).

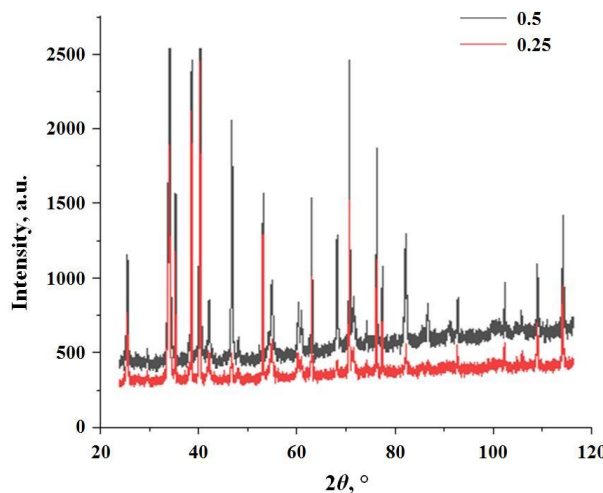


Fig. 3. X-ray diffractograms of the surfaces of electrochemically fabricated TiO₂ nanotubes with an electrodeposited Pd layer. The legend shows the content of noble metal (mg/cm²).

The reflections of platinum on the surface of the TiO₂ nanotubes are covered by strong peaks of elemental titanium. The (1 1 1) plane of the deposited Pt, the

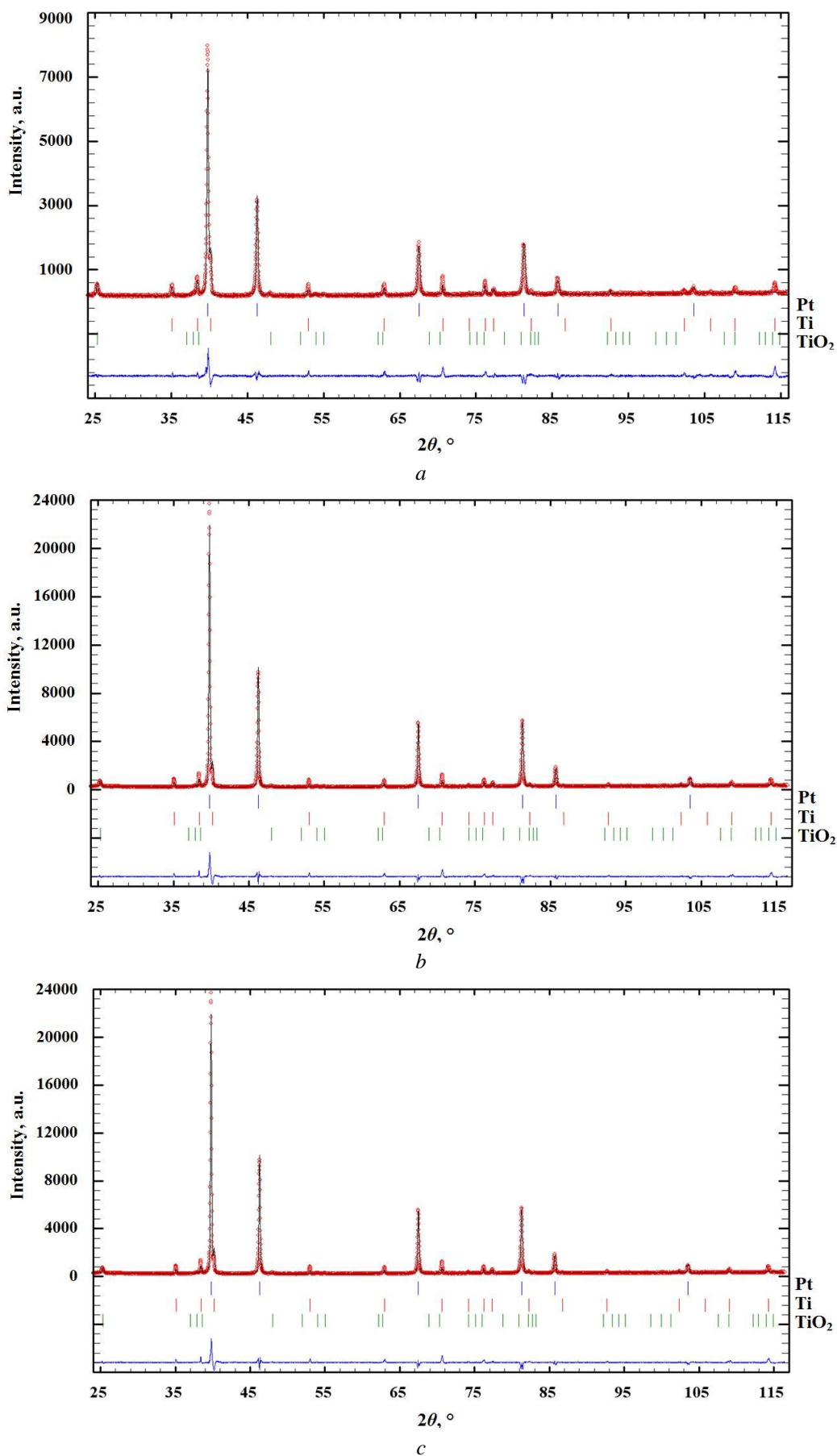


Fig. 4. Observed and calculated X-ray powder profiles for the samples coated with 0.5 (a), 0.25 (b), and 0.1 (c) mg/cm^2 Pt, respectively. The experimental data (circles) and calculated profile (solid line) are presented together with the calculated Bragg positions (vertical ticks) and difference curve (bottom solid line).

strongest peak, overlaps with the peak of elemental titanium at $2\theta = 39.76^\circ$. Other Pt peaks in the X-ray scanning range (at $2\theta = 46.24^\circ$ and 67.48°) correspond to the (2 0 0) and (2 2 0) planes, respectively. The broadening of the peaks is indicative of an amorphous structure, which is consistent with the SEM analysis. This can be attributed to the reduction in crystallite size and surface amorphization due to hydrate formation resulting from the reduction of the coating through cathodic polarization. The presence of PdO was detected on the surface of all thermally treated samples with a surface content of up to 0.5 mg/cm^2 palladium. At $2\theta = 33.88^\circ$, a characteristic reflection of PdO is observed, and its intensity increases with increasing Pd content (Fig. 5).

Since Pd and Pt are isomorphic metals and freely soluble in each other in both the liquid and the solid state, during prolonged heat treatment at a temperature of 500°C , mutual diffusion of the elements occurs. The

diffraction patterns show noticeable narrowing of the peaks, indicating an increase in the crystallinity of the coating [23, 24].

The phase composition of the studied samples, crystallographic data and microstructure parameters for the phases with face-centered cubic (fcc) structure (structural type Cu, space group $Fm-3m$) are presented in Table 2.

The study of the texture, morphology, and atomic structure revealed that the proposed treatment conditions for Ti foil allows forming hierarchically structured anodic oxide coatings characterized by a nanoporous amorphous matrix containing nanostructured anatase phase with elemental titanium, platinum, palladium, and palladium oxide.

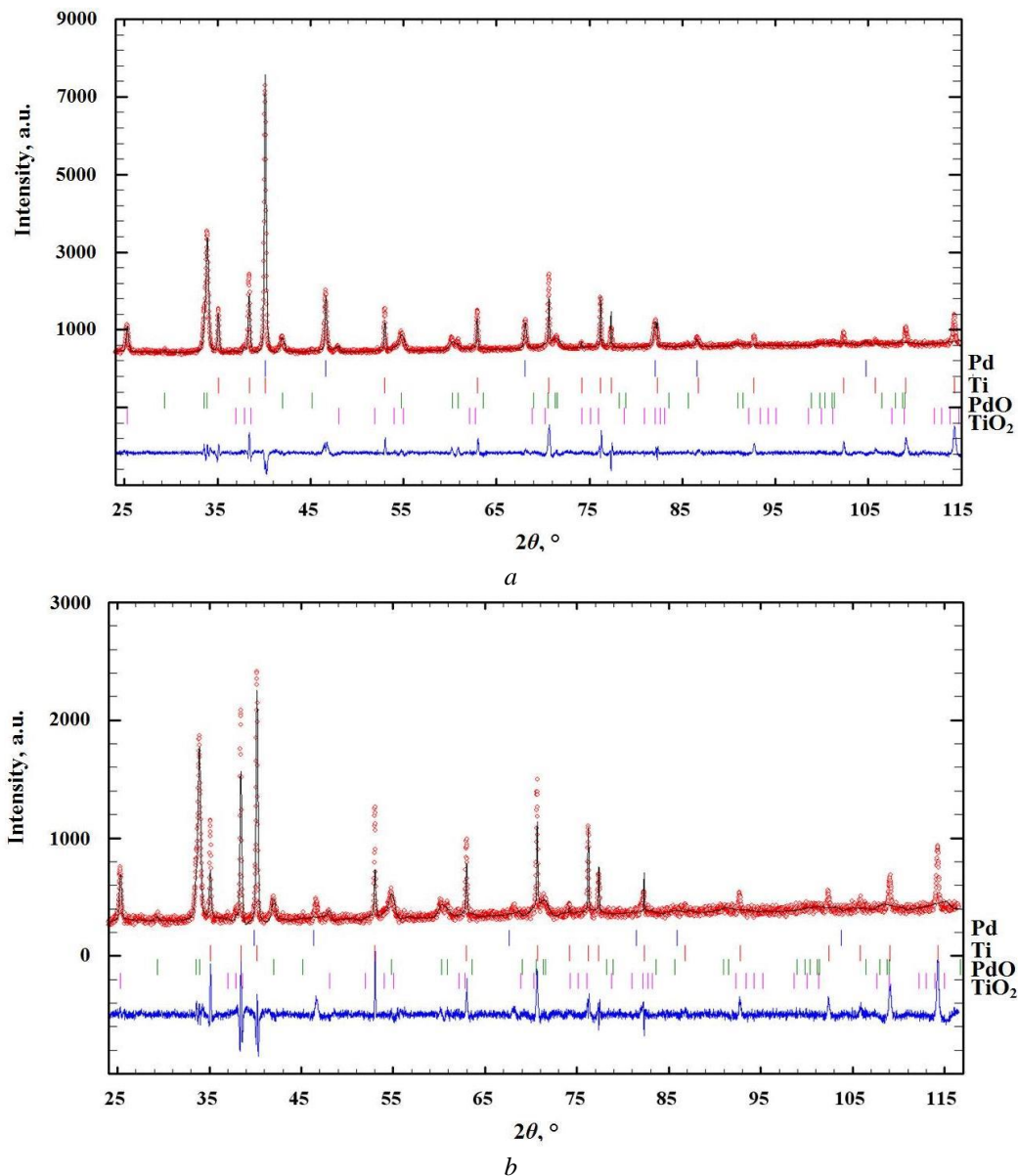


Fig. 5. Observed and calculated X-ray powder profiles for samples coated with 0.5 (a) and 0.25 (b) mg/cm^2 Pd, respectively. The experimental data (circles) and calculated profile (solid line) are presented together with the calculated Bragg positions (vertical ticks) and difference curve (bottom solid line).

Table 2.

Phase composition of the surface of electrochemically coated titania tubes, crystallographic data and microstructural parameters for the phases with fcc structure

Sample	Phases	Lattice parameter <i>a</i> , Å	Unit-cell volume <i>V</i> , Å ³	Crystallite size <i>D</i> , Å / strain ϵ
0.5 mg Pt	Pt 46.2(4) wt.% Ti ¹ 38.5(7) wt.% TiO ₂ ² 15.3(5) wt.%	3.92146(9)	60.304(2)	271 / 0.0036
0.5 mg Pd	Pd 22.8(4) wt.% Ti 43.2(6) wt.% TiO ₂ 12.9(4) wt.% PdO ³ 21.1(3) wt.%	3.89124(13)	58.920(3)	252 / 0.0038
0.5 mg Pt 0.5 mg Pd	Pt 42.8(5) wt.% Pd 19.5(3) wt.% Ti 28.4(4) wt.% TiO ₂ 5.2(2) wt.% PdO 4.1(1) wt.%	3.91689(14) 3.89132(16)	60.093(4) 58.924(4)	243 / 0.0040 231 / 0.0042
0.25 mg Pt 0.25 mg Pd	Pt 28.6(4) wt.% Pd 7.5(3) wt.% Ti 47.8(6) wt.% TiO ₂ 9.7(4) wt.% PdO 6.4(1) wt.%	3.91757(19) 3.8990(4)	60.125(5) 59.275(11)	215 / 0.0046 192 / 0.0051
0.25 mg Pt	Pt 13.4(2) wt.% Ti 49.0(7) wt.% TiO ₂ 37.6(7) wt.%	3.9202(2)	60.246(6)	209 / 0.0047
0.25 mg Pd	Pd Ti TiO ₂ PdO	Note ⁴		216 / 0.0045
1.0 mg Pt	Pt 62.8(4) wt.% Ti 25.4(4) wt.% TiO ₂ 11.8(4) wt.%	3.92233(4)	60.3439(12)	435 / 0.0022

Notes: 1. α -Ti (structure type Mg, space group $P6_3/mmc$).2. TiO₂ anatase (space group $I4_1/amd$).3. PdO (structure type PtS, space group $P4_2/mmc$).

4. The Ti substrate (textured) prevents the correct calculation of the profile of the phase. The content of fcc phase is small (<3 %) and almost all the palladium is present in the form of PdO oxide.

Conclusions

Electrochemically fabricated TiO₂ nanotubes exhibit self-organized tubes with open pores and effective diameters ranging from 40 to 70 nm. The variations in pore sizes across different domains suggest the influence of the mechanism of oxide film dissolution during titanium anodization.

Upon annealing at 500 °C, the surface structure of the nanotubes undergoes certain changes. There is compaction of the defective porous layer, formation of cracks within it, and the appearance of corrugation consisting of smaller nanoscale formations. Deposition of a platinum layer followed by annealing in air leads to a transition from nanotubular mesoscopic surface structure to a microcrystalline structure. The microcrystalline structure consists of randomly arranged particles with linear dimensions of 1-3 μ m, exhibiting the characteristic shape of rutile crystallites.

SEM images of samples covered with a layer of palladium show fused blocks, which is characteristic of the surface morphology of titanium suboxides. The surface is mainly formed by micro-scaled and submicron

aggregates. SEM analysis confirms that even after undergoing crystallization, the tubular structure of the oxide is preserved in samples containing a small amount of metal.

X-ray diffraction showed that the thermally treated samples contain anatase and elemental titanium. The peaks of platinum on the surface of TiO₂ nanotubes are covered by intense peaks of elemental titanium. The broadening of the peaks indicates an amorphous character of the formed material. The presence of PdO was detected on the surface of all thermally treated samples with a surface content of palladium up to 0.5 mg/cm². The intensity of the PdO peak increases with increasing palladium content.

Conflict of interests:

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

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Velichenko Alexander – Doctor of Sciences (Chemistry), Professor, Member of the NAS of Ukraine, Head of the Department of Physical Chemistry, Ukrainian State University of Chemical Technology;

Knysh Valentina – Doctor (Ph.D.), Associate Professor, Associate Professor at the Department of Physical Chemistry, Ukrainian State University of Chemical Technology;

Shmychkova Olesia – Doctor of Sciences (Chemistry), Associate Professor, Professor at the Department of Physical Chemistry, Ukrainian State University of Chemical Technology;

Luk'yanenko Tatiana – Doctor of Sciences (Chemistry), Professor, Professor at the Department of Physical Chemistry, Ukrainian State University of Chemical

Technology;

Pukas Svitlana – Doctor (Ph.D.), Associate Professor, Associate Professor at the Department of Inorganic Chemistry, Ivan Franko National University of Lviv;

Demchenko Pavlo – Doctor (Ph.D.), Senior Researcher, Leading Research Fellow at the Department of Inorganic Chemistry, Ivan Franko National University of Lviv;

Kordan Vasyl – Doctor (Ph.D.), Research Fellow at the Department of Inorganic Chemistry, Ivan Franko National University of Lviv;

Gladyshevskii Roman – Doctor of Sciences (Chemistry), Professor, Member of the NAS of Ukraine, Vice-Rector for Science and Research at the Ivan Franko National University of Lviv.

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Олександр Веліченко¹, Валентина Книш¹, Олеся Шмичкова¹, Тетяна Лук'яненко¹,
Світлана Пукас², Павло Демченко², Василь Кордан², Роман Гладішевський²

Комплексне дослідження фізико-хімічних властивостей матеріалів на основі субоксидів титану

¹Кафедра фізичної хімії, Український державний хіміко-технологічний університет, Дніпро, Україна, o_shmychkova@ukr.net

²Кафедра неорганічної хімії, Львівський національний університет імені Івана Франка, Львів, Україна, svitlana.pukas@lnu.edu.ua

В роботі досліджено структуру поверхні та мікроструктурні зміни пористих діоксидтитанових покриттів з електрохімічно нанесеними шарами платини та/або паладію. Зразки Ti, анодовані у фторовмісному електроліті, демонструють самоорганізовані нанотрубки різного діаметру з відкритими порами. Термічна обробка при 773 К призвела до ущільнення пористого шару, утворення тріщин і появи рифлення поверхні. Осадження платини викликало перехід від нанотрубчастої поверхневої структури до мікрокристалічної структури, що складалася з кристалітів рутилу. Зразки, покриті паладієм, показали розплавлені блоки, характерні для субоксидів титану. Трубочаста структура збереглася навіть після кристалізації. Зображення, отримані на скануючому електронному мікроскопі, демонструють гребінчастий характер у покриттях із різним вмістом металу. Аналіз рентгенівських порошкових дифракційних даних підтвердив наявність анатазу та елементарного титану. На поверхні термічно оброблених зразків виявлено PdO. Для зразків, оброблених спільно Pd і Pt, під час термічної обробки відбулася взаємна дифузія двох металів. Отримані дані розкривають характеристики поверхні, ефекти осадження металу та фазовий склад пористих покриттів із оксиду титану, надаючи цінну інформацію для подальших досліджень.

Ключові слова: нанотрубки, діоксид титану, метали платинової групи, морфологія, фізико-хімічні властивості.