

Article

Development of Multicomponent Nanostructured Nitride Coatings to Protect against Corrosion Products from Titanium Alloy

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Abstract: Phase-structural characteristics and the corrosion resistance of coatings ZrN, (Zr,Ti)N, (Zr,Hf)N, (Zr,Nb)N, (Ti,Zr,Hf)N and (Ti,Zr,Nb)N, which were deposited on a Ti6Al-4V titanium alloy substrate, were investigated. It was found that the titanium substrate has a crystalline structure, including grains with high (up to 24 at.%) and low (less than 2 at.%) vanadium content. Thus, during the deposition process, the coating can form adhesive bonds with local areas of the substrate that have quite different compositions. The diffusion of the coating elements into the substrate takes place up to a depth of 200 nm. The diffusion of titanium alloy elements (primarily titanium and vanadium) into the adhesive sublayer of the coating to a depth of 100 nm is also observed. Corrosion studies were carried out in 1M solutions with acidic (H₂SO₄), alkaline (NaOH) and neutral (NaCl) media at a constant temperature of 50 °C. The actual change in the mass of the samples during corrosion tests is extremely small. The protective coatings under study have very high anti-corrosion characteristics and practically do not react with solutions that imitate the liquid environments of the human body.

Keywords: coatings; diffusion; corrosion protection; nitrides; titanium alloy



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1. Introduction

Titanium alloy Ti6Al-4V is widely used in various fields of production [1,2]. This material is most actively used in the production of medical devices, aircraft construction and products for nuclear energy. It possesses several useful properties, including high strength with relatively low specific gravity and good resistance to corrosion due to the spontaneous formation of a dense protective oxide film on the surface. Along with the obvious advantages, this alloy also has disadvantages, including relatively low wear resistance and the threat of active corrosion when the specified oxide film is destroyed [1,2].

The hardness of titanium alloys is relatively low (for example, Ti6Al-4V HB 293–361 MPa with a coating hardness of 25–38 GPa). Accordingly, the wear resistance of titanium alloys is relatively low compared to ceramic, carbide or nitride coatings. Titanium is also a reactive metal and oxidizes easily. As is known, the resistance of titanium to oxidation

is associated with the formation of a thin (20–30 nm) and dense oxide film on its surface. This film protects titanium from further oxidation. However, in aggressive environments (for example, in the environment of the human body or sea water), this thin film can be destroyed, for example, as a result of electrolysis. In this case, an active reaction of titanium with the environment begins, and in the case of titanium implants, this can lead to metallosis and implant rejection. To eliminate these disadvantages, it is advisable to modify the surface of products made from the Ti6Al-4V alloy via the deposition of special protective coatings. Nitride coatings are thick (2–3 microns, that is, 100–150 times thicker than a spontaneously forming oxide film). With greater hardness and wear resistance, such coatings can provide greater reliability for titanium products, even if they have the same corrosion resistance as the oxide film. Of the available coating deposition methods, in this case, the physical vapor deposition (PVD) method is the most preferable, since it allows the coating to be applied at relatively low temperatures (400 °C and below) while ensuring high adhesion to the substrate, as well as sufficient density and defect-freeness [3,4].

Among the various possible compositions of PVD coatings, zirconium nitride (ZrN) can be distinguished, which has a few important advantages. This coating makes it possible to simultaneously increase wear and corrosion resistance [5,6]. At the same time, ZrN has sufficient plasticity to effectively resist cracking and brittle fracture [7,8], and it has high heat resistance [9]. ZrN coatings are actively used to increase the wear and corrosion resistance of products made from materials such as stainless steel [10,11], magnesium-based alloys [12] and titanium alloys [13–15]. The main phase formed in the coating is fcc ZrN [10,16,17]. At the same time, the formation of the hexagonal h-ZrN phase is also observed [18].

Even though the ZrN coating has high performance, these characteristics can be further enhanced by introducing additional components into the ZrN composition. There are several works demonstrating the effectiveness of introducing hafnium (Hf) or niobium (Nb) into the ZrN coating composition [19]. Hafnium makes it possible to increase corrosion and wear resistance [19–21]; however, high hafnium contents (more than 20 at.%) can lead to an increase in the magnitude of residual compressive stresses [19] and a decrease in corrosion resistance [22].

A similar effect is achieved by introducing niobium into the composition of the ZrN coating [23,24]. In addition to the above, niobium can increase crack resistance and resistance to brittle fracture [24], and it can improve thermal stability [25–27] and reduce the magnitude of residual stresses [28]. It is worth noting that an increase in corrosion resistance is observed only with the introduction of a relatively small amount of niobium (about 2 at.%), but with a high niobium content, corrosion resistance may decrease.

Another direction for improving the properties of a ZrN coating is the introduction of titanium (Ti) into its composition. Such coatings have noticeably better wear resistance and a lower coefficient of friction [29–31] in combination with good anti-corrosion properties [32,33]. Although the (Zr,Ti)N coating has better wear resistance compared to TiN and ZrN coatings [34,35], it also experiences higher compressive residual stresses, which makes it more brittle [36].

The coatings of more complex compositions, including four or more elements, are also considered. In particular, (Ti,Zr,Nb)N coatings are characterized by high wear resistance and a low friction coefficient [37,38].

From the point of view of phase composition, it is worth noting that in the (Zr,Hf)N coating, as a rule, a single fcc phase (Zr,Hf)N is formed, which is a solid solution of Hf in c-ZrN [19,20]. In a (Zr,Nb)N coating, at sufficiently high Nb contents (35 at.% and higher), two phases can form an fcc phase (Zr,Nb)N, which is a solid solution of Nb in ZrN, and hexagonal Nb₂N phases [39] or Nb₄N₃ [40]. In the (Ti,Zr)N coating, depending on the dominance of Ti or Zr, the fcc phase (Zr,Ti)N, which is a solid solution of Ti in c-ZrN, or the fcc phase (Ti,Zr)N, which is a solid solution of Zr in c-TiN, can be formed [31,41,42]. At close Ti and Zr contents, two fcc phases can form: (Zr,Ti)N and (Ti,Zr)N [33,34,43,44].

To increase the adhesion strength between the coating and the substrate, using an intermediate adhesion sublayer consisting of a metal or metal alloy is advisable. In particular, when depositing a ZrN coating, an adhesive Zr sublayer [45] and, for a (Zr,Hf)N coating, a Zr, Hf or Zr sublayer were used [46–48].

Given that the coatings under consideration have been studied previously, a comprehensive comparison of their properties will improve the efficiency of choosing coating compositions for various operating conditions.

As is known, metals are heterogeneous in their structure. On the surface of metal products, there are crystalline grains of various orientations, the composition of which may be different due to microliquation; the alloy itself may have a heterogeneous structure [49,50]. Due to this heterogeneity, different areas of the surface are characterized by different potentials. Areas with a more negative electrode potential play the role of anodes and are destroyed first. Mechanical stress also increases negative potentials, which increases electrochemical corrosion. Factors such as metal heterogeneity, differences in stress values in different areas of the product, and the unequal intensity of corrosion processes cause the formation of various forms of corrosion destruction [51,52].

The corrosion of coated products during long-term exposure to a liquid electrolytic environment under cyclic mechanical loads will obviously proceed mainly via an electrochemical mechanism associated with the emergence of a potential difference in different areas of the surface due to the formation of galvanic couples. A galvanic couple can be formed not only by different metals but also by separate sections of the same metal located in different conditions; therefore, electrochemical corrosion always occurs when the metal meets an electrolyte (or atmospheric moisture) [51,52]. Despite the fact that titanium nitride is characterized by high resistivity (40 $\mu\text{Ohm}\cdot\text{cm}$) and zirconium nitride is a non-conducting high-temperature ceramic, a number of transition metal nitrides (for example, yttrium or hafnium) have a metallic type of conductivity; this results in the possible formation of combined nitride coatings of micro-areas with different potentials, especially after mechanical impact. Although the mechanism of the corrosion process for almost any material under different conditions is also different, according to the nature of surface destruction, corrosion can be divided into uniform and local corrosion. Uniform or general corrosion [53–55] is distributed more or less evenly over the entire surface of the metal; local corrosion [56] is concentrated in specific areas and appears as pits or spots. It is more dangerous than uniform corrosion, since the corrosion process penetrates to great depths and causes local mechanical stress and destruction.

When analyzing available data on the corrosion of various materials, a problem that arises is that it is necessary to compare the results obtained on different equipment and often under different experimental conditions [57]. It was also found that only the rate of surface destruction in a particular corrosive liquid environment does not reflect the characteristics of changes in the surface of the metal matrix [58–60]. Rapid corrosion can occur without the formation of pits and canyons while maintaining the smooth surface of each newly exposed layer of metal. When the part is removed from the corrosive environment, such a surface obviously stops deteriorating and retains its mechanical characteristics. Conversely, significantly slower metal corrosion can lead to the formation of a deeply loose, spongy and mechanically weak layer, the destruction of which can occur unevenly, resulting in the formation of local defects. In this case, removing the part from the corrosive environment will not be an obstacle to its further destruction (under the influence of external forces, depending on the points of application and direction). Thus, the study of the characteristics of corrosion and destruction of double and triple nitride coatings should be carried out comprehensively using various exposure options.

Thus, this work examines the corrosion properties of ZrN, (Zr,Ti)N, (Zr,Hf)N, (Zr,Nb)N, (Ti,Zr,Hf)N and (Ti,Zr,Nb) coatings that were deposited onto a titanium alloy Ti6Al-4V substrate. A comparison of the corrosion properties of the coatings under study will be carried out under identical conditions using a unified methodology. This will allow for a

comprehensive and objective comparison, determining the most preferable coatings for given operating conditions.

2. Materials and Methods

To deposit coatings on titanium alloy samples, a VIT-2 installation (IDTI RAS–MSTU STANKIN, Moscow, Russia) was used. The VIT-2 unit uses two types of evaporators. The first type comprises filtered cathodic vacuum arc deposition (FCVAD) [61–63], which provides up to 98% separation relative to the microparticle phase in combination with a high degree of plasma flow focusing. Evaporators of the second type—the controlled accelerated arc (CAA-PVD) system [64,65]—are distinguished by high energy efficiency and a reduced amount of microparticles compared to traditional arc-type evaporators. In the coating process, Zr (99.98%), Ti (99.99%), Zr-Nb (50:50%) and Zr-Hf (50:50%) cathodes were used.

Before coating deposition, the samples were washed in a washing solution with ultrasonic stimulation; then, it was washed in purified running water and dried in a sterile chamber. The coating deposition process included the following steps:

- Thermal activation (etching) in gas (argon) and metal plasma;
- Deposition of coatings: During coating deposition, the arc current of the titanium and zirconium cathodes was, respectively, 75 and 80 A. The arc current of Zr-Nb (50:50%) and Zr-Hf (50:50%) cathodes was, respectively, 85 and 90 A. The deposition was carried out under the following parameters, and they were identical for all processes: nitrogen pressure of 0.42 Pa; voltage for the substrate at -150 V; and tool rotation speed of 0.7 rpm.

Structural studies of the lamellas were carried out using a transmission electron microscope (TEM) JEM-2100 (JEOL Company, Tokyo, Japan) at an accelerating voltage of 200 kV. SAED (selected area electron diffraction) is a standard technique for obtaining electron diffraction patterns (DPs) from different areas of a sample via a transmission electron microscope. This method examines the electrons that passed through a selected area in a thin sample and that were diffracted on the crystal planes of the sample. The diameter of the region from which diffraction can be obtained varies from approximately hundreds of nm to several microns (depending on the diameter of the selector diaphragm that is currently used in the TEM). Based on the diffraction pattern, the interplanar distances are determined; based on the calculated set of interplanar distances (and intensity), the phase in the region from which this DP was obtained is determined.

To study the elemental composition, TEM with EDX INCA Energy (OXFORD Instruments, Abingdon, Oxfordshire, UK) was used. To obtain samples, the focused ion beam (FIB) method was used on a Strata 205 installation (FEI, Hillsboro, OR, USA).

The structural-phase state of the coatings was studied via X-ray diffraction analysis using a Rigaku Ultima IV diffractometer (Rigaku Co., Tokyo, Japan) that utilized Cu K α radiation-focusing parallel beams. The lattice parameter (a_{hkl}) was calculated using the following equation:

$$a_{hkl} = d_{hkl} \sqrt{h^2 + k^2 + l^2},$$

where d_{hkl} denotes interplanar spacing (determined using PDXL2 Rigaku Data Analysis Software, Version 2.8.4.0) and (hkl) denotes the Miller indices of the corresponding crystallographic plane.

Studies of the corrosion rate of samples of protective coatings on a titanium substrate in highly aggressive environments were carried out according to GOST 9.909-86 [66] in 1 M solutions with acidic (H₂SO₄), alkaline (NaOH) and neutral (NaCl) media at a constant temperature of 50 °C; the exposure duration did not exceed 180 min, and a control interval was used for measuring the mass of samples every 30 min. At least 3 samples were tested in each environment. The corrosion rate was assessed via the increase in or loss of mass per unit of the surface area of the sample after the end of the next time interval. In this case, the sample was washed in a vessel with water and dried with filter paper to obtain

accurate mass changes. The samples were weighed on an electronic analytical balance SARTOGOSM CE224-C (Sartogsm LLC, St. Petersburg, Russia) with an error of ± 0.01 mg. The research results were processed using the following formulas:

1. Change in sample mass during the test Δm , mg

$$\Delta m = m_0 - m_1, \quad (1)$$

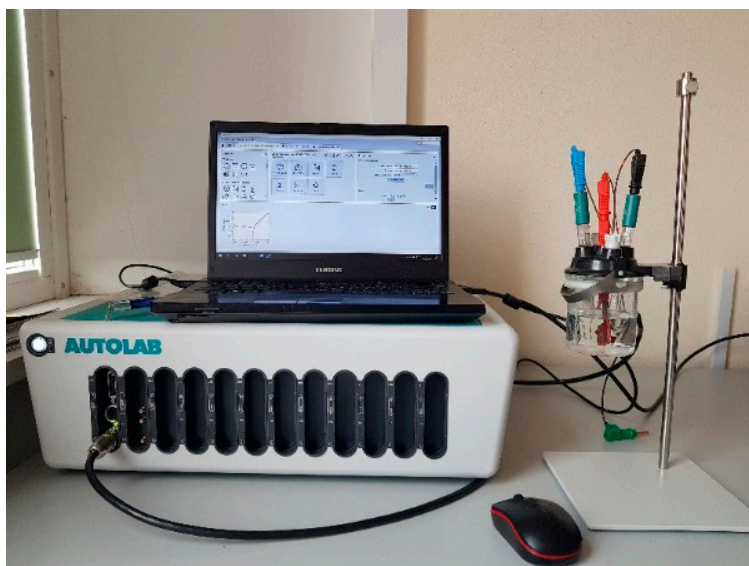
where m_0 is the mass of the sample before testing, mg; and m_1 denotes the mass of the sample after testing, mg.

2. Change in the density of the sample (thickness of the coating of the formed corrosion layer) S_{pr} , mg/cm²

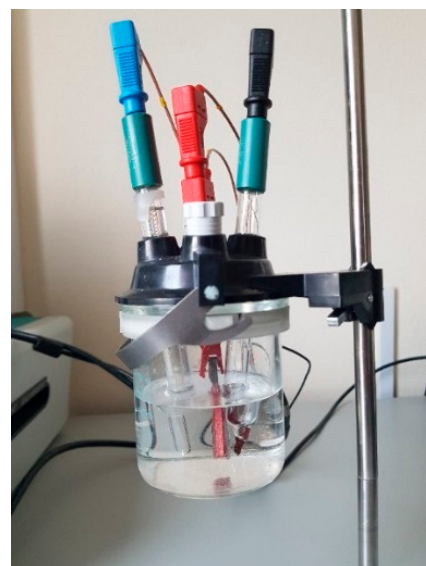
$$S_{pr} = \Delta m_i / A, \quad (2)$$

Here, Δm_i is the change in the mass of the i -th sample, mg; A denotes the sample's surface area, cm². In the case under study, for all samples in the form of disks, $A = 17.89$ cm².

Nitride coating tests for corrosion resistance were also carried out on an Autolab/PGSTAT302N potentiostat–galvanostat (Metrohm Autolab B.V., Utrecht, The Netherlands) (Figure 1a) using the electrochemical method of polarization curves in a standard three-electrode cell (Figure 1b). Corrosion current density was determined via the extrapolation of polarization curves' linear parts (corresponding to the Tafel equation) relative to the corrosion potential. Extrapolation was carried out using Nova 2.1.5 software. The reference electrode was a saturated silver chloride electrode, and the counter electrode was a platinum plate. Before recording the polarization curves, the samples were kept in the solution without polarization for 30 min. At the same time, the dependence of the open-circuit potential on time was recorded. The initial value of the polarization potential was chosen to be 300 mV more positive than the open-circuit potential. Polarization curves were recorded in the potentiodynamic mode at a potential sweep rate of 0.1 mV/s. The working surface area of each sample was 1 cm². All tests were carried out in a solution of 3% NaCl at room temperature and without convection.



(a)



(b)

Figure 1. AUTOLAB potentiostat for recording polarization curves: (a) general view and (b) three-electrode electrochemical cell.

3. Results

3.1. Structure and Composition of Coatings

Studies have shown that when using one Zr-containing cathode, the formation of a single-phase coating based on a ZrN solid solution is observed (Figure 2). When using two cathodes (Zr-containing cathode and titanium cathode), a two-phase coating is formed, containing solid solutions based on ZrN and TiN. In the diffraction patterns of all coatings, the presence of diffraction lines corresponding to α -Zr (Zr-COD 9008559) is observed, which is associated with the formation of an intermediate adhesive metal sublayer. In addition, according to X-ray diffraction analysis data, during the deposition of coatings, the formation of ZrO₂ oxide with a cubic crystal lattice is possible. Since this polymorphic modification of the oxide is high in temperature, its existence at room temperature may be due to both stabilization by other elements present in the coating composition and the possible existence of microstresses that prevent the transition to a low-temperature polymorphic modification.

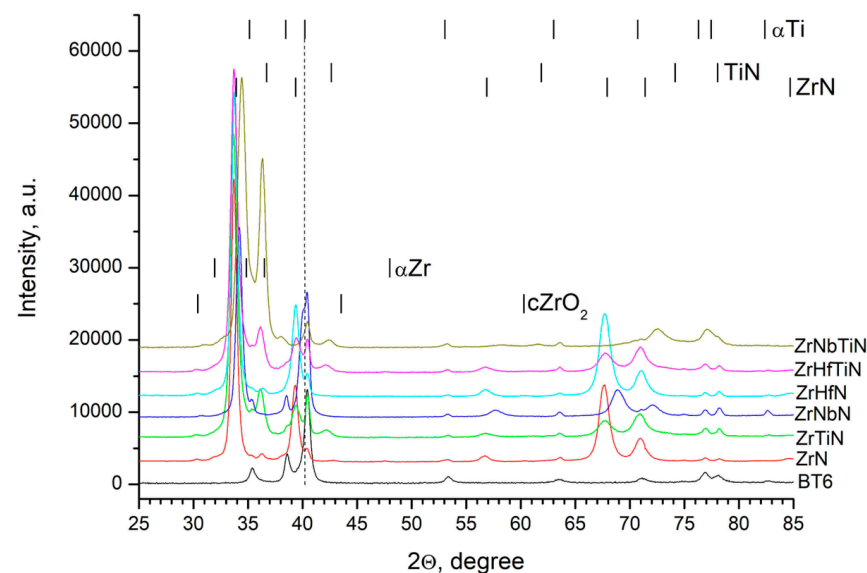


Figure 2. X-ray diffraction patterns of coatings based on ZrN-TiN.

Data obtained as a result of SAED analysis (Figure 3) confirm diffraction patterns. In titanium-containing coatings, two phases are formed—corresponding cubic solid solutions based on ZrN and TiN (ZrN-COD 4303942; TiN-COD 1100033; NbN-COD 1537803). In coatings that do not contain titanium, only one ZrN-based phase is formed. In the substrate (Ti6Al-4V Titanium alloy), the Ti₃AlV phase with space group P6₃/mmc is formed (COD 1527832).

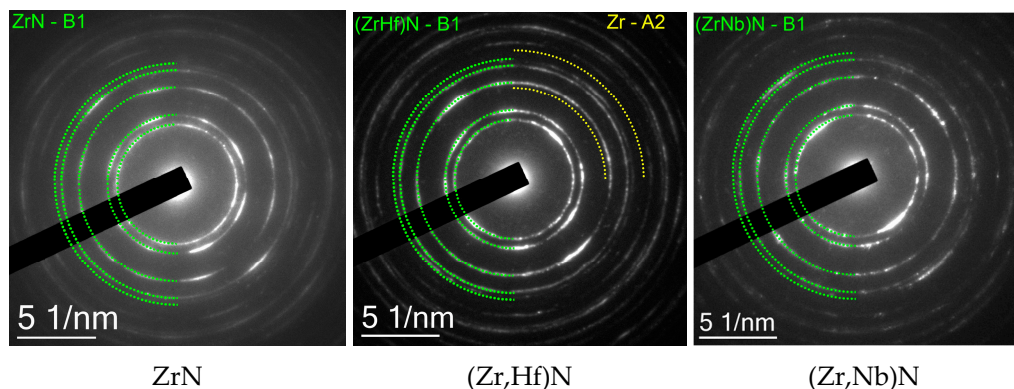


Figure 3. Cont.

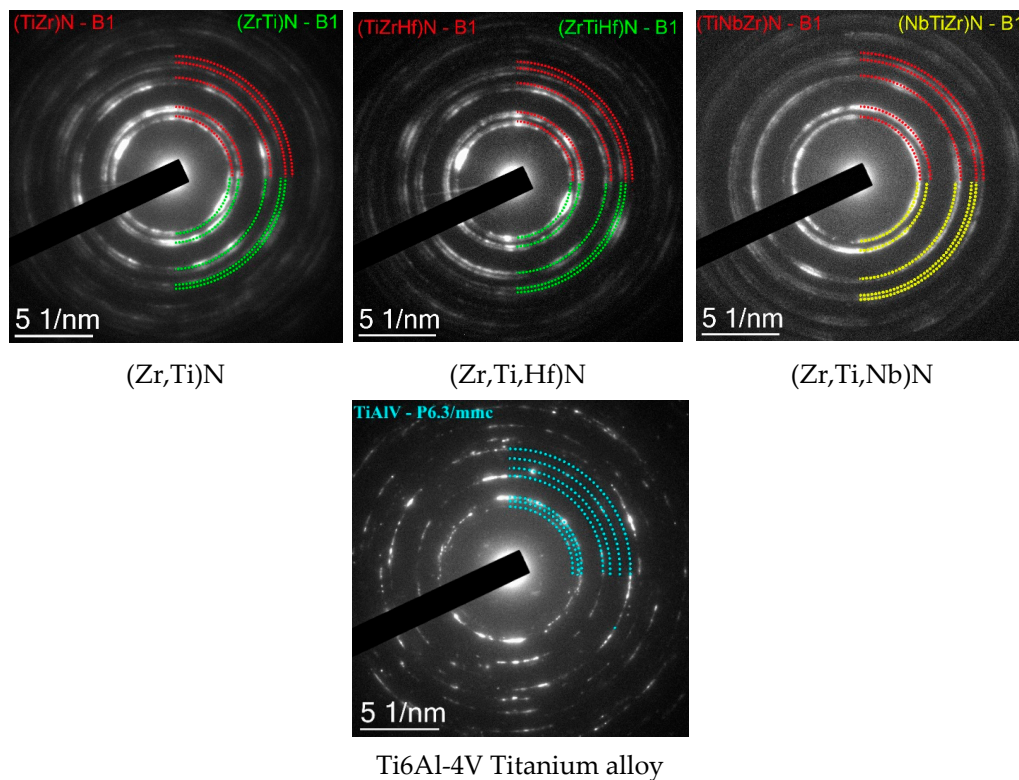


Figure 3. Results of the SAED analysis of the studied coatings and titanium alloy substrate.

Let us consider the structure of the coatings under study. The ZrN coating with an intermediate Zr adhesion layer (Figure 4) has a columnar structure. The structure contains layers associated with the periodic heating of the surface of the deposited coating. The interface between the intermediate adhesion sublayer and the substrate has a rather interesting structure, including a thin (20–30 nm thick) layer with a nanocrystalline structure. This layer may be associated with the interaction between the metallic material of the substrate and the deposited zirconium, as a result of which intermetallic compounds can be formed between zirconium on the one hand and titanium, aluminum, and possibly vanadium on the other hand [67–69]. It is noted that zirconium has high adhesion strength relative to the titanium–aluminum system [69]. This issue requires more detailed study in the future.

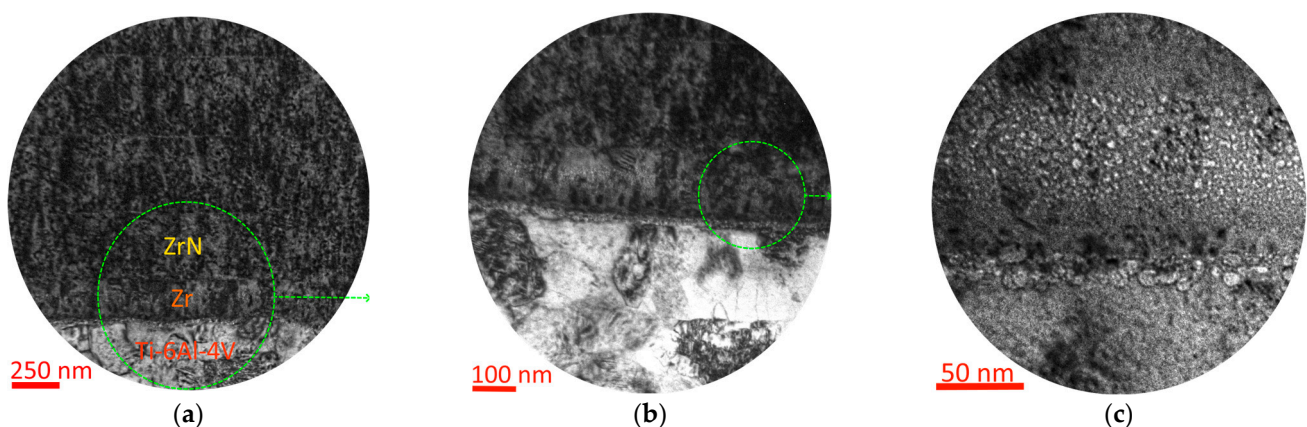


Figure 4. Structure of the ZrN coating: (a) general structure of the coating, (b) region of the adhesive transition sublayer and (c) crystalline structure of the interface of the adhesive sublayer and the titanium alloy substrate.

The (Zr,Hf)N coating also has a columnar structure, in which there are layers associated with the periodic heating of the coating surface during the deposition process. At the interface between the Zr,Hf adhesive sublayer and the titanium alloy substrate, there is a layer with pronounced nanocrystalline structures (see Figure 5b), similarly to that previously considered for the ZrN coating. In addition to this layer, a dark contrast layer is observed (see Figure 5c) with a thickness of about 30 nm. Analyses of the elemental content do not show any noticeable differences in the composition of this layer. Perhaps this layer is associated with the process of etching the surface with a flow of metal (Zr,Hf) plasma, due to which a change in the structure occurred without changing the composition. To better understand the formation process of the interface between the substrate and the adhesion sublayer, an analysis of the elemental content in this area was carried out (Figure 5d–h). The crystalline structure of the Ti-6Al-4V substrate is worth noting, which includes grains with high (up to 24 at.%) and low (less than 2 at.%) vanadium content (Figure 5d,h). The aluminum content has a smaller spread (from 4 to 8 at.%). Thus, during the deposition process, the coating can form adhesive bonds with local areas of the substrate that have quite different compositions. This must be considered when selecting the composition of the adhesive layer.

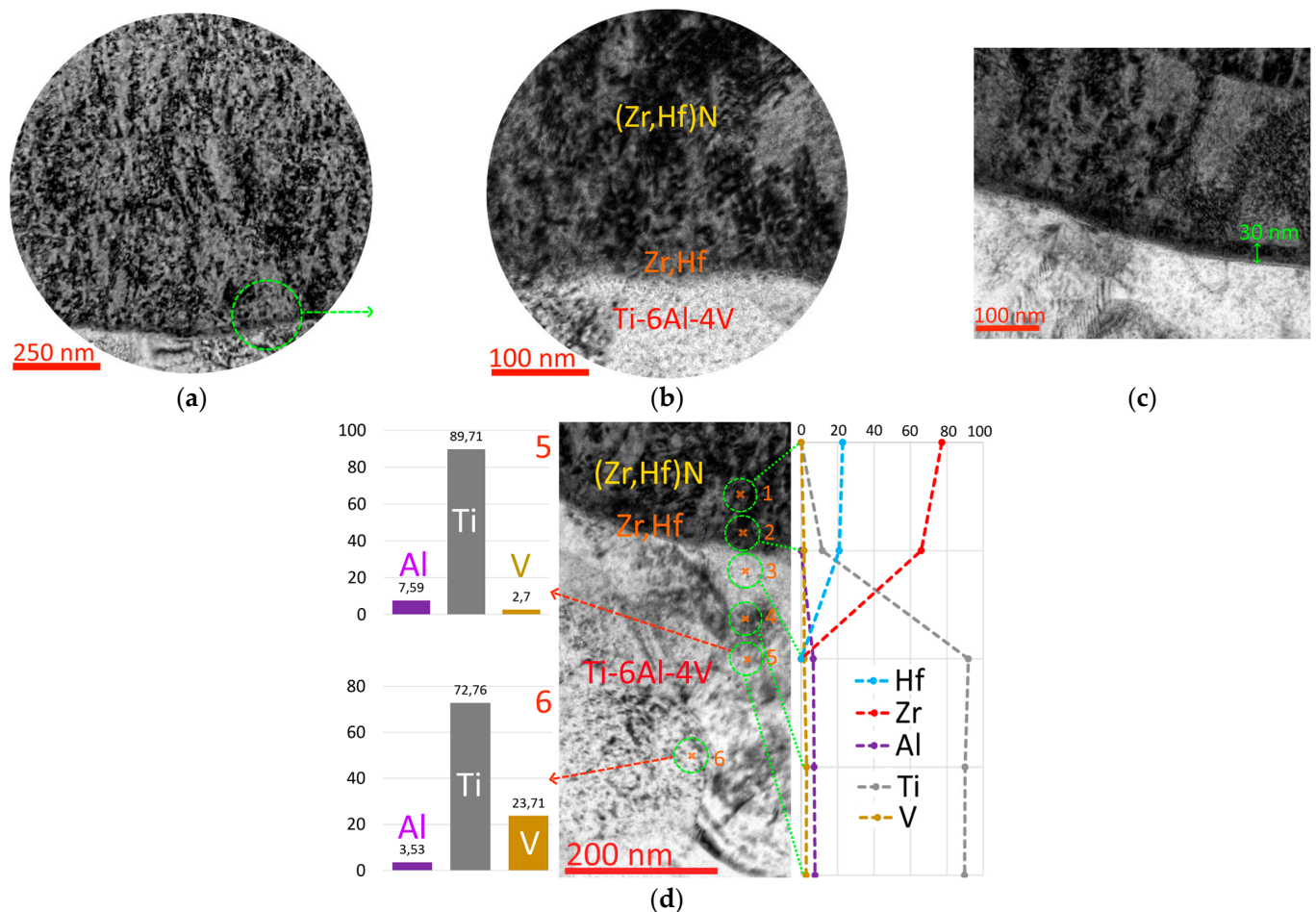


Figure 5. Cont.

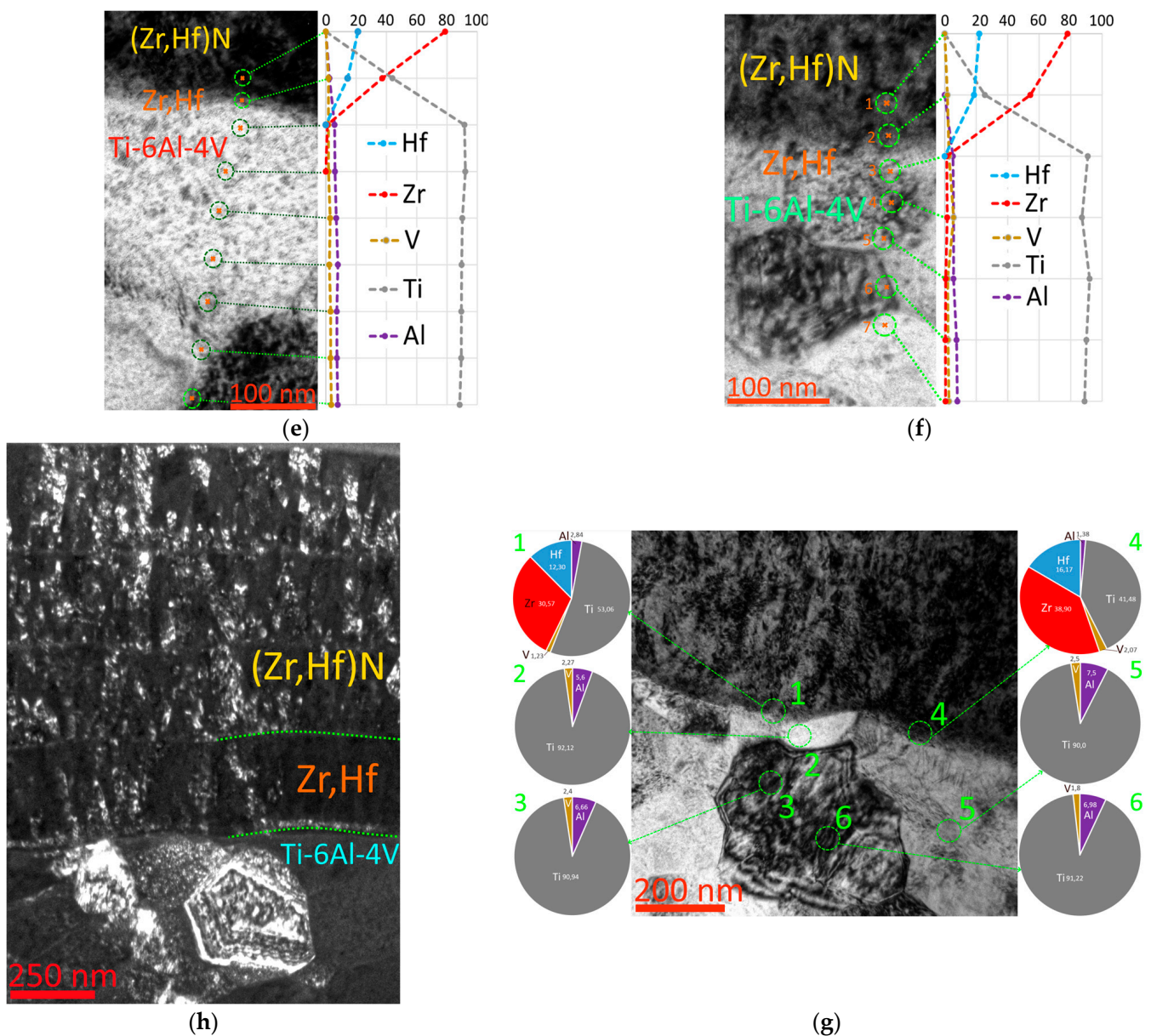


Figure 5. Structure of the (Zr,Hf)N coating: (a) general structure of the coating; (b) region of the transition adhesion sublayer; (c) crystal structure of the interface of the adhesive sublayer and the titanium alloy substrate; (d–f) analysis of elemental content in the interface region; (g,h) analysis of the elemental structure of the crystal structure in the interface region.

The diffusion of zirconium and hafnium from the adhesion layer of the coating into the substrate takes place up to a depth of 200 nm. The diffusion of titanium alloy elements (primarily titanium and vanadium) into the adhesive sublayer of the coating to a depth of 100 nm is also observed. These interdiffusion processes can increase the strength of the adhesive bond.

The structure of the (Zr-Nb)N coating is similar to the previously considered coatings (Figure 6). There is a columnar structure with layers formed by the periodic heating of the coating's surface. In this case, the layer with a nanocrystalline structure is absent or weakly expressed. The interface between the substrate and the adhesion sublayer is more clearly defined than that of ZrN and (Zr,Hf)N coatings.

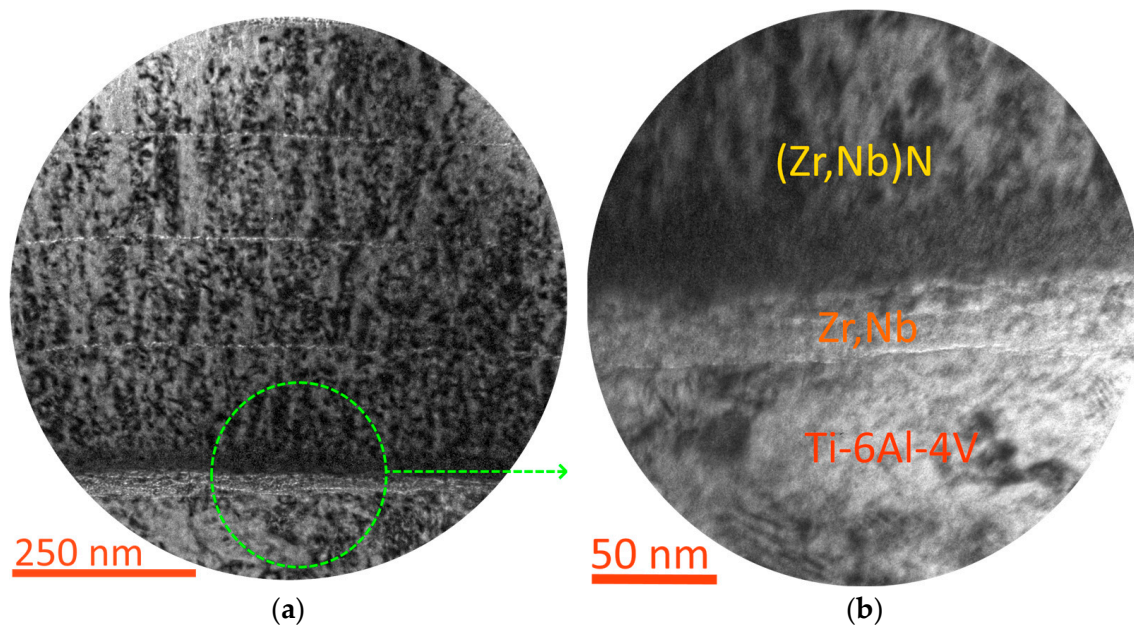


Figure 6. Structure of the (Zr,Nb)N coating: (a) general structure of the coating and (b) region of the transition adhesion sublayer.

The structure of coatings containing titanium is significantly different. Since coating deposition occurs during the simultaneous operation of two cathodes, one of which is titanium and the second is made of zirconium or a corresponding zirconium alloy, a nanolayer structure is formed in all coatings with Ti [47,70]. In particular, such a nanolayer structure is present in the (Ti,Zr)N coating (Figure 7) and is formed by alternating layers with high titanium (light in contrast) and zirconium (dark in contrast) contents. The adhesion sublayer of Zr is well differentiated from the functional layer (Ti,Zr)N. Delamination can be seen forming between the substrate and the adhesive sublayer. Given that the composition of the adhesion layer is identical to the ZrN coating, the formation of this delamination may be associated with the high compressive stresses that are characteristic of the (Ti,Zr)N coating [36].

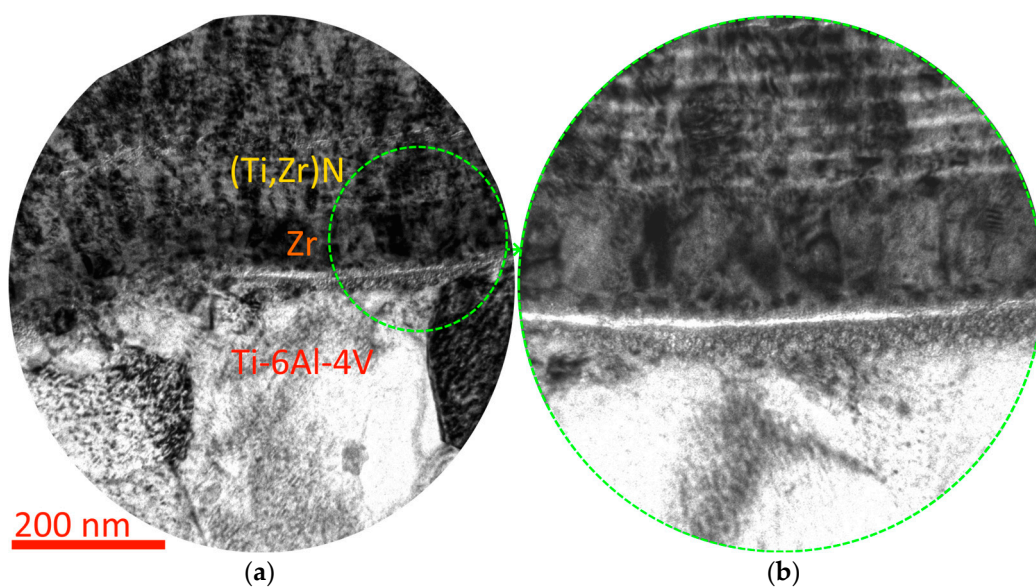


Figure 7. Structure of the (Ti,Zr)N coating: (a) general structure of the coating and (b) region of the transition adhesion sublayer.

(Ti,Zr,Hf)N and (Ti,Zr,Nb)N coatings have a nanolayer structure (Figures 8 and 9), similarly to the previously discussed (Ti,Zr)N coating. In the (Ti,Zr,Hf)N coating, the previously considered layer with a nanocrystalline structure is observed in the interfacial area of the substrate and the adhesive sublayer (Figure 8).

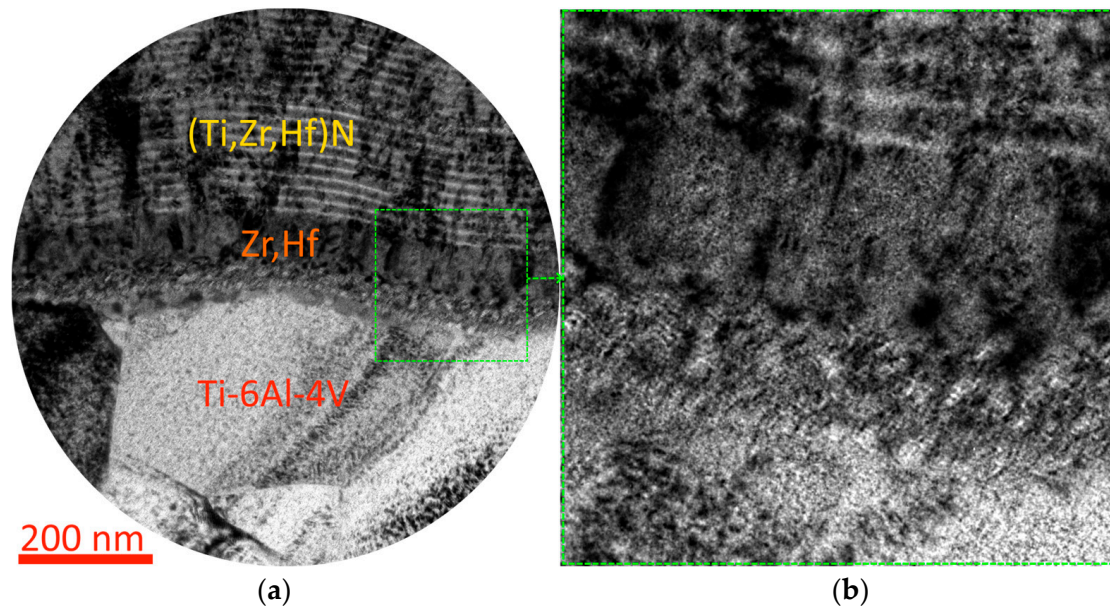


Figure 8. Structure of the (Ti,Zr,Hf)N coating: (a) general structure of the coating and (b) region of the transition adhesion sublayer.

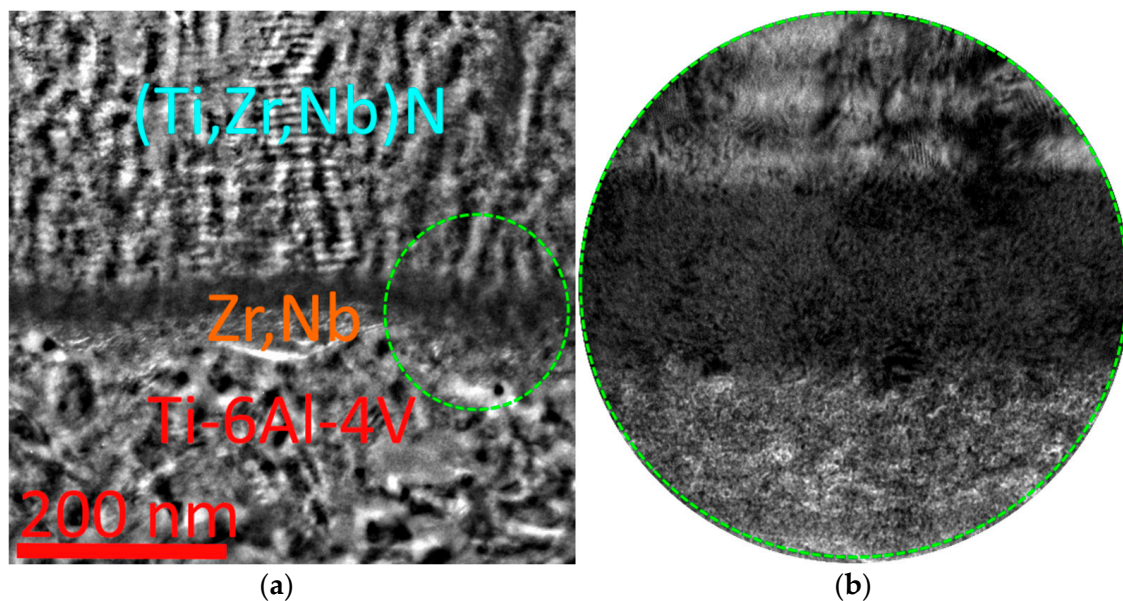


Figure 9. Structure of the (Ti,Zr,Nb)N coating: (a) general structure of the coating; (b) region of the transition adhesion sublayer.

Based on X-ray diffraction data, the crystal lattice parameters of the solid solution based on ZrN (Figure 10) and TiN (Figure 11) were determined. As observed in Figure 10, for ZrN, (Zr,Ti)N, (Zr,Hf)N and (Zr,Ti,Hf)N coatings, the lattice parameter of the ZrN-based solid solution determined from (111) and (311) diffraction lines) is slightly larger than that of the standard, including the lattice parameter of the ZrN coating. This may be due to the nonstoichiometry of the coating's composition or the appearance of additional sub-dimensional impurities (for example, C). The use of a Zr-Nb cathode leads to a sharp

decrease in the lattice parameter of the (Zr,Nb)N solid solution in (Zr,Nb)N and (Zr,Ti,Nb)N coatings (Figure 10). The reason for the decrease in the lattice parameter is the smaller radius of Nb atoms (0.164 nm) compared to Zr atoms (0.175 nm).

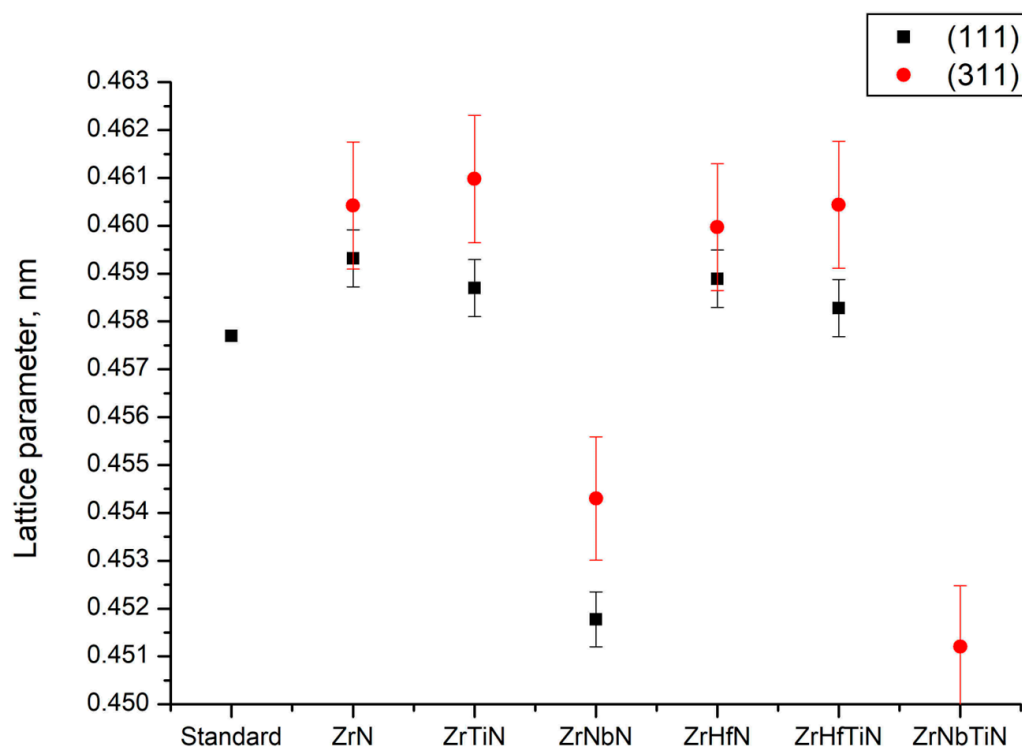


Figure 10. Crystal lattice parameter of the ZrN-based solid solution in deposited coatings.

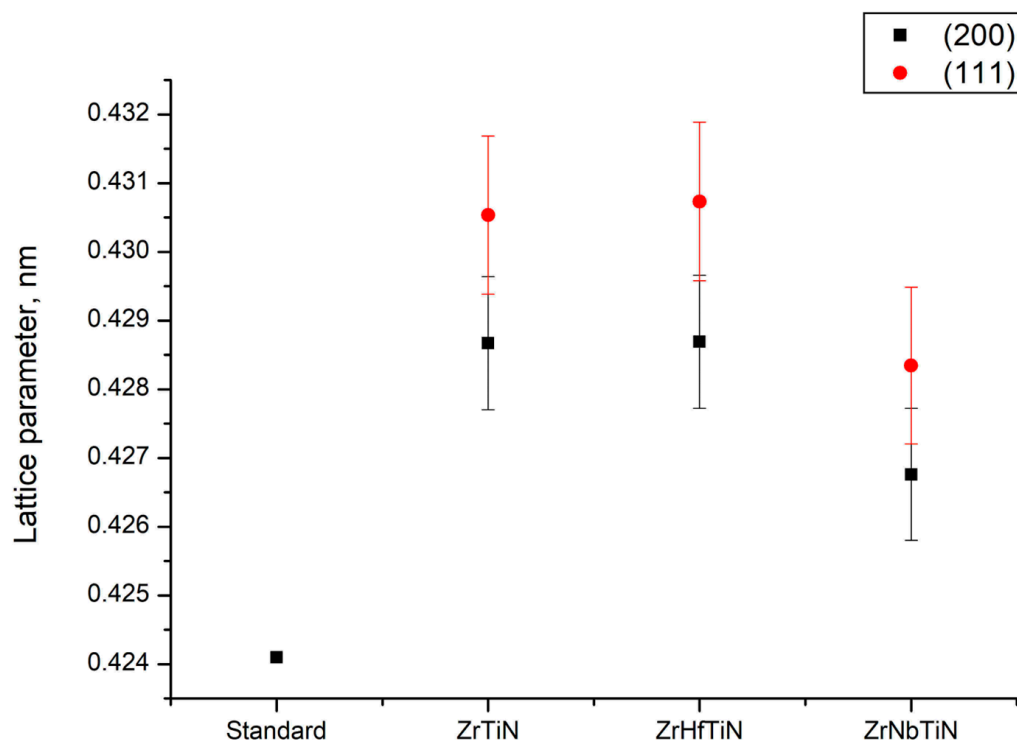


Figure 11. Crystal lattice parameter of the TiN-based solid solution in deposited coatings.

Similar effects are observed for the TiN-based solid solution (Figure 12). In particular, the use of a Zr-Nb cathode leads to a sharp decrease in the lattice parameter of the TiN-based solid solution in the (Zr,Ti,Nb)N coating, which suggests the formation of a solid (Ti,Nb)N solution. The results of the study of the elemental composition of coatings are presented in Table 1. The data were obtained without considering possible impurities, such as carbon and oxygen. From the data presented in the table, it is clear that the predominant metal element in multicomponent coatings is zirconium (with the exception of the (Zr,Nb,Ti)N coating in which titanium predominates). In (Zr,Nb)N and (Zr,Nb,Ti)N coatings, the ratio of metal elements Zr and Nb is close to the ratio of these elements in the Zr-Nb cathode: 1:1. In (Zr,Hf)N and (Zr,Hf,Ti)N coatings, the ratio of the metal elements Zr and Hf (~8:1) differs from the ratio of these elements in the Zr-Hf cathode: 1:1. For all types of coatings, the nitrogen concentration is close to 50 at.%.

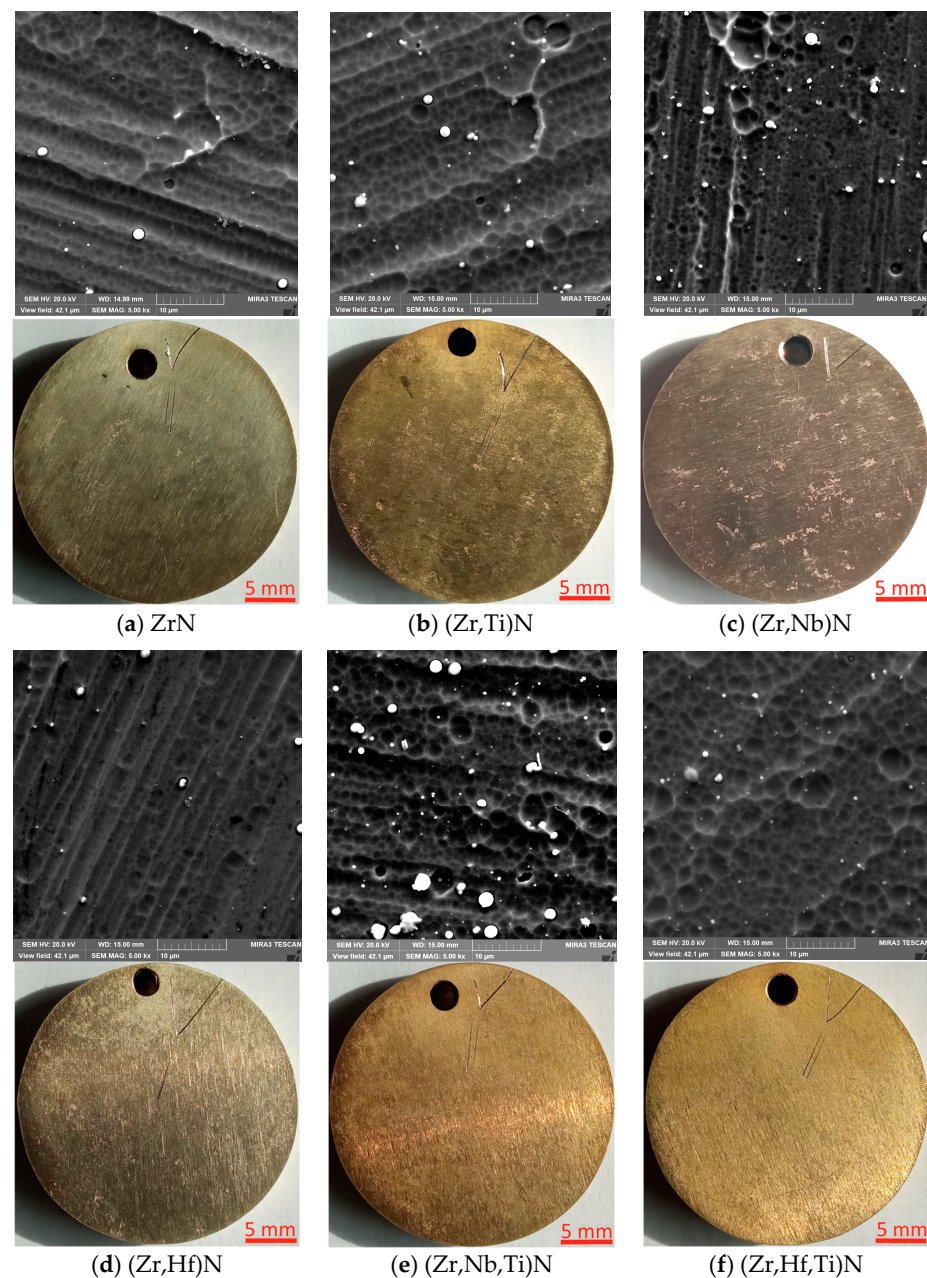
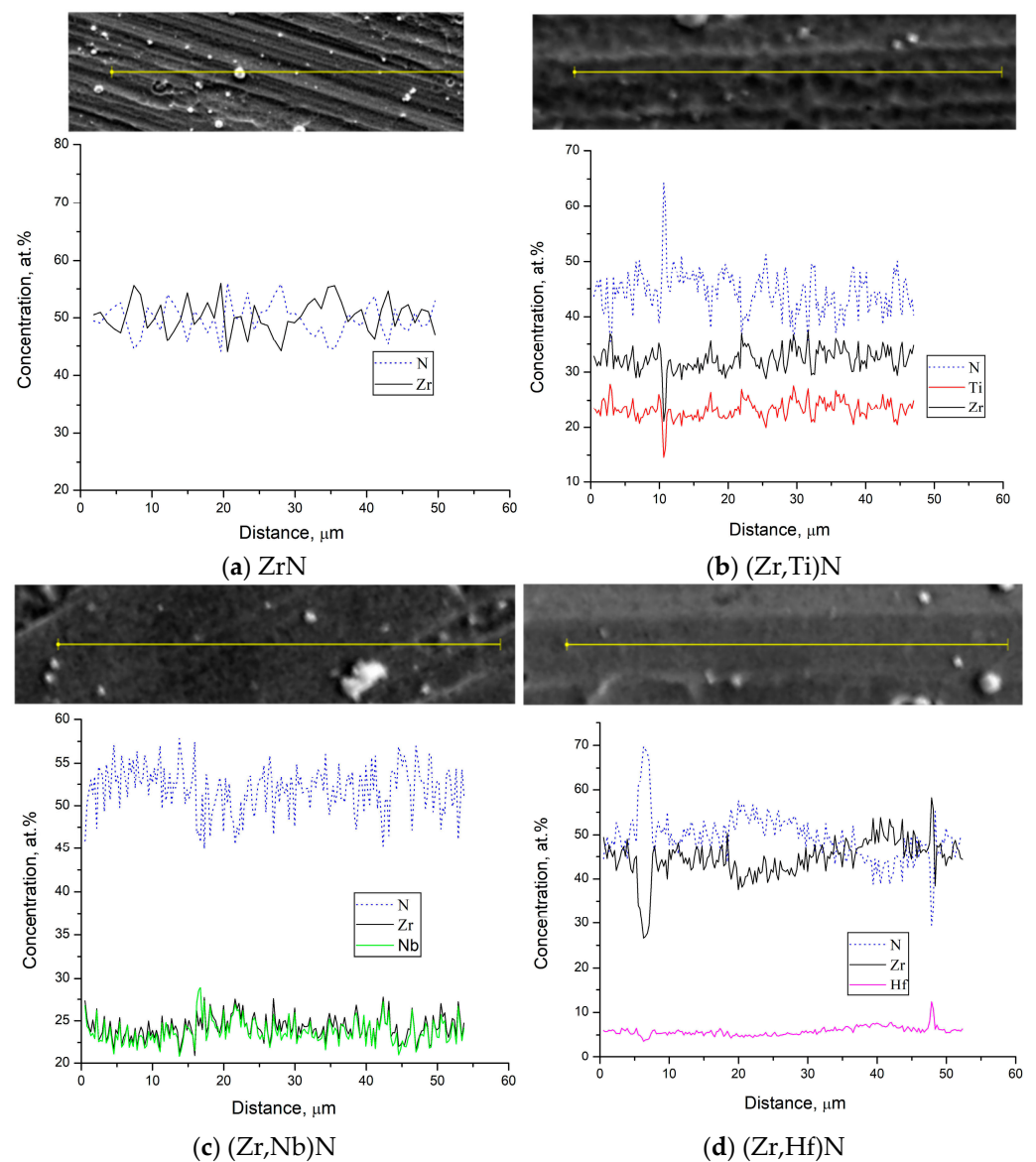


Figure 12. Surface morphology (from above) and the general view of the coating sample (below): (a) ZrN, (b) (Zr,Ti)N, (c) (Zr,Nb)N, (d) (Zr,Hf)N, (e) (Zr,Nb,Ti)N and (f) (Zr,Hf,Ti)N.

Table 1. Average concentration of elements in coatings.

Coating	Concentration of Elements in the Coating, at. %				
	Ti	Zr	Nb	Hf	N
ZrN	0.17	48.61	-	-	51.22
ZrTiN	22.15	30.53	-	-	47.32
ZrNbN	-	23.50	23.41	-	53.10
ZrHfN	-	43.52	-	5.72	50.77
ZrNbTiN	36.99	7.47	7.51	-	48.03
ZrHfTiN	22.53	26.60	-	3.38	47.48

Figures 12 and 13 show the surface morphology and distribution of coating elements along the surface. Surface morphology is characterized by the presence of droplets from the cathodes formed in the arc during coating deposition (Figure 12).

**Figure 13.** Cont.

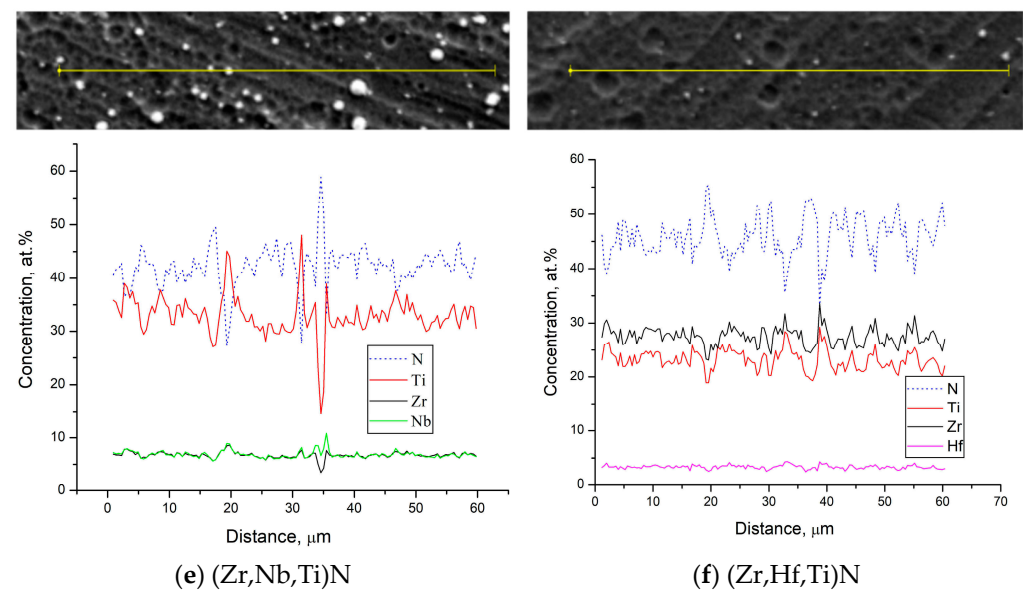


Figure 13. Distribution of coating elements when scanning along a line on the surface of samples: (a) ZrN, (b) (Zr,Ti)N, (c) (Zr,Nb)N, (d) (Zr,Hf)N, (e) (Zr,Nb,Ti)N and (f) (Zr,Hf,Ti)N.

In most cases, the distribution of elements over the surface is uniform (Figure 13). However, on the (Zr,Hf)N coating (Figure 13d), there are local areas in which the concentration of coating elements (N–69 at.%, Zr–26 at.% and Hf–5 at.%) differs from the average concentration presented in Table 1. It should be noted that those that are the most uniform with respect to chemical composition are ZrN and (Zr,Nb)N coatings.

3.2. Accelerated Testing in Aggressive Environments

The exposure of metals and alloys with coatings to corrosion-active solutions at elevated temperatures (35–50 °C) significantly accelerates the corrosion aging of the material. This helps simulate the corrosion resistance of specific products over long periods relative to their real use under the conditions of exposure to an aggressive external environment and promotes an informed choice regarding the best coating options, application methods, optimal thicknesses, technologies and the materials themselves. This type of corrosion test was carried out in this work just to evaluate the coatings' corrosion resistance within the entire pH range (acidic, neutral and alkaline media) and determine external conditions for coatings application.

The results of the statistical processing of experimental measurement data are presented in Table 2.

As observed in the presented data, in fact, there is no change in the mass of the samples during accelerated corrosion tests in all cases; minor fluctuations at $\pm 0.1\text{--}1.8 \text{ g/cm}^2 \times 10^{-5}$ probably correspond to the adsorption of water vapor and gases or the microfibers of filter paper on the microroughness of a solid surface, and they are on the verge of corresponding to the confidence interval of the measurements of analytical balances. Consequently, the studied nitride coatings, in the absence of mechanical microdamage, are not susceptible to corrosion in aggressive liquid environments for a sufficiently long period of time, and they are determined by the standards of machine parts and mechanisms and medical products.

Table 2. Average weight loss Δm , $\text{g}/\text{cm}^2 \times 10^{-5}$, of samples with protective coatings in aggressive 1M environments.

Uncoated Ti Alloy			
Time, min	NaCl	NaOH	H ₂ SO ₄
30	−2.2	−0.4	−1.9
60	−2.6	−1.7	0.2
90	−2.8	−1.9	−0.6
(Zr,Nb)N			
Time, min	NaCl	NaOH	H ₂ SO ₄
30	10.4	2.4	17.7
60	12.1	32.8	−1.5
90	12.3	3.4	3.0
(Zr,Hf)N			
Time, min	NaCl	NaOH	H ₂ SO ₄
30	30.0	0.0	1.7
60	10.0	6.7	10.1
90	20.0	3.9	3.7
(Zr,Ti)N			
Time, min	NaCl	NaOH	H ₂ SO ₄
30	3.4	4.5	0.0
60	0.6	1.3	0.0
90	1.3	2.6	1.1
ZrN			
Time, min	NaCl	NaOH	H ₂ SO ₄
30	2.8	5.2	0.4
60	−0.4	1.7	−0.2
90	−1.1	1.9	−0.6
(Zr,Hf,Ti)N			
Time, min	NaCl	NaOH	H ₂ SO ₄
30	0.4	2.0	1.1
60	0.6	0.2	1.1
90	0.2	2.2	−0.2
(Zr,Nb,Ti)N			
Time, min	NaCl	NaOH	H ₂ SO ₄
30	0.0	1.5	0.2
60	−0.6	1.1	−1.1
90	−0.2	0.7	0.4

3.3. Forced Electric Potential Tests

At the preliminary stage, a study of the corrosion process of coatings using voltammetry (VAM) with the construction of Tafel logarithmic polarization curves showed that in a 3% NaCl environment, which is an imitation of the environment in the body (saline), the corrosion current density ranges from 2.2×10^{-5} to 3.5×10^{-9} A/cm² (Table 3, Figure 14). The ZrN coating possesses the lowest corrosion rate among other single nitrides. One can observe that the corrosion potential of YN coatings was strongly shifted into the area of

negative potentials. Its corrosion current density was a few orders of magnitude higher than that of other nitride coatings and even uncoated Ti alloys. The decomposition of YN in water solutions was the main reason for such behavior [71,72].

Table 3. Corrosion current density (i_{cor}) of titanium-based nitride coatings, A/cm².

Material	i_{cor}
Uncoated Ti alloy	3.9×10^{-8}
TiN	3.0×10^{-8}
ZrN	3.5×10^{-9}
CrN	1.3×10^{-8}
YN	2.2×10^{-5}
(Zr,Nb)N	1.0×10^{-8}

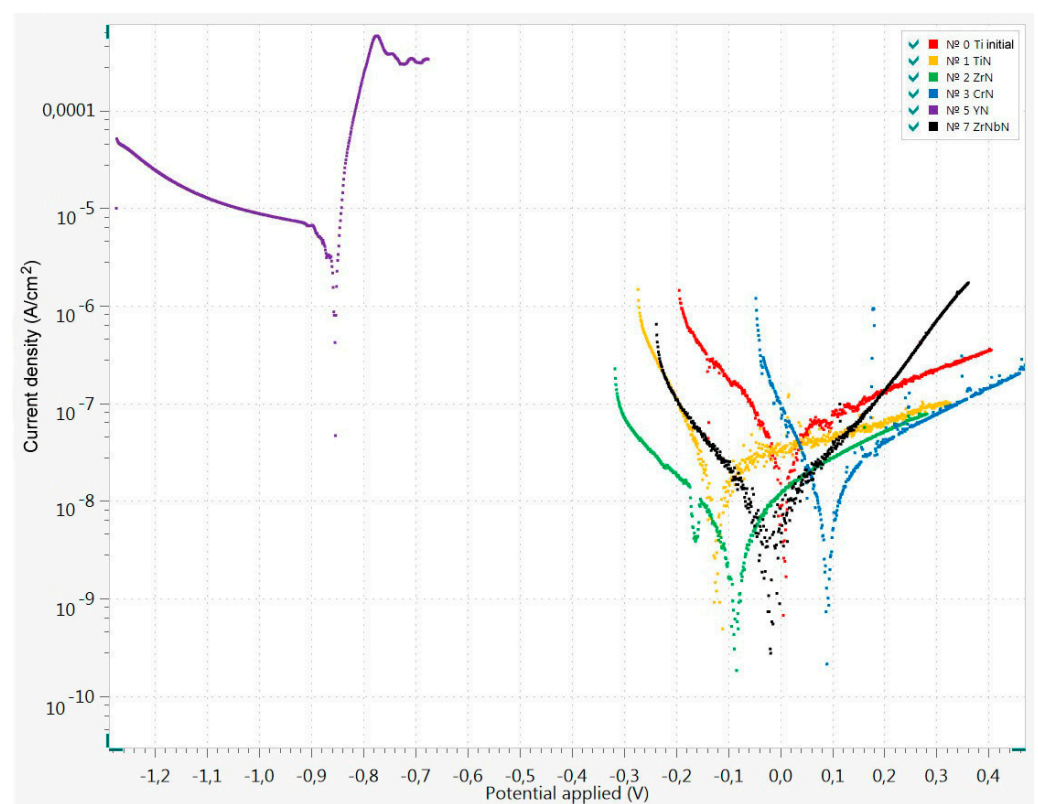
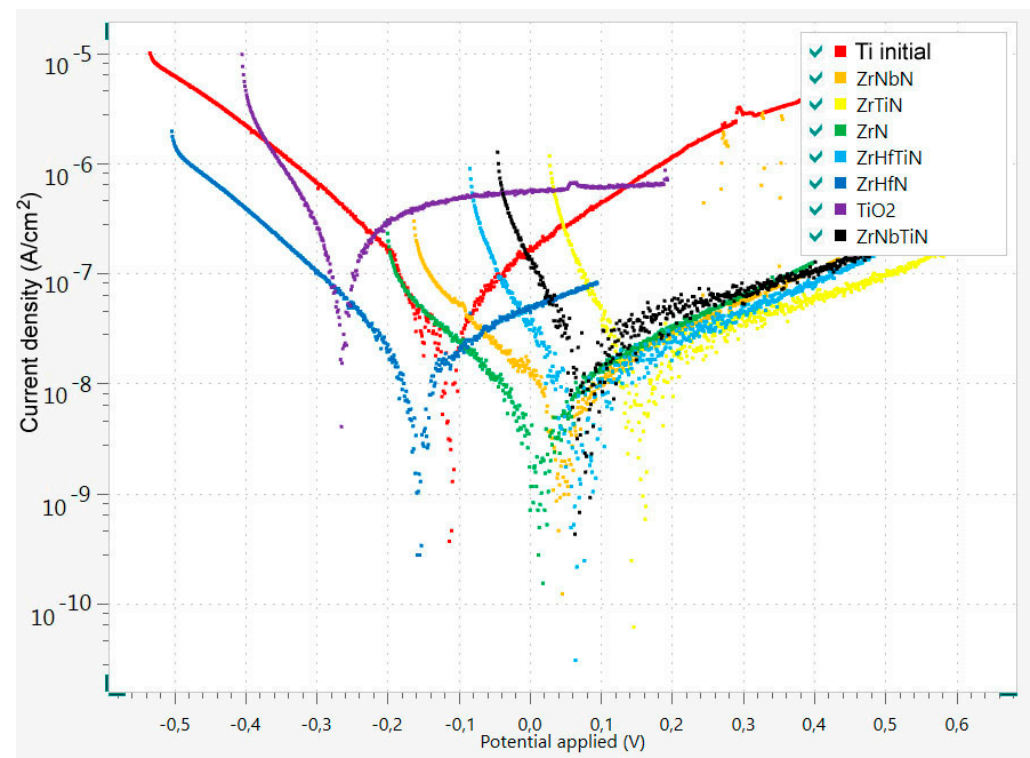


Figure 14. Logarithmic polarization curves for nitride coatings on titanium in a 3% NaCl environment. Preliminary study for double nitrides and (Zr,Nb)N.

The subsequent determination of the corrosion current density of coatings based on zirconium nitride (Table 4, Figure 15) showed that it almost corresponds to that of single nitrides. According to VAM data, corrosion current density for the studied coatings in a 3% NaCl environment was changed in the range from 7.9×10^{-9} to 2.6×10^{-8} A/cm², which confirms the high corrosion resistance of the materials under study. It should also be noted that ZrN coatings provided higher corrosion resistance than solid solutions on their basis. But in any case, TiO₂ magnetron coatings that are frequently used as protective medical implant coatings showed higher corrosion rates than nitride coatings.

Table 4. Corrosion current density (i_{corr}) of nitride coatings deposited on a titanium alloy, A/cm².

Material	i_{corr}
Uncoated Ti alloy	3.9×10^{-8}
(Zr,Nb)N	1.0×10^{-8}
(Zr,Hf)N	1.4×10^{-8}
(Zr,Ti)N	7.9×10^{-9}
ZrN	3.5×10^{-9}
(Zr,Hf,Ti)N	9.2×10^{-9}
(Zr,Nb,Ti)N	2.6×10^{-8}
TiO ₂	1.4×10^{-7}

**Figure 15.** Logarithmic polarization curves for nitride coatings on a titanium alloy in a 3% NaCl environment. Generalized research for all samples.

3.4. Long-Term Testing under Conditions Simulating Real-Life Operations

In order to study the characteristics of the corrosion of nitride coatings under conditions closest to real ones, long-term tests (4 months) were carried out in a climate chamber. Samples with the coatings under study were immersed in a 3% NaCl solution (a physiological solution that simulates the liquid environment in the body) and placed in closed containers in an automatic thermostat at 37 °C for long-term testing.

After the completion of tests, all studied samples, both nitride coatings and the original titanium alloy substrate, had no external signs of destruction; the solutions practically did not change in terms of color and transparency, which indicates the absence of metal dissolution products in the liquid medium. The results of the statistical processing of the experimental measurements of changes in the mass of samples are presented in Table 5.

Table 5. Average change in mass Δm , $\text{g}/\text{cm}^2 \times 10^{-4}$, of samples with protective coatings after long-term tests in a liquid environment simulating conditions in the body.

Material	Δm , $\text{g}/\text{cm}^2 \times 10^{-4}$
Uncoated Ti alloy	1.36
(Zr,Ti)N	0.01
(Zr,Hf)N	4.20
(Zr,Nb,Ti)N	3.05
ZrN	0.42
(Zr,Hf,Ti)N	0.13
(Zn,Nb)N	0.78

4. Conclusions

- The Ti-6Al-4V substrate has a crystalline structure, including grains with high (up to 24 at.%) and low (less than 2 at.%) vanadium content. Thus, during the deposition process, the coating can form adhesive bonds with local areas of the substrate that have quite different compositions. This must be considered when selecting the composition of the adhesive layer. The diffusion of the adhesion-layer elements of the coating into the substrate takes place to a depth of up to 200 nm. The diffusion of titanium alloy elements (primarily titanium and vanadium) into the adhesive sublayer of the coating up until a depth of 100 nm is also observed. These interdiffusion processes can increase the strength of the adhesive bond.
- The use of a Zr-Nb cathode leads to a sharp decrease in the lattice parameter of the (Zr,Nb)N solid solution in the (Zr,Nb)N and (Zr,Ti,Nb)N coatings, as well as the TiN-based solid solution in the (Zr) coating, Ti,Nb)N.
- Forced electric potential tests showed the high corrosion resistance of ZrN nitride coatings and coatings based on ZrN solid solutions in 3% NaCl solutions. All these coatings possess lower-corrosion-rate TiO_2 magnetron coatings, which are frequently used for medical implant protection. The actual change in the mass of samples during corrosion tests in acidic (H_2SO_4), alkaline (NaOH) or neutral (NaCl) media at elevated temperature is insignificant; fluctuations in some cases are on the verge of a systematic error of analytical balances and can be caused by the adsorption of ions, the microcrystals of salt and water vapor on the surface of samples.
- The studied protective coatings based on d-element nitrides have very high anti-corrosion characteristics and practically do not react with body fluids.

The next stage of research may be the study of the corrosion patterns of these materials after various types of mechanical impacts, simulating operational damage.

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