

Article



# Features of the Application of Coatings Based on the ZrN System to Increase Resistance to Mechanical Wear and Corrosion of Titanium Alloy Products

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**Abstract:** The coatings of ZrN, (Zr,Ti)N, (Ti,Zr,Hf)N and (Ti,Zr,Nb)N deposited on the titanium alloy substrate were compared. The wear resistance in the pin-on-disk test together with the Al<sub>2</sub>O<sub>3</sub> indenter and the corrosion resistance in 3.5% NaCl solution were studied. It was found that the (Zr,Nb,Ti)N coating has the best resistance to wear, but has low corrosion resistance. The (Ti,Zr,Hf)N coating, on the contrary, has the best corrosion resistance, but low resistance to wear. The ZrN coating has good corrosion resistance combined with good resistance to wear. This coating is best suited for use in friction conditions with a ceramic counterbody under the influence of seawater. An important resource for increasing the properties of coatings is increasing their adhesion to the substrate, which can be achieved in two combined ways: (1) complete removal of the original oxide layer from the surface of the substrate and (2) the use of optimal compositions of the adhesive sublayer, which have not only high adhesive properties in relation to both the substrate and the coating, but also high strength. While the introduction of Nb into the ZrN coating composition increases wear resistance and the introduction of Hf increases corrosion resistance, the ZrN coating without additives best resists wear and corrosion simultaneously.

Keywords: wear resistance; coatings; corrosion resistance; adhesive sublayer; titanium alloy

# 1. Introduction

Titanium alloys are widely used in various industries. The combination of high strength, relatively low specific gravity and good corrosion resistance make this material very promising in such industries as medicine, aerospace, energy and others [1–3]. Further expansion of the scope of the application of titanium alloys can be achieved via modifying the surface properties, in particular, increased resistance to corrosion and mechanical wear. In some cases (for example, in shut-off valves of special-purpose pipelines), tribopairs "ceramics—titanium alloy" can be used, operating in various aggressive environments [4–8]. Obviously, in such a pair, the dominant wear of the titanium alloy component is observed. At the same time, replacing the titanium component with a second ceramic one is not always possible or technologically feasible. Thus, there is a need to increase the wear



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**Copyright:** © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). resistance of the titanium component. Another problem in the operation of such a pair is the possibility of the destruction of the protective oxide film on the titanium component during tribocontact, which can lead to its intense oxidation [9,10]. Thus, the simultaneous increase in resistance to corrosion and mechanical wear of titanium alloy products operating in a tribopair with ceramics is a pressing task.

Coating deposition is widely used in various fields (metal-cutting tools, friction pairs, medical products, etc.) as an effective method of surface modification. At the same time, ensuring good adhesion between the titanium alloy substrate and the nitride PVD coating is a certain difficulty compared with, for example, a stainless steel substrate [4]. This is due, in particular, to the fact that titanium alloys exhibit active elastic recovery under various deformations [4,11–14]. As a result, significant shear forces arise in the area of the coating and substrate interface, which can lead to peeling of the coating. Thus, even very hard coatings may not provide a sufficient increase in wear resistance due to delamination from the substrate and rapid destruction [12]. Since the properties of the coating and the substrate differ quite significantly, it is advisable to use an adhesive sublayer that firmly binds the coating and the substrate and has properties that are transitional between the substrate and the coating [15–21]. To increase adhesion, it is also important to remove as much microcontamination and chemical (most often oxide) films from the substrate sur-face as possible during preliminary ion etching [22–25]. Another way to increase adhesion is to pretreat the substrate to increase its roughness and thus increase the active contact surface [26]. Ion beam etching [27] or laser micromachining [26,28,29] are suggested as such treatments. In this case, an increase in roughness can lead to an increase in the defectiveness of the surface layer and thus reduce the adhesion strength of the substrate and coating [30,31]. The ratio between the hardness of the coating and substrate affects the adhesion strength between them. On the one hand, an increase in the hardness of the substrate makes the gap in the properties of the coating smaller and thus leads to an improvement in the adhesion between them. On the other hand, the presence of softer and more plastic phases in the substrate can ensure the absorption of the deformation energy of the coating [32]. To bring the properties of the coating and substrate closer together, ion implantation of the surface layer of the substrate with elements such as Ti, Cr, as well as preliminary plasma nitriding are also used [33,34]. Depending on the composition of the substrate and coating, the following elements are used as the adhesion layer: Ti [17,35–38], Zr [39–42], Cr [43–45], Mo [20,44,46,47], Al [20,48], Nb and Ta [20,49], W and Ag [20], as well as intermetallic compounds Fe<sub>2</sub>Ti [35], Zr,Hf [50,51] and Cr,Mo [52]. The comparison showed that the best adhesion was provided by metals such as Ti, Nb, Zr and Cr [20].

To increase the corrosion resistance of parts, coatings of various compositions were used. ZrN coating was effectively used as an anticorrosive [53,54]. In [55], NbN coating was used, which was deposited on Mg-Y-RE (WE43) alloy and allowed shifting of the corrosion potential to the positive side and significantly reduced the corrosion current density. In [56], it is indicated that the corrosion potential of AZ91 alloy without coating is -1830 mV, and with a two-layer ZrN/Zr coating it shifts to -1420 mV in physiological fluid. In [57], ZrN coatings were used to protect Ti-6Al-4V alloy from corrosion in an isotonic solution of 0.9% NaCl. It was found that the polarization curves for Ti-6Al-4V alloy samples with and without a ZrN coating were characterized in 0.9% NaCl due to the presence of a passivation pad in the potential range of -0.40 to +0.65 V [57]. In the course of complex corrosion studies of samples with Ti-TiN, Zr-ZrN, Zr-(Zr,Hf)N and Zr-(Zr,Nb)N coatings in a 3% NaCl environment [58], it was shown that the introduction of hafnium into zirconium nitride with the formation of mixed nitride (Zr,Hf)N made it possible to reduce the corrosion currents from  $0.127 \,\mu\text{A/cm}^2$  to  $0.118 \,\mu\text{A/cm}^2$ , which was due to the formation of a denser microstructure of the (Zr,Hf)N coating in comparison with ZrN. At the same time, the deposition of Zr-(Zr,Nb)N increased the corrosion current by 3.5 times, to 0.127  $\mu$ A/cm<sup>2</sup>, due to the oxidative effect of corrosion products containing Nb<sup>+5</sup>-based compounds [58,59].

Although the ZrN coating has high hardness combined with good anticorrosion properties in isotonic solutions [49,50] and salt media [52], problems with adhesion arise when it is deposited on a titanium alloy substrate [60]. The value of the fracture resistance of the ZrN coating deposited on a titanium alloy is significantly lower compared with CrN or TiN coatings [61]. At the same time, adding an adhesive Zr layer between the coating and the substrate can significantly improve this indicator. The adhesion of the ZrN coating with the Zr adhesive layer when deposited on a titanium alloy is significantly better than when using a Ti adhesive layer [31,62]. In addition to increasing the adhesion between the substrate and the coating, the adhesive layers help to restrain the development of cracks and increase the overall strength of the coating–substrate system [63–65]. Despite the significant interest in the use of modifying coatings for titanium alloys, as well as in the issues of wear resistance and adhesion strength to the substrate of these coatings, there has been little research into the issues of comparing different coatings simultaneously in terms of wear resistance and corrosion resistance. Wear resistance, in turn, includes the hardness and strength of the coating itself and the strength of the adhesive bond with substrate.

Thus, in this work, such properties of samples made of titanium alloy Ti-6Al-4V with ZrN, (Zr,Ti)N, (Ti,Zr,Hf)N and (Ti,Zr,Nb)N coatings as wear resistance in a pin-on-disk test with an Al<sub>2</sub>O<sub>3</sub> counterbody and corrosion resistance in a 3.5 wt.% NaCl solution were simultaneously compared. The objective of this study was to determine the composition of the coating that best increases the wear resistance of titanium alloy products operating in an aggressive environment (seawater). Previously conducted studies of wear resistance and corrosion resistance of coatings of various compositions deposited on a titanium alloy substrate yielded separate results that are difficult to systematize, since the tests were conducted by different authors under different conditions. In this present study, a simultaneous comparison conducted under identical conditions of wear resistance and anticorrosive properties of a number of coatings deposited on a substrate of uniform size and composition, is carried out.

#### 2. Materials and Methods

The coating deposition was carried out using the VIT-2 installation (IDTI RAS—MSUT "STANKIN", Russia), a detailed description of which is contained in publications [44,51,52,66–68]. Controlled Accelerated Arc (CAA-PVD) technology was used [50,69,70]. This technology allows for a reduction in the number of microparticles while maintaining high efficiency of the deposition process and reducing energy costs.

Zr (99.98%) and Ti (99.99%) cathodes, as well as Zr-Nb (50%:50%) and Zr-Hf (50%:50%) alloy cathodes, were used. Samples of titanium alloy Ti-6Al-4V in the form of cylinders with a diameter of 30 mm and a thickness of 4 mm were manufactured in-house by the university.

Before depositing the coating, special preparation of the samples was carried out, as follows:

- Washing in a specially selected alkaline detergent at a temperature of 80 °C with ultrasonic stimulation;
- Rinsing in purified running water (prepassed through a special filter—a fine-mesh membrane and activated carbon);
- Drying in a stream of hot purified air (passed through a special filter).

Before the deposition of the main coating layer, an adhesion layer was deposited (in an argon atmosphere; the deposition time was 5 min, the thickness was 30–70 nm), consisting of pure metal or a mixture of metals: Zr for coatings ZrN and (Zr,Ti)N; Zr,Hf for (Ti,Zr,Hf)N; and Zr,Nb for (Ti,Zr,Nb)N.

During the coating deposition process, the arc current of the titanium cathode was 75 A, and of the zirconium cathode, 80 A. The arc current of the Zr-Nb (50%:50%) cathode was 85 A, and of the Zr-Hf (50%:50%) cathode, 90 A. The differences in the arc current for each material were due to the available experience and a large volume of research (conducted since the 1990s) that determined the optimal arc current for each material [71–75]. If the arc current is too high, the formation of the microparticle phase is activated, while if it

is too low, the plasma flow density decreases and the coating defectiveness increases. This study uses metals with significant differences in such parameters as atomic weight, melting/evaporation temperature and electronegativity (e.g., zirconium and hafnium). Accordingly, for efficient arc burning and the formation of a dense plasma flow with a low microparticle content, there is an optimal arc current for each cathode composition, which we used. At the same time, I completely agree with the reviewer that a change in arc current can affect the coating structure and residual stresses.

At an arc current of 75 A, the Zr-Hf cathode (50%:50%) burns very poorly and the arc constantly breaks down, and for titanium and zirconium cathodes, an arc current of 90 A leads to a sharp increase in the microparticle phase. Thus, with a unified arc current, it is impossible to obtain high-quality coatings from cathodes of different compositions. To form a tungsten-based coating, the arc current of a tungsten cathode can reach 200 A (an additional row of transformers must be connected), though a titanium cathode will simply explode at such a current.

Other parameters were the same for all processes: the nitrogen pressure was 0.42 Pa, the substrate supply voltage was 150 V, and the rotation speed of the turntable was 0.7 rpm.

Immediately before the test, as well as before measuring or weighing, the samples were cleaned and dried. Non-film-forming and chlorine-free cleaning agents and solvents were used to prepare the samples.

The surface morphology and structure of the samples were studied using a scanning electron microscope (SEM) EVO 50 (Carl Zeiss, Jena, Germany) with an EDX X-Max—80 mm<sup>2</sup> system (OXFORD Instruments, Abingdon, UK) and a transmission electron microscope (TEM) TEM JEM 2100 (JEOL, Tokyo, Japan). The elemental composition was studied using TEM with EDX INCA Energy (OXFORD Instruments, Abingdon, UK). Samples for TEM were prepared using a focused ion beam (FIB) on a Strata 205 device (FEI, Hillsboro, OR, USA).

Hardness and elastic modulus were measured on an SV-500 nanotester (Nanovea, Irvine, CA, USA) using a Berkovich indenter, and the maximum load was 20 mN. Twenty measurements were taken based on the results of which the average value was determined.

Wear resistance was studied in accordance with the ASTM regulations "Standard Test Method for Wear Testing with a Pin-on-Disk Apparatus" [76]. A spherical indenter with a diameter of 6 mm made of aluminum oxide at a load of 10 N and a rotation speed of 100 rpm (Figure 1) was used. The duration of the test was 1 h. An  $Al_2O_3$  indenter was used to simulate the contact between the ceramics and coated titanium alloy, with a track diameter of 20–23 mm.



**Figure 1.** Scheme of the study of wear resistance of samples: 1—wear groove, 2—indenter, 3—rotating disk (sample).

To study the corrosion behavior of ZrTiN, ZrN, (Ti,Zr,Nb)N and (Ti,Zr,Hf)N coatings on the surface of titanium alloy Ti-6Al-4V in solutions, polarization studies were carried out via the cyclic voltammetry method (potential scan rate 1 mV/s) with electrode polarization of  $\pm 800$  mV using an AUTOLAB PGSTAT302 N potentiostat-galvanostat (Utrecht, The Netherlands) in 3.5 wt.% NaCl (which corresponds to the average salinity of seawater), using a standardized YSE-2 electrochemical cell with three electrodes, a graphite additional electrode and a saturated silver chloride reference electrode at a temperature of 40 °C. This was required by the ASTM G48 corrosion test [59]. The area of the working electrode was 1 cm<sup>2</sup>.

All potential values measured relative to the saturated silver chloride reference electrode were converted to the standard hydrogen electrode scale [58]. Corrosion currents were calculated using the functions of mathematical modeling of the corrosion process in the Nova 2.0 program using the polarization resistance method based on processing experimentally obtained data at low polarizations ( $\eta = \pm 20$  mV) [60]. This method is based on

$$\eta \approx \frac{RT}{nF} \frac{i}{i_0} = R_0 i \tag{1}$$

where  $R_0 = \frac{RT}{i_0 nF}$  is the resistance to charge transfer, which is measured in ohms ( $\Omega$ ) [60].

We limited ourselves to only the polarization resistance method based on experimental data at low polarizations because the method of the extrapolation of cathodic and anodic curves (Tafel method) does not allow us to correctly determine the corrosion currents for these samples [60].

#### 3. Results and Discussion

This study of the coatings showed that the (Ti,Zr,Nb)N coating had the maximum microhardness and the (Zr,Ti)N coating had the minimum. The spread of values was  $\pm$  HV 152 ... 210 (Figure 2a). The elemental composition of the coatings was investigated (see Figure 2b).



Figure 2. Hardness (a) and elemental composition of the studied coatings (b).

Wear resistance studies have shown that all coatings provided some increase in wear resistance of the samples (Figure 3a). The best wear resistance was demonstrated by the sample with the (Ti,Zr,Nb)N coating, and the highest wear intensity was observed in the sample with the (Ti,Zr,Hf)N coating. The samples with the ZrN and (Zr,Ti)N coatings had average wear resistance among the samples with the coatings under consideration, which was practically identical for these two coatings. The wear value of the Al<sub>2</sub>O<sub>3</sub> indenter (ball) was insignificant and incomparable with the wear of the titanium alloy samples.



(**d**)

**Figure 3.** Results of the study of wear resistance of samples in contact with an Al<sub>2</sub>O<sub>3</sub> indenter. (a) Wear rate of coated and uncoated samples, (b) average wear rate based on five measurements, (c) mass loss by the indenter, (d) coefficient of friction (COF) of samples.

The average wear rate was determined based on the results of five measurements (Figure 3b).

Measurements of the indenter mass after testing show that the indenter wear was significantly lower than the wear of all coated samples (Figure 3c). The maximum level of mass loss was observed when testing a sample without a coating and with a (Ti,Zr,Hf)N coating, and the lowest was for a sample with a (Zr,Nb,Ti)N coating, which also had the greatest hardness.

The study of the friction coefficient (FC) of the samples showed that all the coatings under study provided a noticeable reduction in FC (Figure 3d). The lowest FC value was provided by the ZrN coating. A noticeable reduction in FC was also provided by the (Zr,Nb,Ti)N and (Ti,Zr,Hf)N coatings.

Of significant interest is not only the resulting value of wear resistance, but also the nature of the destruction of the coatings.

#### 3.1. Wear Pattern of Samples after Pin-on-Disk Test

Let us take a closer look at the wear pattern of samples with coatings after the pin-ondisk test. To conduct this, we first examined the boundaries of the wear area using SEM, and then carried out more in-depth studies using TEM.

#### 3.2. ZrN Coating

In the ZrN-coated sample, along the edges of the wear area, the formation of a sequence of cracks (Figure 4a,b) was observed.

A study of the transverse section of the boundary of the worn area (Figure 4c) showed that in this area the adhesive bond of the coating was maintained, even in places of noticeable plastic deformation of the substrate. During the wear process, the coating was destroyed and its fragments were pressed into the substrate material. A study of the nature of crack formation in the coating (region A in Figure 4c, discussed in more detail in Figure 4d) showed that, upon reaching a more plastic substrate, the crack branched and faded. This mechanism of crack attenuation during the transition from a harder to a more plastic layer was considered earlier in [44,52]. Since the ZrN coating did not have a nanolayer structure, crack development in it occurred along the boundaries of columnar grains.



Figure 4. Cont.







**Figure 4.** Study of the features of destruction of the ZrN coating (pin-on-disk test): boundary of the destruction area (**a**), formation of cracks in the coating (**b**), transverse section of the boundary of the worn area (**c**), crack in the coating structure (**d**).

#### 3.3. Coating (Zr,Ti)N

Despite the fact that the sample with the (Zr,Ti)N coating showed wear resistance almost identical to the sample with the ZrN coating, the nature of their destruction had certain differences. The (Zr,Ti)N coating also exhibited minor delamination from the substrate at the wear zone boundary (Figure 5a). At the same time, the sample with the (Zr,Ti)N coating exhibited slightly less active crack formation. Since the (Zr,Ti)N coating had a nanolayer structure with alternating dominance of the ZrN and TiN phases, the nature of the destruction of this coating had certain features. Along with the defoliation of the coating and the substrate (adhesive failure), delamination between the coating nanolayers also occurred (cohesive failure) (Figure 5a). In turn, studying the interface between the coating and the substrate showed that defoliation occurred due to the formation of a longitudinal crack in the outer layer of the substrate, which differed in structure from the deeper layers (Figure 5b). Analysis of the elemental composition (Figure 5c) showed the presence of oxygen, which may indicate that this layer was the remains of an incompletely removed oxide outer layer of the titanium substrate. It can be seen (Figure 5b) that there was both delamination of this layer and the adhesive sublayer of the coating as well as delamination from the substrate. Thus, the presence of residual oxide layer reduced the adhesion strength of the coating and the substrate.

Analysis of the change in element content in the coating (Figure 5c) showed that interdiffusion of zirconium and vanadium and, obviously, titanium, took place (determining the diffusion of titanium is complicated due to the fact that titanium was contained in both the substrate and the coating). Given that the coating had a nanolayer structure, its destruction may be like the destruction of the ZrN coating with a monolithic structure discussed above. Through transverse cracks were formed, the development of which was little determined by the structure of the nanolayers (Figure 5d). This development of cracks was associated with similar characteristics of ZrN and TiN. As noted earlier [44,51], the nanolayer structure of the coating can inhibit crack development only in the case of alternating harder and more plastic nanolayers. The pressing of fragments of the destroyed coating into the substrate material was also observed (Figure 5d). The presence of such hard coating fragments may have had some effect on further wear of the substrate.





**Figure 5.** Study of the features of destruction of the (Zr,Ti)N coating (pin-on-disk test): zones of cohesive and adhesive failure (**a**), nature of defoliation in the area of the coating–substrate interface (**b**), distribution of elements in the worn coating (**c**), pressing of destroyed fragments of the coating into the substrate material (**d**).

# 3.4. Coating (Ti,Zr,Hf)N

The destruction of the (Ti,Zr,Hf)N coating was associated with moderate defoliation from the substrate combined with some cracking (Figure 6a,b). Unlike the (Zr,Hf)N coating, which had a similar Zr,Hf adhesion sublayer, the adhesion of the (Ti,Zr,Hf)N coating and the substrate was quite good. Areas of extensive defoliation characteristic of the (Zr,Hf)N coating were not observed. This fact may indicate that for good adhesion to the substrate, not only are the properties of the adhesive sublayer important, but also the combination of the properties of this sublayer and the coating. A more detailed study of the coating failure boundary showed that between the substrate and the Zr,Hf adhesive sublayer, there was a substrate layer with a different structure (Figure 6c). The structure of this layer looked less dense and it was in this structure that longitudinal cracks developed, ultimately leading to defoliation of the coating and substrate (Figure 6c,e). Therefore, the surface oxide layer of the substrate must be completely removed, otherwise it will have a negative impact on the adhesion strength of the coating and the substrate. The presence of a residual oxide layer and, accordingly, an identical mechanism of defoliation of the coating and substrate was previously observed for the (Zr,Ti)N coating. A distinctive feature of the wear of the (Ti,Zr,Hf)N coating was the formation of a fairly smooth inclined wear boundary (Figure 6c,d). In this case, the nanolayer structure of the coating affected the shape of this boundary. In some places, this boundary had a stepped shape, considering the interfaces between the nanolayers. Analysis of the phase composition of the wear boundary region showed the presence of two initial phases—(Ti,Zr,Hf)N (TiN-based solid solution) and (Zr,Ti,Hf)N (ZrN-based solid solution) (Figure 6f).

### 3.5. Coating (Ti,Zr,Nb)N

The (Ti,Zr,Nb)N coating had fairly good adhesion to the substrate (Figure 7). No noticeable delamination zones were observed at the coating destruction boundary. Microchipping of the coating along the wear boundary was observed. Apparently, in this case, microchipping is the key mechanism of coating destruction.





(a)

Figure 6. Cont.

(b)



**Figure 6.** Study of the features of destruction of the (Ti,Zr,Hf)N coating (pin-on-disk test): general view of the boundary of the destruction area (**a**,**b**), transverse section of the wear zone boundary area (**c**), wear boundary and nanolayer structure of the coating (**d**), formation of a longitudinal crack in the structure of the adhesive sublayer (**e**), results of SAED analysis of the coating failure boundary (**f**).

With a more detailed (using TEM) study of the nature of destruction of the (Zr,Nb,Ti)N coating, one can see the formation of extensive delaminations between the nanolayers of the coating (Figure 8). Directly near the fracture boundary (right side of the image in Figure 8a) there was a slight defoliation of the adhesive sublayer from the substrate. At the same time, directly at the fracture boundary, despite noticeable plastic deformation and bending of the coating, the adhesive bond with the substrate was fully preserved. There was a diffusion of coating elements into the substrate to a depth of up to 300 nm (Figure 8b). Diffusion of



vanadium into the coating was also observed. Since titanium was simultaneously part of the coating and the substrate, it was impossible to draw a conclusion about its diffusion.

**Figure 7.** Study of the features of destruction of the (Zr,Nb,Ti)N coating during the pin-on-disk test: microchipping of the coating (**a**,**b**).

Let us consider the effectiveness of using adhesive sublayers of various compositions. Theoretically, the use of an adhesive sublayer of Zr,Hf when depositing coatings on titanium alloys may be appropriate based on the following premises. Hafnium, like zirconium, increases the thermal stability of the titanium alloy structure, increases the creep strength, strength at low and medium temperatures and improves the weldability of titanium-based alloys [77–80], respectively, and it can increase the diffusion strength between the coating and the titanium substrate. In liquid and solid states, hafnium and titanium form continuous series of solid solutions. In addition, hafnium with zirconium is a neutral hardener of titanium-based solid solution, acting according to the mechanism of solid solution hardening. Moreover, in this series of experiments, the Zr,Hf sublayer did not provide enough adhesion of the coating to the substrate. It is worth noting that defoliation between the coating and the substrate in these cases was not associated with the loss of adhesion between the Zr,Hf sublayer or the wort layer with residual oxides.

The Zr sublayer provided the average adhesion strength of the studied samples. In the scratch test, low adhesion to the substrate was observed, but in the pin-on-disk test, adhesion was slightly better, especially for the ZrN coating.

The best adhesion was provided by the Zr,Nb sublayer. Alloys of the Zr–Nb system have high fatigue endurance and their elastic modulus is in the range of 58–90 GPa, depending on the initial structural-phase state and impurity content [81–84]. In a (Zr,Nb)N coating, adhesion failure occurs predominantly between the Zr,Nb adhesive sublayer and the coating, while the adhesive sublayer itself shows very good adhesion to the substrate. However, in the (Ti,Zr,Nb)N coating, detachment of Zr,Nb from the substrate was observed while maintaining adhesion to the coating. Thus, the strength of the adhesive bond with the substrate was affected not only by the composition of the sublayer, but also by the composition and structure of the coating. Defoliation occurred at the interface that was weakest in terms of adhesion (with the substrate or with the coating).



**Figure 8.** Study of the features of destruction of the (Zr,Nb,Ti)N coating during the pin-on-disk test: delamination between coating nanolayers (**a**), defoliation of the adhesive sublayer, analysis of changes in the content of elements in the area of coating destruction (**b**).

# 3.6. Corrosion in 3.5 wt.% NaCl Solution at 40 $^\circ\mathrm{C}$

The tendency of (Ti,Zr)N, ZrN, (Ti,Zr,Nb)N and (Ti,Zr,Hf)N coatings on the surface of titanium alloy Ti-6Al-4V to corrosion was estimated using the nature of the polarization curves in 3.5% NaCl at 40 °C (Figure 9).



**Figure 9.** Potentiodynamic curves of the studied coatings (Ti,Zr)N, ZrN, (Ti,Zr,Nb)N and (Ti,Zr,Hf)N on the surface of Ti-6Al-4V alloy in 3.5% NaCl at 40  $^{\circ}$ C (Vp = 1 mV/s).

The open circuit potential (OCP) after 60 min exposure in 3.5% NaCl at 40 °C indicated that the coatings did not have any possible defects in the structure. The maximum OCP value was observed for the uncoated sample, which was associated with the onset of the oxidation process of the titanium and vanadium components in the uncoated alloy. The OCP value for (Ti,Zr,Nb)N coatings indicated the oxidation of niobium as observed in [58,60,85].

For the anodic polarization curve of the Ti-6Al-4V alloy, a passivation region was observed in the potential range of +0.3 ... +0.8 V, which is consistent with the previously studied behavior of Ti-6Al-4V in 3.0% NaCl at 25 °C [60]. It should be noted that the corrosion potential for the Ti-6Al-4V alloy was +0.268 V, which was significantly more positive than the corrosion potentials of samples with (Ti,Zr)N, ZrN and (Ti,Zr,Hf)N coatings (Table 1). The most probable reason for such a shift was the self-passivation of the titanium component of the alloy upon contact with a 3.5% NaCl solution. However, the titanium oxide coating formed during titanium passivation did not have a high electrical resistance of 0.41 MOhm and did not adequately protect the alloy from corrosion dissolution. The corrosion currents of the uncoated sample did not exceed 63.6 nA/cm<sup>2</sup>.

**Table 1.** The value of the open circuit potential (OCP) after 60 min of exposure in 3.5% NaCl at 40 °C and results of the calculation of the corrosion process in the Nova 2.0 program using the method of determining the polarization resistance in the corrosion potential region in 3.5% NaCl at 40 °C.

	Coating	E <sub>OCP</sub> , V	E <sub>cor</sub> , V	<b>Polarization Resistance Method</b>		
				i <sub>cor</sub> , nA/cm <sup>2</sup>	P, μm/year	Ro, MOhm
1	ZrN	+0.199	+0.099	7.9	0.070	3.299
2	TiZrN	+0.296	+0.060	62.1	0.548	0.420
3	TiZrHfN	+0.238	+0.083	8.7	0.077	2.986
4	TiZrNbN	+0.319	+0.281	248.9	2.195	0.105
5	Uncoated	+0.357	+0.268	63.6	0.561	0.410

Despite the fact that the corrosion potential for (Ti,Zr)N, ZrN and (Ti,Zr,Hf)N coatings was shifted to the negative region relative to the corrosion potential of the Ti-6Al-4V alloy,

the corrosion current density for these nitride coatings was lower in comparison with the corrosion current density of the Ti-6Al-4V alloy.

Thus, on the anodic branch of the polarization curve for the (Ti,Zr)N coating in 3.5% NaCl after the dissolution region, a passivation plateau in the range of +0.08 ... +0.12 V was observed, which was also due to the oxidation of titanium with the formation of oxide layers on the surface. The corrosion currents for the sample with the (Ti,Zr)N coating were comparable with the corrosion currents of the Ti-6Al-4V alloy itself in 3.5% NaCl at 40 °C and did not exceed 62.1 nA/cm<sup>2</sup> (see Table 1).

At the same time, the introduction of hafnium into the (Ti,Zr)N system allowed for significant suppression of corrosion in 3.5% NaCl at 40 °C and reduced corrosion currents to 8.7 nA/cm<sup>2</sup>. In this case, the formation of a dense film of oxynitrides and oxides of zirconium [49,50] and hafnium with a polarization resistance of 2.986 MOhm was observed.

It should be noted that the use of ZrN coating also allowed for a significant reduction of the corrosion currents in 3.5% NaCl at 40 °C to 7.9 nA/cm<sup>2</sup>, which was explained via the formation of a more homogeneous oxide film of zirconium oxide during primary oxidation. The value of polarization resistance for the Ti-6Al-4V sample with ZrN coating was 3.299 MOhm in 3.5% NaCl at 40 °C (Figure 10), which is consistent with previously obtained data [58,60].



**Figure 10.** Combined diagram of polarization resistance values for (Ti,Zr)N, ZrN, (Ti,Zr,Nb)N and (Ti,Zr,Hf)N coatings on the surface of Ti-6Al-4V alloy in 3.5% NaCl at 40 °C.

When analyzing the diagram (Figure 10), it should be noted that the polarization resistance for the sample with the (Ti,Zr,Nb)N coating was low, amounting to 0.105 MOhm, and the corrosion currents were 248.9 nA/cm<sup>2</sup> (see Table 1). At the same time, for the (Ti,Zr,Nb)N coating, a shift in the corrosion potential to a more electropositive region was observed in comparison with pure Ti-6Al-4V, which was probably due to the oxidation of niobium to soluble oxo ions, which promote further corrosion [58,60].

Thus, ZrN, (Ti,Zr,Hf)N coatings, allowed for the reduction of the corrosion currents of Ti-6Al-4V alloy by 7–8 times to 7.9–8.7 nA/cm<sup>2</sup> in 3.5% NaCl at 40 °C, which was due to the formation of a dense film of nonstoichiometric zirconium and/or hafnium oxychloride and oxide with a polarization resistance of 2.986–3.299 MOhm.

# 4. Conclusions

1. After 3900 s (65 min) of the pin-on-disk test, the best wear resistance was observed for the sample with the (Zr,Nb,Ti)N coating, and the worst among the coated samples

was for (Zr,Ti,Hf)N. Samples with ZrN and (Zr,Ti)N coatings showed identical wear resistance. At the same time, all coated samples showed much (2.5–3.3 times) better wear resistance compared with the uncoated sample.

- 2. Of significant importance is not only the strength of the adhesion of the sublayer to the substrate and coating, but also the strength of the adhesive sublayer itself. The boundary of defoliation of the coating from the substrate often passed inside the adhesive sublayer itself, i.e., defoliation occurred not because of poor adhesion to the substrate but due to insufficient strength of the adhesive sublayer. Peeling of the coating from the substrate can also occur due to destruction in the structure of the intermetallic layer (e.g., Zr, Ti, Hf), which can form during the deposition of the adhesive sublayer on the thermally activated surface of the substrate.
- 3. The surface oxide layer of the titanium substrate must be completely removed, otherwise it will have a negative impact on the adhesion strength of the coating and the substrate.
- 4. The strength of the adhesive bond with the substrate was affected not only by the composition of the adhesive sublayer, but also by the composition and structure of the coating. Delamination occurred at the weakest interface from the point of view of adhesion (with the substrate or with the coating).
- 5. It was found that the Ti-6Al-4V alloy samples with ZrN and (Ti,Zr,Hf)N coatings had the highest corrosion resistance in a 3.5% NaCl solution at 40 °C, with a corrosion current density of 7.9 and 8.7 nA/cm<sup>2</sup>, respectively. This was due to the formation of a dense film of nonstoichiometric zirconium and/or hafnium oxychloride and oxide with a polarization resistance of 2.986–3.299 MOhm.
- 6. The introduction of niobium into the (Ti,Zr)N system significantly reduced the corrosion resistance of the Ti-6Al-4V alloy itself in a 3.5% NaCl solution at 40 °C, increasing the corrosion currents from 62.1 nA/cm<sup>2</sup> (Ti,Zr)N to 248.9 nA/cm<sup>2</sup>, which was also significantly greater than the corrosion current of Ti-6Al-4V equal to 63.6 nA/cm<sup>2</sup>. This phenomenon was probably due to the oxidation of niobium to soluble oxo ions, which promote further corrosion.

Thus, the (Zr,Nb,Ti)N coating had better pin-on-disk fracture resistance, but low corrosion resistance. The (Ti,Zr,Hf)N coating, on the contrary, had better corrosion resistance, but low fracture resistance. The ZrN coating had good corrosion resistance combined with good pin-on-disk fracture resistance. This coating is best suited for use in friction with a ceramic counterbody under seawater conditions.

An important resource for increasing the performance properties of coatings was in-creasing their adhesion to the substrate, which can be achieved in two combined ways:

- Complete removal of the original oxide layer from the surface of the substrate;
- Use of optimal compositions of the adhesive sublayer, which have not only high adhesive properties in relation to both the substrate and the coating, but also high strength.

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