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Synthesis of Titanium-Containing Coatings in Aqueous-Organic Electrolytes

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Abstract: The conditions and results of low-temperature electrochemical synthesis, allowing for the targeted production of phases of a given composition on the titanium surface, are considered. Functional coatings were obtained on thin (10÷15 μm) titanium layers in the potentiostatic mode at potential values of 4÷10 V and a maximum current of no more than 0.02 A in aqueous-organic electrolytes based on ethylene glycol, in the presence of additives of various salts in the concentration range from 0.05 to 0.5 wt. %. As a result of electrochemical treatment of the titanium surface in electrolytes, solid electrically conductive films with a mirror surface from light yellow to bronze shades are formed. The microhardness of the coatings, measured by the Vickers method, is at least 946 HV 0.1, which indicates the high mechanical strength of the materials. The specific resistance of the coatings does not exceed 2.1 Ohm·cm. X-ray photoelectron spectroscopy studies of the elemental composition and chemical states of the resulting coatings reveal the presence of titanium, oxygen, carbon, and nitrogen on the sample surfaces, with oxygen primarily present in the upper oxidized layer. Coatings obtained in all studied electrolytes contain the $Ti(C_XN_Y)$ phase and oxide phases (TiO, Ti_2O_3, TiO_2).

Keywords: Electrochemical modification of titanium, X-ray photoelectron spectroscopy, Chronoamperograms, Phase composition, Titanium carbonitride.

Introduction

The importance of titanium and its alloys to modern industry is difficult to overestimate. Its unique physical, chemical, and mechanical properties determine its widespread use in virtually all industries. Surface modification techniques for titanium and its alloys allow for targeted modification of their properties, enhancing their performance characteristics. Surface oxidation is most commonly used through electrochemical, plasma-electrolytic, or microarc oxidation. This allows for the production of biocompatible implant materials with a porous coating that mimics bone structure, accelerating the process of osseointegration. It has been shown that the morphology, thickness, crystallinity, chemical composition, mechanical properties, corrosion resistance, and bioactivity of coatings are highly dependent on the parameters of electrochemical processes (voltage, process duration, electrolyte composition and temperature, etc.) (Makurat-Kasprolewicz & Ossowska, 2023; Brocklebank et al., 2022; Huang & Yoshimura, 2023; Gangqiang Li et al., 2023).

Titanium nitride films are also widely used, having proven themselves as decorative coatings, coatings for friction surfaces, and functional layers in microelectronics, increasing their wear resistance, reliability, and durability.

Furthermore, Ti_xN_y compounds exhibit good conductivity, high hardness, chemical and temperature stability, and are resistant to aging processes (Maryeva & Popova, 2016; Brover et al., 2023).

Titanium carbide-containing coatings can increase hardness and corrosion resistance and reduce the friction coefficient of cutting and milling tools. The structure and mechanical properties of TiCx films also depend on the synthesis parameters (Sumanya et al., 2023). Most often, titanium carbide films are obtained by plasma spraying or magnetron sputtering. It has been established that an optimized *x* value is a key factor in improving the performance characteristics of TiCx films used under extreme wear conditions (Xie et al., 2023; Abegunde et al., 2021; Tamarkin et al., 2023). The combination of several types of alloying additives in the coating composition makes it possible to vary their properties depending on the technical tasks and operating conditions of the final product. For example, a TiO_2-TiN composite coating has been created, which has significant potential for the creation of surface structures of vascular stents (Xin Chen et al., 2023). The authors of Xiao Chen et al. (2023) succeeded in combining the good mechanical properties of TiN film (surface hardness, elastic modulus, cytocompatibility) with the excellent anticoagulant properties of TiO_2. Coating implants with films of TiO_2-TiC_x composition also showed good results (Veronesi et al., 2017).

In a study (Jie Jin et al., 2021), the continuous field unbalanced ion sputtering (CFUMSIP) technology was used to produce TiCN coatings with high electrical conductivity and excellent corrosion resistance by simultaneously feeding acetylene (C_2H_2) and nitrogen (N_2) into the chamber. The resulting TiN-TiCN-based coatings were proposed for use in membranes in fuel cells. Titanium carbonitride films also exhibit electrocatalytic properties (Gujral et al, 2022; Roca-Ayats et al, 2020), as well as outstanding specific capacitance, low internal resistance, and high cyclic stability, making them promising for the fabrication of symmetrical supercapacitors (Iffat Ashraf et al., 2023).

Each of the above coatings has its own advantages and disadvantages. Improving performance characteristics and reducing resource and energy consumption during the coating application process remains a pressing issue. A synergistic effect is expected from creating composite coatings while maintaining environmental and economic efficiency. The aim of this work is to establish the relationship between the synthesis conditions and the properties of multicomponent titanium carbonitride-containing coatings obtained using environmentally friendly soft chemistry methods.

Method

Electrochemical Syntheses

Electrochemical syntheses were carried out in potentiostatic mode using a P-30I potentiostat at ambient temperature (approximately 20°C). The electrolyte base for the syntheses was ethylene glycol (EG) with the addition of 10% water. Electrically conductive additives included ammonium, sodium, potassium, and lithium fluorides, as well as $LiClO_4$, NH_4SCN, and other compounds. The anodes were titanium plates with a surface area of 2–2.5 cm², which were fabricated by thermal spraying of titanium layers (99.99% purity) onto glass-ceramic substrates with a thickness of ~15 µm. A titanium plate with an area of 2 cm² served as an auxiliary electrode. Before each synthesis, the electrodes were cleaned using cathode-anodic polarization. The end time of the synthesis was determined from the I–t dependence, when the current became zero. The studied samples were obtained at potentials of 4 ÷ 10 V relative to (Ag/AgCl, KCl(sat)). The electrical conductivity of electrolyte solutions was measured using an OK-102/1 conductometer (Radelkis).

Microstructure and Properties of Coatings

Micrographs of the samples were obtained using a Quanta 200 scanning electron probe microscope. To determine the microhardness of the titanium nitride layers, a method established in accordance with GOST 9450-76 was used. This method requires the use of a PMT-3 microhardness tester and involves indenting a square diamond tip into the sample under a load of 0.981 N for 10-15 seconds, followed by analysis of the recovered indentation. The specific resistance of the samples was determined using the four-probe method.

Elemental and Phase Composition of Coatings

Analysis of the elemental composition and chemical states of atoms was performed for samples synthesized in electrolytes of the following composition:

1 – (EG + 10% H_2O + 0.5% NH_4SCN);
2 – (EG + 10% H_2O + 0.5% LiF);
3 – (EG + 10% H_2O + 0.5% $LiClO_4$);
4 – (EG + 10% H_2O + 0.25% NH_4F).

The elemental composition of the coatings was studied by X-ray photoelectron spectroscopy (XPS) on a K-Alpha spectrometer (Termo Scientific) with an AlK_α X-ray source (1486.6 eV). During the measurements, the pressure in the analyzer chamber did not exceed 2.3×10^{-9} mbar. When analyzing the photoelectron spectra, secondary electron background subtraction was performed using the Shirley method. To compensate for the shift of photoelectron lines due to possible charge accumulation on the surface, a compensating gun was used during measurements. The binding energies of the lines were calibrated using the position of the component corresponding to the sp^2-hybridized carbon state with a binding energy of 284.8 eV (C÷C). To analyze the ratios of coating components in different chemical states, the Gauss-Maxwell peak decomposition method was used. The spectrometer was calibrated using the following lines: Au $4f_{7/2}$–83.96 eV, Cu $2p_{3/2}$–932.62 eV and Ag $3d_{5/2}$–368.21 eV.

Immediately prior to spectroscopic studies of the composition and chemical states of the coatings, the surface was cleaned of any contaminating layer by bombardment with argon ions (as a rule, titanium nitride films synthesized by the electrochemical method are coated with an oxide layer on top). Potential shifts due to residual charge were monitored using the position of the sp^2-hybridized carbon peak with a binding energy of 284.8 eV, which is part of the residual surface contamination.

To describe the titanium peak in the metallic state, the LA (1,1.5,7) function with its characteristic asymmetry (Biesinger et al., 2010) was used, and to describe the remaining chemical states, the Voigt GL(30) function in the CASAXPS program was used.

Results and Discussion

Features of Electrochemical Modification of Titanium in Various Electrolytes

During the electrochemical modification of titanium in electrolytes with NH_4F as a conductive additive, a relationship is observed between the NH_4F concentration and the nature of the resulting products. In particular, the formation of predominantly titanium carbides and nitrides or titanium oxide is possible. In ethylene glycol with an NH_4F concentration in the range of 0.05 ÷ 0.25 wt. % and a corresponding electrolyte conductivity of 0.2 10^{-3} ÷ 0.7 10^{-3} S/cm, the formation of titanium carbonitrides was observed in the potential range of 2 ÷ 14 V (Maryeva & Popova, 2016). A characteristic chronoamperogram for this process (curve 1) is shown in Figure 1 in comparison with the chronoamperogram corresponding to the formation of TiO_2 at an NH_4F concentration of 0.5 wt.% (curve 2).

Electrochemical modification of titanium in the absence of nitrogen-containing electrolytes also results in the formation of titanium carbides and nitrides. The increase in oxidation potential is visually accompanied by a change in the surface color of the modified layers. The chronoamperograms of processes occurring at different anode potentials differ in nature. In the curves corresponding to potentials in the range of 3–6 V (Figure 2, a), the current density decreases steadily. In contrast, in the chronoamperograms of processes occurring at anode potentials of 7–10 V (Figure 2, b), the current density initially decreases and then, after 30–50 seconds, slowly increases.

Presumably, at higher synthesis potentials (and hence higher initial current values) in the presence of fluorides, the formed Ti(CXNY) is subject to destruction as a result of, for example, an oxidation reaction leading to the formation of titanium oxide (Maryeva & Popova, 2016):

$$TiN + O_2 = TiO_2 + \frac{1}{2} N_2 ,$$

The calculated Gibbs energy change for this reaction is –582.2 kJ/mol.

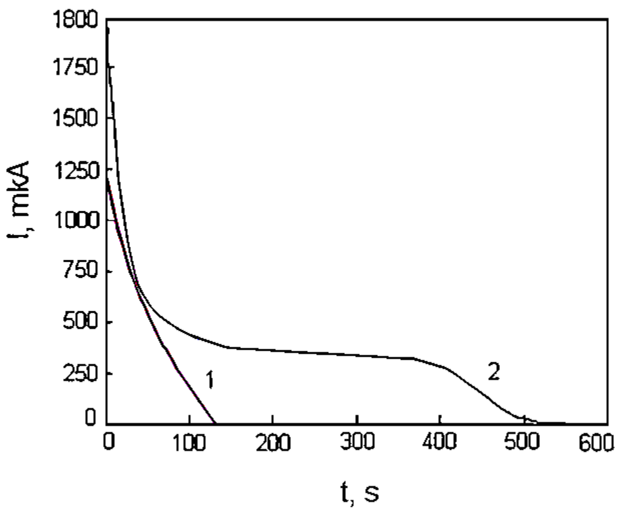


Figure 1. Chronoamperograms at an anode potential of 4 V: 1 – the process of $Ti(C_XN_Y)$ formation in the electrolyte EG–H_2O–NH_4F (89.8–10.0–0.2 wt.%); 2 – the process of TiO_2 formation in the electrolyte EG–H_2O–NH_4F (89.5–10.0–0.5 wt.%)

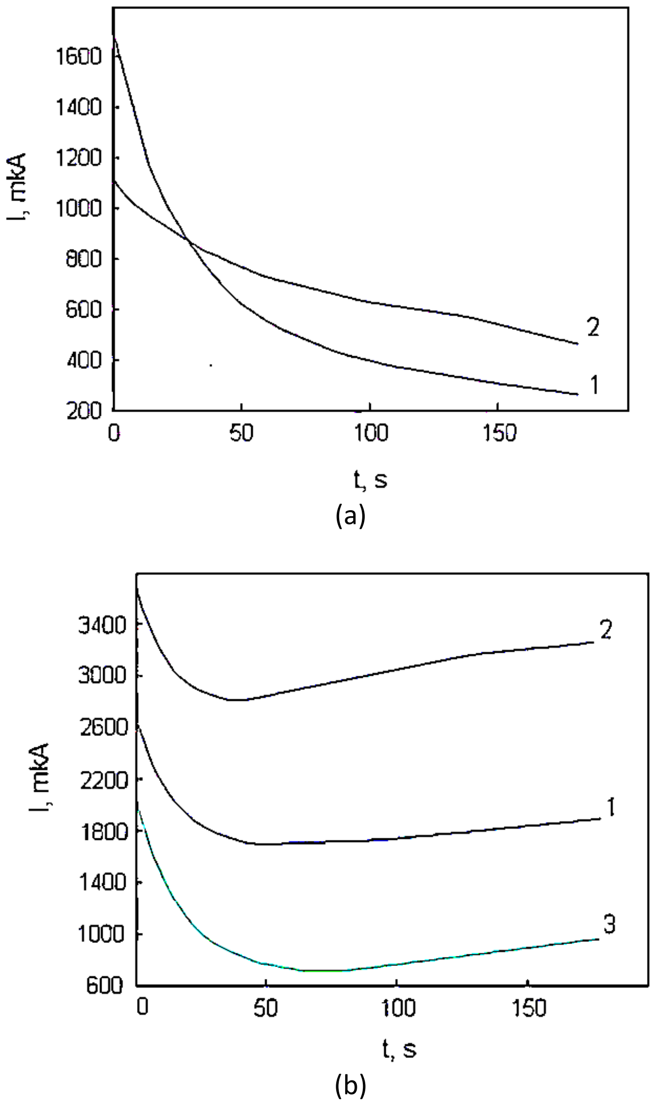
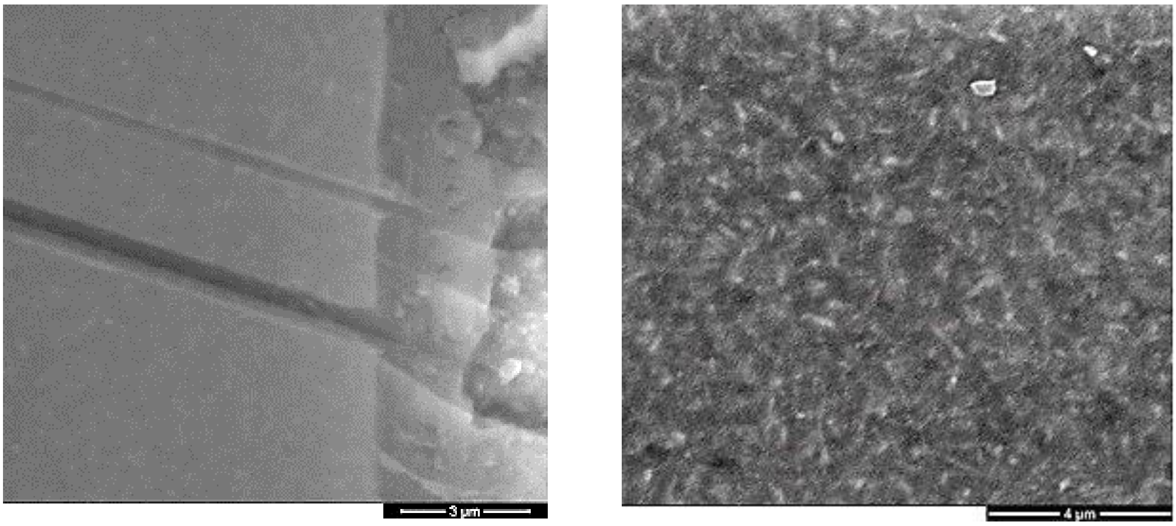


Figure 2. Chronoamperograms of processes at potentials of 4 V – (1a); 6 V – (2a); 8 V – (1b); 10 V – (2b) in the electrolyte (EG + 10% H_2O + 0.27 mol/l KF); at a potential of 10 V – (3b) in the electrolyte (EG + 10% H_2O + 0.27 mol/l LiF)

Study of Microstructure and Properties of Coatings

Electrochemical processing of titanium layers in these electrolytes produces conductive coatings with a wide range of color shades, from light yellow to bronze. Films of samples 1–3 are characterized by the formation of an almost homogeneous layer with a mirror surface, practically free of defects. These films adhere tightly to the base substrate and precisely replicate its microrelief (Figure 3, a). The layer from sample 4 (conductive additive NH_4F) exhibits structural unevenness due to the distinct presence of various phases (Figure 3, b). The microhardness of the coatings from samples 1–3, measured using the Vickers method, is at least 946 HV 0.1, indicating the high mechanical strength of these materials. The specific resistance of the films does not exceed 2.1 Ohm·cm.



a b

Figure 3. Microstructure of the surface of the synthesized coating at a potential of 6 V (×20000): (a) in the EG–H_2O–$LiClO_4$ electrolyte (89.5–10–0.5 wt.%); (b) in the EG–H_2O–NH_4F electrolyte (89.75–10.0–0.25 wt.%)

Analysis of the Elemental Composition and Chemical States of Atoms of the Synthesized Coatings

Below are the results of XPS analysis for the surface of sample 1, obtained in an electrolyte of the composition EG+H_2O+NH_4SCN (89.5–10.0–0.5 wt.%). The overview spectrum shows the presence of mainly titanium, oxygen, carbon, and nitrogen on the surface (Figure 4, Table 1), with the amount of oxygen being much greater than the other components, indicating the presence of an oxidized layer.

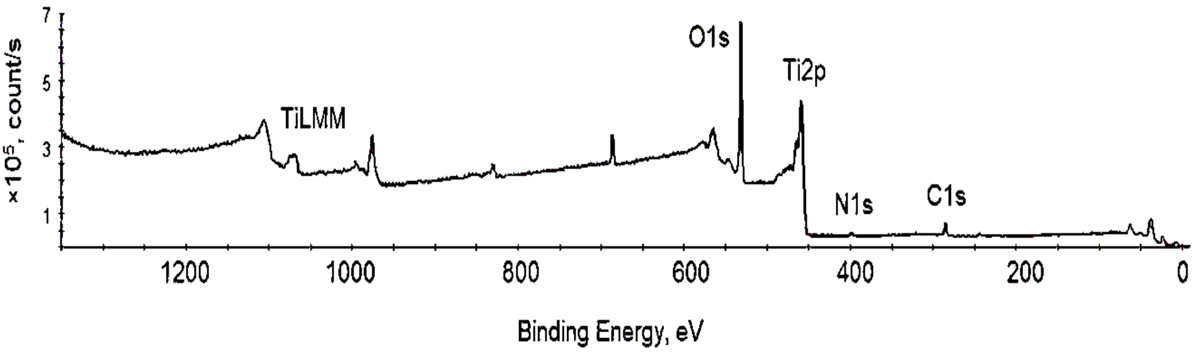
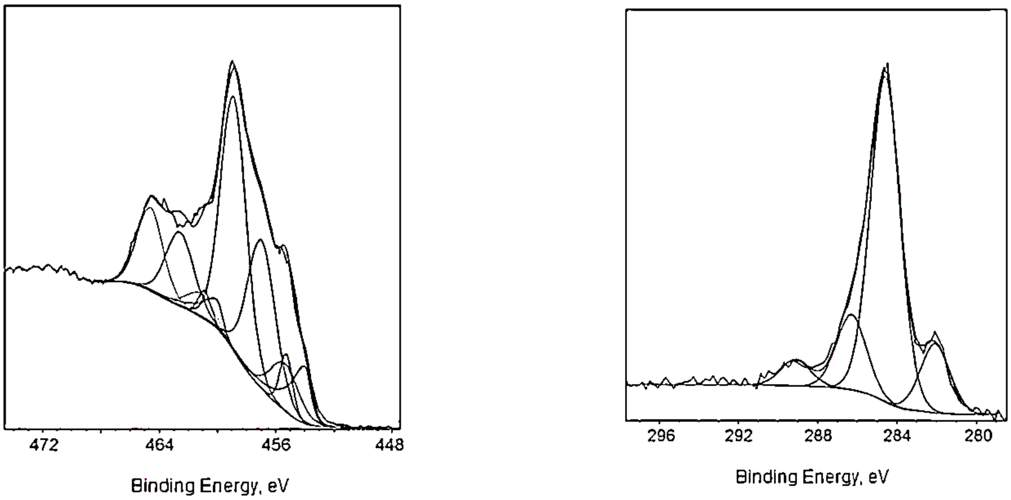


Figure 4. Survey spectrum of the surface of sample 1

Table 1. Chemical composition of the surface of sample 1

Lines of elements	O	Ti	C	F	N
Content of elements, at.%	46,22	20,33	12,29	8,99	3,06

The chemical states of the components on the surface of sample 1 were analyzed by decomposing the photoelectron peaks into their components. The obtained data are in good agreement with studies of TiCN using XPS (Miller et al., 2012; Xin Feng & Li-Yi Shi, 2005).

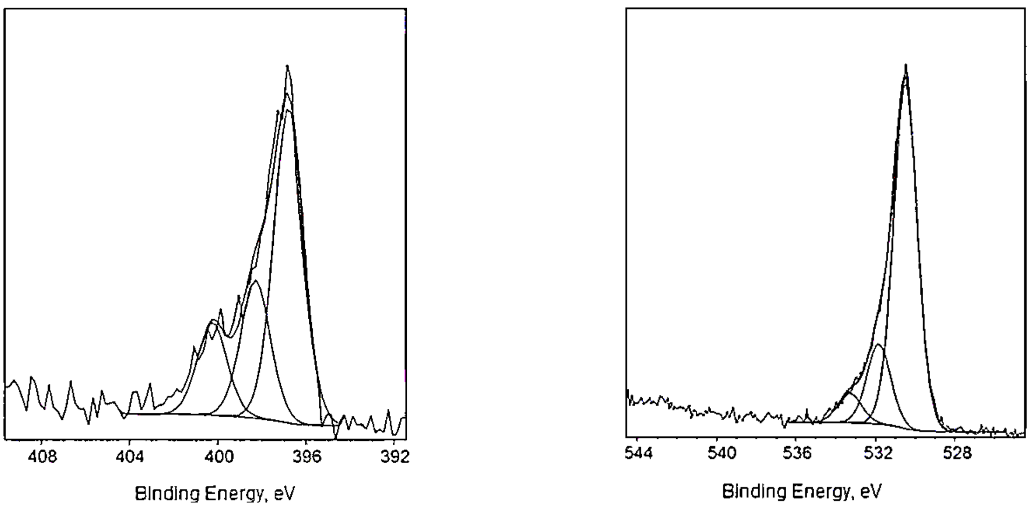


a b

Figure 5. Analysis of chemical states: spectrum of titanium Ti 2p (a) and carbon C 1s (b) on the surface of sample 1

Figure 5a shows the decomposition results for the peak of the titanium Ti 2p doublet. The small amount of metallic titanium present on the surface, which was probably formed as a result of cleaning the sample surface by bombardment with argon ions, is 10.85 at.%. This state of titanium Ti $2p_{3/2}$ corresponds to a binding energy of 454.0 eV. Titanium with oxygen forms the following states: Ti II (455.41 eV – 9.99 at.%), Ti III (457.0 eV – 30.78 at. %), and Ti IV (458.9 eV – 43.03 at. %). The state of titanium with carbon and nitrogen corresponds to the compound TiCN (455.3 eV – 5.35 at. %).

Carbon atoms are primarily present in the residual contaminant layer on the surface, which corresponds to a binding energy of 284.5 eV. According to the spectrum and the results of chemical state analysis in the region of the C 1s line (Figure 5b), this peak remains the most intense even after surface cleaning. Furthermore, a carbon peak at 282.08 eV is clearly visible, corresponding to the Ti–CN bond (13.87 at. % of the total carbon on the surface). Carbon in the C–O/C–N and C=O states, which are part of the contaminant layer, corresponds to binding energies of 286.3 and 289.1 eV. Nitrogen forms the compounds C–N (400.26 eV – 17.04 at.%), N–O (400.26 eV – 17.04 at.%), and Ti–CN (396.8 eV – 57.74 at.%) (Figure 6, a) (Miller et al., 2012). The oxygen spectrum (Figure 6, b) is represented by the states: lattice oxygen Ti–O (530.5 eV –75.88 at.%), N–O (531.84 eV –17.6 at.%), C–O (533.3 eV – 6.52 at.%) (Miller et al., 2012). The results of the study of the stoichiometry of the phase composition of the obtained coatings are presented in Table 2.



a b

Figure 6. Analysis of chemical states: spectrum of nitrogen N 1s (a) and spectrum of oxygen O 1s (b) on the surface of sample 1

Table 2. Stoichiometric composition of $Ti(C_XN_Y)$ phases obtained in different electrolytes

Components	at. %	(C+N)/Ti	$Ti(C_XN_{1-X})$
Sample 1: Electrolyte (EG + 10% H_2O + 0,5% NH_4SCN)			
Ti	65,73		
C	27,43	0,52	$Ti(C_{0,8}N_{0,2})$
N	6,84		
Sample 2: Electrolyte (EG + 10% H_2O + 0,5% LiF)			
Ti	76,67		
C	16,7	0,3	$Ti(C_{0,74}N_{0,26})$
N	6,63		
Sample 3: Electrolyte (EG + 10% H_2O + 0,5% $LiClO_4$)			
Ti	79,03		
C	14,53	0,26	$Ti(C_{0,69}N_{0,31})$
N	6,44		
Sample 4: Electrolyte (EG + 10% H_2O + 0,5% NH_4F)			
Ti	82,21		
C	11,88	0,21	$Ti(C_{0,66}N_{0,34})$
N	5,91		

X-ray photoelectron spectroscopy analysis of the composition and chemical states of the samples revealed that the $Ti(C_XN_Y)$ phase was present in all four samples. The highest content of this phase was found in sample 1 (NH_4F, an electrically conductive additive). In the other three samples, the $Ti(C_XN_Y)$ phase content was significantly lower, and oxide phases (TiO, Ti_2O_3, TiO_2) played a significant role.

Conclusion

During electrochemical modification at low potentials (4–10 V) and a maximum current of no more than 0.02 A in water-containing ethylene glycol in the presence of various conductive additives, titanium carbonitride and oxide phases are formed. The composition of the resulting products varies depending on the conductive additive and the potential during synthesis. Titanium oxide formation is characteristic in the presence of ammonium fluoride and largely depends on its concentration. In the presence of Li, Na, and K fluorides, titanium oxide formation begins at potentials of 8–10 V. Coatings formed in electrolytes with the other conductive additives studied are primarily composed of titanium nitrides and carbides. The stoichiometric composition of the $Ti(C_XN_Y)$ phases in the resulting coatings was determined.

Scientific Ethics Declaration

* The authors declare that the scientific, ethical, and legal responsibility of this article, published in the EPSTEM journal, belongs to the authors.

Conflict of Interest

* The authors declare that they have no conflicts of interest

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