



Article

Wear Resistance and Failure Mode of Coatings Based on the ZrN System with the Introduction of Ti, Nb, and Hf Deposited on a Titanium Alloy Substrate

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Abstract: The article presents the results of a comparison of the wear resistance of coatings with a two-layer architecture (adhesion layer-wear-resistant layer) of Zr-ZrN, Zr-(Zr,Ti)N, Zr,Hf-(Zr,Hf)N, Zr,Nb-(Zr,Nb)N, Zr,Hf-(Ti,Zr,Hf)N, and Zr,Nb-(Ti,Zr,Nb)N coatings, deposited on a titanium alloy substrate. The wear resistance was studied using two different counterbodies: Al_2O_3 and steel. When in contact with the Al_2O_3 counterbodies, the best wear resistance was demonstrated by samples with Zr,Hf-(Zr,Hf)N and Zr,Nb-(Zr,Nb,Ti)N coatings. In tests conducted in contact with the steel counterbody, the best resistance was demonstrated by samples with Zr-ZrN and Zr,Hf-(Ti,Zr,Hf)N coatings. The wear resistance of samples with (Zr,Hf)N and (Zr,Nb,Ti)N coatings was 2.5-3.3 times higher than that of the uncoated sample. The Zr,Nb adhesion layer ensures better adhesion of the coating to the substrate. It was found that not only the adhesion strength of the adhesion layer to the substrate and coating is of significant importance but also the strength of the adhesion layer itself. The surface film of titanium oxide must be completely etched off to ensure maximum strength of the adhesive bond between the coating and the substrate. It has been established that the adhesion of the coating and the titanium substrate is also affected by the characteristics of the outer (wear-resistant) coating layer, which is the composition and structure of the wear-resistant coating layer. Delamination can occur both at the boundary of the adhesive layer with the substrate and at the boundary of the wear-resistant and adhesive layers of the coating depending on the strength of the adhesive bonds in the corresponding pair. It is necessary to ensure a good combination of properties both in the substrate-adhesion layer system and in the adhesion layer-wear-resistant layer system.

Keywords: wear resistance; titanium alloy; coatings; pin-on-disk test; adhesion



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1. Introduction

Titanium alloy parts are widely used in various fields of life [1-3]. Possessing high strength with relatively low specific gravity, this material also provides effective corrosion resistance due to the dense protective oxide film formed on its surface. Titanium alloy products often function as parts of various tribological pairs, which causes their mechanical wear. Being a fairly soft material, titanium, under such conditions, resists wear quite poorly (compared, for example, to ceramics). At the same time, in a number of cases, there is a technological need to use titanium parts in contact with counterbodies that are both identical in hardness (for example, titanium and other metals) and harder (for example, ceramics) [4–10]. When the tribological pair "titanium alloy-ceramics" functions, the high wear rate of the titanium component becomes a significant problem. One of the effective ways to increase the wear resistance of parts made of various materials is the deposition of wear-resistant coatings on their working surfaces [11–13]. Due to their high (20 GPa and more) hardness, nitride coatings provide a significant increase in wear resistance. When depositing nitride coatings on a titanium alloy substrate, a significant problem is ensuring a strong adhesive bond between them. It was found that even with the same scratch test groove depth on a steel and titanium substrate with a coating (deposited by magnetron sputter), more intense destruction of the coating is observed on the titanium substrate [4]. Elastic recovery is more important for titanium alloys than for steel [4,14,15]. Due to the deformations that occur in the titanium substrate during the scratch test, significant shear forces arise at the boundary of the coating and the substrate. It is worth considering the fact that without taking into account fatigue and interphase properties, even extremely hard coatings will not necessarily be effective and reliable [16]. Thus, for coatings deposited on titanium alloy products, adhesion to the substrate is of particular importance. There are a number of methods that can increase the strength of the adhesive bond. In particular, to improve the adhesion of the coating, it is proposed to increase the roughness of the substrate [17]. For this purpose, ion beam etching (IBE) [18] and laser micromachining [16,19–21] are used. Good adhesion, in this case, is achieved by matching the chemical properties of the coating and the substrate and increasing the area of the active surface of the substrate. At the same time, it has been shown that a decrease in the roughness of the substrate surface increases the adhesion of the coating by reducing the number of surface defects [22]. With a decrease in roughness from Ra = 1.348 to Ra = 0.037, the L_{C2} value of the Ti-TiN-Zr-ZrN coating increased from 31 to 58 N [23]. Thus, the roughness of the substrate surface can both improve and worsen adhesion depending on a number of factors [24]. There is a correlation between the coating adhesion and the substrate hardness [25]. Harder substrates provide a better level of adhesion to the coating. It has been established that for Zr or ZrN coatings, the adhesion between the coating and the substrate increases linearly with increasing substrate hardness [26]. At the same time, softer and more plastic phases of the substrate allow for an increase in the resistance to cohesive failure due to plastic deformation and the formation of a disordered atomic layer that absorbs the deformation energy of the coating [25]. Thus, not only is the substrate hardness important, but the combination of the properties of the coating and the substrate is also important. To ensure a balance of these properties, duplex processing methods are used, which allow modifying the structure and properties of the surface layers of the substrate before coating deposition [27,28]. Such a modification is possible both as a separate technological operation and as part of the general process of coating deposition. The ion implantation of Ti, Cr, and N into the surface layers of the substrate allows for an increase in the hardness of these layers and the adhesion of the deposited coating [29]. Preliminary plasma nitriding is also effective [30]. Both of these processes can be carried out in one technological cycle with the deposition of coatings, which is their undoubted advantage.

Another approach (including one that complements those described above) to improve adhesion involves introducing an intermediate adhesive layer between the coating and the substrate [31-35]. Depending on the substrate material and the coating composition, the following metal components were used as the adhesion layer: Ti [31,36–38], Zr [39–44], Cr [45–47], Mo [46,48,49], and Al [50]. Comparisons were also made of various adhesion layer materials: Nb, Cr, and Ta [51] and W, Mo, Nb, Cr, Ti, Ag, and Al [34]. Intermetallic compounds were also considered—Fe₂Ti [36], ZrHf [52,53], and CrMo [54]. Of the materials considered, the best indicators for increasing adhesion were shown by Ti, Nb, Zr, and Cr. The high Zr content in the three-component coatings allows for increased wear resistance. With an increase in the Zr content in the CrN/ZrN coating from 50 to 71 at%, the wear resistance of the coating increased significantly [55]. The arc-PVD ZrN coating deposited on a titanium alloy substrate did not have very high adhesion (critical failure load L_{C2} = 29.4 N) [56]. The adhesion of ZrN deposited on a titanium alloy was significantly lower than that on a nickel or chromium-molybdenum alloy. When deposited on a Ti-29Nb-13Ta-4.6Zr alloy, the modeled using density functional theory adhesion strength of the coatings (critical point L_{C2}) was 39 MPa for CrN, 37 MPa for TiN, and 29 MPa for ZrN [57]. The introduction of Ti or Zr layers between the TiN and ZrN layers increased the adhesion energy, with Zr layers increasing adhesion more effectively than titanium layers [24,58]. The double glow plasma alloying method was also used to improve adhesion in the Ti-ZrN system [59]. In this case, a transition layer was formed between the ZrN and Ti layers, which contained both metallic and ceramic phases. By varying the deposition parameters, it was possible to ensure sufficiently good adhesion of PVD-deposited ZrN on a titanium alloy substrate [60]. Metallic sublayers of the PVD coatings prevented crack propagation and increased the critical failure load [61]. Close values between the residual stresses of the substrate before deposition and the deposited coating led to good adhesion. Differences in hardness between the materials of the adhesion sublayer, coating, and substrate had a greater effect on adhesion than differences in the modulus of elasticity [34]. Bias voltage also had a significant effect on the adhesion strength of the ZrN coating, with the optimal value of this parameter depending on the properties of the substrate [62].

This paper presents the results of a comparison of the properties of ZrN, (Zr,Ti)N, (Zr,Hf)N, (Ti,Zr,Hf)N, (Zr,Nb)N, and (Ti,Zr,Nb)N coatings deposited on the Ti-6Al-4V titanium alloy substrate. These coatings have adhesion layers of Zr, Zr,Hf, and Zr,Nb, respectively. The pin-on-disk test will be conducted using two different counterfaces: Al₂O₃ and 52100 bearing steel. The ceramic counterbody (Al₂O₃) simulates the contact conditions in the titanium–ceramic pair, which simulates the operating conditions of some groups of products (e.g., shut-off valves in pipelines) under conditions when one of the elements of the tribological pair has a hardness significantly exceeding the hardness of the second element. The metal counterbody (52100 bearing steel) simulates contact in a metal-to-metal pair when two elements of the tribological pair have close hardness values. Thus, the studies will allow not only the determination of the wear resistance of titanium alloy samples with coatings of different compositions but also the study of the effect of the material and properties of the counterbody (indenter) on the wear pattern of samples with coatings. Particular attention will be paid to the disruption or preservation of strong adhesive bonds between the coating and the substrate during the tests.

2. Materials and Methods

A specialized physical vapor deposition (PVD) unit VIT-2 (IDTI RAS—MSUT STANKIN, Moscow, Russia) was used for coating deposition [39,40,46,52,53]. Controlled Accelerated Arc (CAA-PVD) evaporators were used [54,63]. Zr (99.98%), Ti (99.99%) cath-

odes, as well as cathodes made of Zr-Nb (50:50%) and Zr-Hf (50:50%) alloys, were installed in the CAA-PVD evaporators.

The samples were disks made of titanium alloy Ti-6Al-4V. The deposition surfaces of the coatings were ground, and the surface roughness after grinding was Ra 0.53–0.36.

- Before the deposition of the coatings, the samples were prepared in a special way:
- Washing in a special water solution (NaOH 15 g/L, sodium carbonate 15 g/L, aqueous alkaline solution of sodium silicates Na₂O(SiO₂)_n), 3 g/L) at a temperature of 80 °C with ultrasound stimulation,
- Rinsing in purified running water,
- Drying in a stream of hot purified air (temperature is about 100 °C).

The arc current of the titanium cathode was set at 75 A, and for the zirconium cathode, it was -80 A. For the alloy cathodes Zr-Nb (50:50%) and Zr-Hf (50:50%), the arc current was set at 85 and 90 A, respectively. The remaining parameters were the same for all processes: nitrogen pressure of 0.42 Pa, voltage on the substrate of 150 V, and a tool rotation speed of 0.7 rpm. The surface temperature of the samples during coating deposition was 400–430 °C. Ten samples were produced with coatings of identical composition.

The deposited coatings have adhesive layers of Zr, Zr, Hf or Zr, and Nb, with a thickness of 150–200 nm and a total coating thickness of about 3 μ m. In the future, for ease of perception, the coatings will be designated only by the composition of the wear-resistant nitride layer.

The ASTM standard was used to test the wear resistance "Standard Test Method for Wear Testing with a Pin-on-Disk Apparatus" [64,65]. The indenter was spherical in shape with a diameter of 6 mm, a load of 10 N, and a rotation speed of 100 rpm.

Two counterbodies were used:

- Al₂O₃ ball, which has high hardness and low plasticity. The diffusion and chemical interaction of samples with this counterbody is predictably low or absent.
- AISI 52100 bearing steel ball (ASTM A295 [66]). This material is more plastic and is close to Ti-6Al-4V in a number of mechanical properties (see Table 1). An active interdiffusion interaction is possible upon contact with this indenter.

	Strength			14 11 0	T 1 67 1		
	Tensile Yield Strength σ_B	$\begin{array}{l} \text{Compressive} \\ \text{Strength } \sigma_{\text{C}} \end{array}$	Bending Yield Strength σ_f	$\sigma_{\rm T}$	$\frac{\delta_5}{\delta_5}$	Fracture Toughness K _{Ic}	Hardness HB
	MPa	MPa	MPa	MPa	%	MPa m ^{1/2}	MIIa
AISI 52100	590-730	600–750	395	370–410	20	15–18	179–433
Ti-6Al-4V	835-1050	885	300	75–105	6–10	84–107	293–361
Al ₂ O ₃	255-260	2550-3100	282-470	1500	-	3–5	1620-2000

Table 1. Properties of the indenter materials (Al₂O₃ and AISI 52100 bearing steel) and the Ti-6Al-4V titanium alloy substrate (adapted from [67–73]).

The test duration was 3800 s upon contact with the Al_2O_3 indenter and 16,700 s upon contact with the AISI 52100 bearing steel indenter.

A comparison of the properties of the materials of both indenters and the titanium substrate material is presented in Table 1. The properties of the Ti-6Al-4V substrate are much closer to those of AISI 52100 bearing steel than to Al_2O_3 . In terms of hardness (and presumably wear resistance), Ti-6Al-4V and AISI 52100 are identical. However, the hardness (and wear resistance) of Al_2O_3 is significantly higher.

A scanning electron microscope (SEM) Quanta 600 FEG (Materials & Structural Analysis Division, Hillsboro, OR, USA), equipped with an EDX system X-Max (OXFORD Instruments, Abingdon, Oxfordshire, UK), was used to study the microstructure of the coatings; a transmission electron microscope (TEM) TEM JEM 2100 (JEOL Company, Tokyo, Japan) was used to study the nanostructure of the coatings. TEM with EDX INCA Energy (OXFORD Instruments, Abingdon, Oxfordshire, UK) was used to determine the chemical composition of the coatings. A focused ion beam (FIB) system on a Strata 205 device (FEI, Hillsboro, OR, USA) was used to cut out lamellas. An SV-500 nanoindentometer (Nanovea, Irvine, CA, USA) with a Berkovich indenter installed was used to study the hardness, at a load of 20 mN. Average values were calculated based on the results of 20 measurements.

3. Results

3.1. Subsection

The thickness of the studied coatings is within the range of 2970–3310 nm (Figure 1), which can be considered identical in thickness when taking into account the spread of coating thickness during deposition by the PVD method [74]. When titanium and zirconium are present in the coating composition simultaneously, a clearly expressed nanolayer structure is formed (for coatings (Ti,Zr,Hf)N, (Zr,Ti)N, (Ti,Zr,Nb)N). For coatings based on ZrN (ZrN, (Zr,Nb)N and (Zr,Hf)N), the formation of a nanolayer structure is not observed. In all coatings, a metal adhesion layer with a thickness of 150–220 nm is observed (Figure 1).



Figure 1. Structure and thickness of the coatings under study (left); structure and thickness of the adhesion layer (right) (TEM). (a) ZrN; (b) (Zr,Nb)N; (c) (Zr,Hf)N; (d) (Ti,Zr,Hf)N; (e) (Zr,Ti)N; (f) (Ti,Zr,Nb)N.

3.2. Hardness and Elemental Composition of the Coatings Under Study

The greatest hardness (see Table 2) is possessed by (Zr,Hf)N and (Ti,Zr,Nb)N coatings. ZrN, (Ti,Zr,Hf)N and (Zr,Ti)N coatings also have fairly high hardness. Based on the results obtained, the (Zr,Nb)N coating has the lowest hardness. It is worth noting that the research object is a composite consisting of a very hard and thin coating on a much softer and thicker titanium substrate. In addition, there are irregularities, defects, and microparticles on the surface of the coating. These factors make the object under study very difficult to measure, even using a nanoindentometer. To obtain adequate results, it is necessary to perform many measurements (at least 30), discard obviously unreliable values (for example, those associated with a microparticle), and determine the average value. This explains the rather large measurement error.

Coating	Hardness HV _{0.02}	Elastic Modulus, GPa
ZrN	2993 ± 145	230 ± 15
(Zr,Ti)N	2727 ± 86	210 ± 18
(Zr,Hf)N	3350 ± 120	280 ± 27
(Zr,Nb)N	2336 ± 115	180 ± 30
(Ti,Zr,Hf)N	2860 ± 95	260 ± 25
(Ti,Zr,Nb)N	3110 ± 135	310 ± 31

Table 2. Hardness and elastic modulus.

The average contents of elements in the coating are presented in Table 3. The content of elements is presented without taking into account nitrogen, the content of which is about 50 at%. The nitrogen content in the composition of nitride coatings deposited under similar parameters was previously studied in a number of works and, according to various researchers, was 45.5–51.5 at% [75], 48.7 at% [76], 50 ± 3 at% [77], 48 at% [78], 54 at% [79], 42-47 at% [80], and 49.2-52.1 at% [81]. During planetary rotation, the sample passes through plasma regions with a dominant content of various elements, so the composition of the coating changes gradiently [39,46,52]. In the (Zr,Hf)N coating, a fairly low hafnium content is observed, while in the (Zr,Nb)N coating, the zirconium and niobium contents are almost identical. Given that the Zr-Hf cathode has a composition of 50/50%, the density of zirconium (6.50 g/cm³) is significantly lower than the density of hafnium (13.31 g/cm³), while the density of niobium (8.57 g/cm^3) is comparable to the density of zirconium. The atomic mass of hafnium (178.49 g/mol) is also noticeably higher than that of zirconium (91.22 g/mol) and niobium (92.91 g/mol). Thus, it can be assumed that heavier and dense hafnium particles require more energy to reach the substrate surface compared to zirconium and niobium particles and, thus, the hafnium content in the (Zr,Hf)N coating is noticeably lower than the zirconium content.

Table 3. Content of elements in the coating composition (excluding nitrogen, the content of which is about 50 at. %, the content of all metals is taken as 100 at. %).

Casting	Elements Content, at. %				
Coating -	Zr	Nb	Hf	Ti	
ZrN	100	-	-	-	
(Zr,Ti)N	57.63	-	-	42.37	
(Ti,Zr,Nb)N	14.08	14.39	-	71.53	
(Ti,Zr,Hf)N	42.98	-	13.77	43.25	
(Zr,Nb)N	49.72	50.28	-	-	
(Zr,Hf)N	77.25	-	22.75	-	

An important parameter influencing the coating deposition process is the sputtering rates of the sprayed materials. For the metals used in this series of experiments, the sputtering rates are, respectively, [82–86] Ti—1.1–1.6 mcg/s; Zr—3.7–4.6 mcg/s; Hf—9.3 mcg/s; Nb—1.9 mcg/s. Thus, sputtering rates for Zr are significantly higher than for Ti, which correlates to a sufficient degree with the predominance of zirconium in the composition of the (Zr,Ti)N coating. At the same time, sputtering rates for Hf are significantly higher, and for Nb, they are significantly lower than for Zr. At the same time, in the (Zr,Nb)N coating, there is an almost identical content of Zr and Nb, and in the (Zr,Hf)N coating, there is a dominant content of Zr. Based on the above, it can be concluded that the content of elements in the coating composition is not determined by any one factor but is the result of a process that is affected by a large number of different factors, including process parameters and the configuration of the sample arrangement in the installation chamber. Predicting the composition and properties of the coating, based on the composition of the cathodes and process parameters, is a complex and not fully resolved problem.

The results of the phase (SAED) analysis of the studied coatings show that in the coatings without titanium, one fcc phase of the solid solution based on ZrN is formed. In the coatings with titanium inclusion, two fcc phases of the solid solution are formed—based on ZrN and TiN (Figure 2).



Figure 2. Phase SAED analysis of the studied coatings. (a) ZrN; (b) (Zr,Nb)N; (c) (Zr,Hf)N; (d) (Ti,Zr,Hf)N; (e) (Zr,Ti)N; (f) (Ti,Zr,Nb)N.

3.3. Wear Resistance in Pin-on-Disk Test

The results of the pin-on-disk wear resistance studies of the samples are shown in Figure 3a. It can be seen that in contact with the Al₂O₃ counterbody, the sample with the (Zr,Hf)N coating showed the best wear resistance. Samples with (Zr,Nb,Ti)N coating also demonstrate relatively high wear resistance. The worst wear resistance among the samples with coatings is observed for the sample with the (Zr,Nb)N coating (wear resistance at the level of the sample without coating). The wear resistance of samples with (Zr,Hf)N and (Zr,Nb,Ti)N coatings was 2.5–3.3 times higher than that of the uncoated sample. It is also worth noting the significantly larger spread of values on the wear graph for the uncoated



sample, which may be associated with both a decrease in surface roughness for coated samples and a higher coefficient of friction and adhesion between the uncoated sample and the indenter.

Figure 3. Results of wear resistance study using pin-on-disk technique (**a**) Al_2O_3 , (**b**) 52100 bearing steel. Comparison of tribological properties of samples with and without coatings. (**c**) Al_2O_3 , (**d**) 52100 bearing steel, after 3825 s.

In tests conducted in contact with the 52100 bearing steel counterbody, the best resistance was demonstrated by samples with ZrN and (Ti,Zr,Hf)N coatings (Figure 3b).

Studies of the tribological properties of samples have shown that all coatings under consideration can significantly reduce the friction coefficient (Figure 3c,d). The lowest friction coefficient (about 0.25) is demonstrated by the ZrN-coated sample. The highest value of the friction coefficient for coated samples was shown by a sample with a (Zr,Nb)N coating. Samples with other studied coatings showed similar values of the friction coefficient (0.32–0.42). In this case, the friction coefficient for the uncoated sample is about 0.45.

A comparison of the data on the final mass losses of the samples and the indenter (Figure 4) shows that the Al_2O_3 indenter wears out incomparably less than the samples with all types of coatings and without coatings. In order to compare these values on one diagram, the indenter mass loss was increased by 10 times (this value is close to the measurement accuracy limit of the scale, so a correct comparison of the values is impossible here). Since the parameters of the titanium alloy Ti-6Al-4V and 52100 bearing steel are comparable (see above), their wear rates are also comparable. It is worth considering the difference in geometry between the indenter (ball) and the sample (flat surface). In two cases (for samples with ZrN and (Ti,Zr,Hf)N coatings), the indenter wears out more



intensively than the sample. Thus, by applying a coating, it is possible not only to increase the wear resistance of parts but also to ensure (with the appropriate choice of coating composition) a uniform wear of elements in a tribological pair.

Figure 4. Weight loss of specimens and indenter during wear resistance testing using the pin-on-disk technique (**a**) Al_2O_3 (weight loss of indenter ×10, for clarity of comparison), (**b**) 52100 bearing steel.

3.4. Wear Pattern of Samples

Let us consider in more detail the wear pattern of the coated samples after the pinon-disk test (Figure 5). Upon contact with the Al₂O₃ counterbody, a clearly defined wear groove is formed on all samples (upper row). Upon contact with the 52100 bearing steel counterbody, a continuous wear groove is not formed on the sample with the (Ti,Zr,Hf)N coating; only fragmentary wear of the coating is observed. The wear intensity of the steel indenter, in this case, exceeds the wear intensity of the coated sample itself. For the ZrNcoated sample in a tribo-pair with the 52100 bearing steel indenter, only the destruction of the outer layers of the coating is observed, while its inner layers are preserved. This sample is also characterized by more intense wear of the indenter.



Figure 5. View of wear tracks of samples with the studied coatings.

When analyzing the distribution maps of chemical elements on the surface of the samples (Figure 6), it is obvious that in the area of wear tracks of samples with ZrN and (Ti,Zr,Hf)N coatings, an increased content of iron and oxygen is observed, and the configurations of the areas of content of these elements coincide, which may indicate the formation of iron oxide. The high iron content correlates well with the high wear

intensity of the steel indenter during friction in contact with these samples. At the same time, in these samples, titanium is present in a high concentration in the form of separate islands and coincides with similar areas of a high vanadium concentration (the area with insignificant titanium intensity in the (Ti,Zr,Hf)N coating is associated with the presence of this element in the coating itself, close titanium intensity is observed on the surface of all titanium-containing coatings). Thus, it is obvious that the coating on these samples has been largely preserved. The remaining samples show complete destruction of the coating in the wear track area. There is an area of high Ti/V intensity corresponding to the surface of the uncoated sample.



Figure 6. Mapping the distribution of elements in the wear track area of coated and uncoated samples.

The examination of the surface of the coatings before the tests does not show the presence of oxygen. Oxygen is either absent or present in extremely small quantities, which are inaccessible to detection by the methods used. After the pin-on-disk test, the presence of oxygen in significant quantities is observed only in the wear track area (apparently mainly in titanium and iron oxide compounds). The content of zirconium and oxygen has an opposing character; that is, in areas with a high zirconium content, oxygen is absent or present in extremely small quantities. Based on the mapping data, it is obvious that all coatings prevent oxidation processes in the air atmosphere, and oxidation is characteristic only in areas where the coating is destroyed.

A more detailed study of the wear pattern of the samples that demonstrated the best wear resistance showed the following. When testing with the 52100 bearing steel counterbody, the best wear resistance was demonstrated by samples with (Ti,Zr,Hf)N and ZrN coatings with adhesive layers of Zr,Hf and Zr, respectively. The sample with the (Zr,Hf)N coating with the Zr,Hf adhesive layer demonstrated the best wear resistance when in contact with the Al₂O₃ indenter. For a better understanding of the role of the adhesive layer in the nature of coating failure, let us also consider the (Zr,Nb)N sample with the Zr,Nb adhesive layer.

3.4.1. ZrN Coating

In the pin-on-disk test in contact with the Al_2O_3 indenter, brittle failure of the ZrN coating is observed (Figure 7a,b). Zirconium microparticles continue to maintain contact with the substrate even when the surrounding ZrN coating is destroyed (Figure 7a). Thus, it can be concluded that the adhesive bond between zirconium and titanium alloy is strong enough. Examination of the cross-section of the destruction zone shows that the coating as a whole continues to maintain good contact with the substrate (Figure 7c). Individual fragments of the coating are pressed into the substrate during interaction with the Al_2O_3 indenter. Analysis of the distribution of elements across the coating thickness after the pin-on-disk test (Figure 7d) shows the presence of a titanium alloy adherent on the coating surface; oxygen is present in this adherent (possibly due to titanium oxidation). Titanium diffusion takes place both on the coating surface (from the adherent to a depth of up to 100 nm) and at the substrate–coating boundary (to a depth of up to 250 nm). In the substrate–coating boundary area, oxygen is also present in small quantities, which may indicate the preservation of oxide film fragments in this area.

When a sample with a ZrN coating and a steel indenter come into contact, the indenter wears more actively than the sample wears. The indenter material is actively oxidized, and a layer of AISI 52100 steel adherence with noticeable diffusion of zirconium from the coating composition is formed on the coating surface (Figure 8). Iron diffusion from the indenter into the coating to a depth of 200 nm is observed. Oxygen diffusion to a similar depth is also observed. The coating fully maintains adhesion to the substrate. There is a slight presence of oxygen at the boundary of the coating and the substrate, which may be due to the presence of oxide film fragments.



Figure 7. (**a**,**b**) Destruction of the ZrN coating due to crack formation upon contact with the Al_2O_3 counterbody, (**c**) the coating maintains good adhesion to the substrate, while fragments of the destroyed coating are pressed into the substrate, (**d**) distribution of elements across the coating thickness after the pin-on-disk test.



Figure 8. Contact area of the ZrN-coated sample and the AISI 52100 bearing steel counterbody. (a,b) analysis of the distribution of elements across the coating thickness.

3.4.2. Coating (Zr,Ti,Hf)N

When in contact with the Al₂O₃ indenter, active cracking followed by a brittle fracture is observed in the (Zr,Ti,Hf)N coating. Figure 9c shows a cross-section of the coating fracture area. On the coating surface, a titanium alloy deposit is extruded from the substrate under the action of the indenter. Diffusion of zirconium from the coating into the deposit is observed. At the boundary of the coating and the substrate, a longitudinal crack is observed passing through the Zr,Hf adhesion layer. A study of the elemental composition of this layer shows a fairly noticeable presence of oxygen (Figure 9c,d, areas 9–12). Thus, it can be assumed that, in this case, there is a preserved layer of titanium oxide that was not completely removed during the ion-etching process.





Figure 9. The nature of the destruction of the (Zr,Ti,Hf)N coating upon contact with the Al_2O_3 counterbody (**a**,**b**) defoliation of the coating and substrate and the nature of cracking, (**c**,**d**) change in the content of elements in the area of coating destruction.

When a sample with a (Zr,Ti,Hf)N coating and an AISI 52100 bearing steel indenter are rubbed, the coating is preserved, while active wear of the indenter is observed (Figure 10a,b).

There is active oxidation of the steel in the contact zone with the coating. The interdiffusion of zirconium and titanium from the coating into the indenter material (to a depth of up to 50 nm) and iron from the indenter into the coating (to a depth of up to 200 nm) is



observed (Figure 10c–e). The presence of a high concentration of oxygen in the adherent area indicates the active oxidation of the indenter material (primarily iron).

Figure 10. Cross-section of the wear area of a specimen with a (Zr,Ti,Hf)N coating in contact with an AISI 52100 bearing steel indenter. (**a**) general view of the coating with an adhesion of the indenter material, (**b**) nature of the adhesion of the indenter elements, (**c**–**e**) study of the elemental composition at the boundary of the coating and the adhesion of the indenter material.

3.4.3. Coating (Zr,Hf)N

The nature of the (Zr,Hf)N coating failure differs significantly from the failure of the (Zr,Ti,Hf)N and ZrN coatings. The (Zr,Hf)N coating is characterized by a large area of defoliation from the substrate (Figure 11a). Although cohesive failure (delamination between nanolayers) also occurs along with adhesion failure (Figure 11b), the main failure factor is precisely defoliation from the substrate and a brittle fracture of the coating.

The detachment of the (Zr,Hf)N coating from the substrate occurs not due to the detachment of the coating from the adhesion layer or detachment of the adhesion layer from the substrate but due to a failure in the structure of the Zr,Hf layer itself (see Figure 11d,e). That is, it is this layer that turns out to be the weak link in the substrate–adhesion layer-coating system. When examining the cross-section of the wear zone boundary, it is evident that the coating chipping occurs with the formation of a surface that is almost perpendicular to the substrate surface (Figure 11d). There is a brittle fracture without the formation of a crack network, which is typical for brittle materials. Extended defoliation is also observed on a significantly larger scale than that of the (Zr,Ti,Hf)N and ZrN coatings. Defoliation occurs to a greater extent inside the (Zr,Hf)-layer.



Figure 11. Study of the nature of destruction of the (Zr,Hf)N coating (indentor Al_2O_3). (**a**,**b**) boundary of the fracture area, (**c**) cross-section of the wear zone boundary area indicating areas for further study, (**d**,**e**) delamination in the area of interface between the coating and the substrate.

Although the (Zr,Hf)N coating formally demonstrated better wear resistance due to its high hardness and sufficient strength, its weak point is the relatively low strength of the adhesive layer. Analysis of the nature of destruction in the pin-on-disk test shows the practical absence of a transition region. There is a clearly defined boundary of the wear region, outside of which there are no signs of coating destruction.

The formation of transverse cracks passing through the structure of the (Zr,Hf)N coating is also observed upon contact with the AISI 52100 bearing steel indenter (Figure 12). This fact indicates the high brittleness of this coating. The substrate material adherent present on the coating surface is partially introduced into the crack. The diffusion of titanium from the adherent into the coating is observed. The presence of oxygen indicates the oxidation of the adherent material (primarily titanium). The crack completely cuts through the coating layer and passes into the substrate (Figure 12).



Figure 12. Features of destruction of the (Zr,Hf)N coating upon contact with an indenter made of AISI 52100 bearing steel, analysis of the content of chemical elements in the crack zone.

3.4.4. Coating (Zr,Nb)N

The (Zr,Nb)N coating has a fairly low wear resistance, especially when in contact with an Al_2O_3 indenter (the wear resistance is actually at the level of the uncoated sample). A branched network of cracks is formed, which results in the intensive destruction of the coating (Figure 13).



Figure 13. The nature of the destruction of the (Zr,Nb)N coating upon contact with an indenter. (**a**,**b**) formation of a crack network and chipping of the coating.

The (Zr,Nb)N coating has relatively low strength and hardness. An area of active cracking and chipping of the coating along the wear boundary is visible (Figure 14a,b). From this point of view, the (Zr,Nb)N coating has opposite properties to the (Zr,Hf)N coating, which is characterized by higher hardness. This type of destruction of the (Zr,Nb)N coating correlates well with its lowest hardness among the studied coatings. Along with low strength, the (Zr,Nb)N coating also demonstrates a rather low adhesion strength to the substrate (Figure 14d). It is evident that the disruption of the adhesive bond occurs

predominantly between the Zr,Nb adhesive layer and the coating. At the same time, the Zr,Nb adhesive layer itself, on the contrary, demonstrates very good adhesion to the substrate. This adhesive bond is not disrupted even under conditions of significant plastic deformation (see Figure 14c–e). Analysis of the distribution of elements in the area of indentation of fragments of the destroyed adhesive layer into the substrate material (Figure 14f) shows that oxygen penetration into the substrate structure is possible through cracks in the coating. Both diffusion of Zr and Nb into the substrate and diffusion of substrate elements (mainly titanium) into the coating occur.



Figure 14. Study of the nature of destruction of the (Zr,Nb)N coating (pin-on-disk test Al_2O_3). (**a**,**b**) cracking and spalling of the coating at the boundary of the wear zone, (**c**–**e**) defoliation of the coating and substrate under the influence of plastic deformation, plastic deformation and destruction of the coating, preservation of sublayer adhesion Zr,Nb and the substrate under conditions of noticeable plastic deformation, (**f**) distribution of elements in the area of pressing fragments of the destroyed adhesive layer of the coating into the substrate material.

4. Discussion

Let us consider the efficiency of using adhesive layers of different compositions. Theoretically, the use of the Zr,Hf adhesive layer during the deposition of coatings on titanium alloys may be advisable based on the following assumptions. Hafnium, like zirconium, increases the thermal stability of the titanium alloy structure, increases the creep limit and the strength at low and medium temperatures, and improves the weldability of titanium-based alloys [82,87–89]; accordingly, it can increase the strength of diffusion between the coating and the titanium substrate. In both liquid and solid states, a continuous series of solid solutions are formed between hafnium and titanium. In addition to the above, hafnium, together with zirconium, is a neutral hardener of a titanium-based solid solution, acting according to the mechanism of solid-solution hardening. At the same time, in this series of experiments, the Zr,Hf layer did not provide sufficient adhesion of the coating to the substrate. The Zr layer provided an average adhesion strength for the samples studied. The Zr,Nb layer provided the best adhesion. Alloys of the Zr–Nb system are characterized by such properties as high fatigue endurance. The elastic modulus of these alloys is in the range of 58–90 GPa, depending on the initial structural-phase state and impurity content [90–94]. In the (Zr,Nb)N coating, adhesion failure occurs mainly between the Zr,Nb adhesion layer and the coating, but the adhesion layer itself exhibits a high strength of adhesive bonds with the substrate. However, in the (Ti,Zr,Nb)N coating, Zr,Nb peels off from the substrate while maintaining adhesion to the coating. Thus, the strength of the adhesion of the coating to the base depends not only on the composition and structure of the adhesive layer but also on the composition and structure of the wear-resistant coating layer. Delamination occurs at the weakest interface (with the base or with the wear-resistant coating layer).

Thus, summarizing the results of the study, we can obtain the following table (Table 4).

Coating	Hardness and Resistance to Brittle Fracture	Adhesive Layer	Adhesion Strength to Substrate
ZrN	A fairly hard coating, but at the same time it has good resistance to brittle fracture	Zr	Provides fairly good adhesion to the substrate
(Zr,Ti,Hf)N	A hard but rather brittle coating prone to cracking	Zr,Hf	The adhesion strength to the substrate is insufficient
(Zr,Hf)N	Very hard, but at the same time very brittle coating	Zr,Hf	The adhesion strength to the substrate is insufficient
(Zr,Nb)N	Brittle coating, prone to formation of a network of cracks. Hardness is relatively low.	Zr,Nb	Provides high adhesion strength to the substrate

Table 4. Comparison of the properties of coatings and the properties of the adhesion layer.

5. Conclusions

- When in contact with the Al₂O₃ counterbody, the best wear resistance was demonstrated by the sample with the (Zr,Hf)N coating. Quite good wear resistance was also observed for the sample with the (Zr,Nb,Ti)N coating. When tested in contact with the 52100 bearing steel counterbody, the best resistance was demonstrated by the samples with the ZrN and (Ti,Zr,Hf)N coatings.
- 2. By applying the coating, it is possible not only to increase the wear resistance of the parts but also to ensure (with the appropriate choice of the coating composition) the uniform wear of the elements in the tribological pair. When in contact with the 52100 bearing steel counterbody, the indenter wear for the sample with the ZrN and (Ti,Zr,Hf)N coatings was more intense than for the sample without the coating. The

wear resistance of samples with (Zr,Hf)N and (Zr,Nb,Ti)N coatings was 2.5–3.3 times higher than that of the uncoated sample.

- 3. To ensure the overall strength of the coating, it is important not only to have the adhesive layer adhere to the base on one side and the coating on the other side but also the strength of the adhesive layer itself. The boundary of the coating's destruction and its separation from the substrate sometimes passes inside the adhesive layer itself. In this case, the peeling occurs not because of poor adhesion to the base but because of the adhesive layer's insufficient strength.
- 4. The surface oxide film must be completely removed from the titanium substrate, as this film will have a negative effect on the adhesion strength of the coating and the substrate.
- 5. The composition and structure of the wear-resistant layer have a significant impact on the overall strength of the adhesive bond between the coating and the substrate. Delamination occurs at the weakest interface in terms of adhesion (with the substrate or with the coating). It is necessary to ensure a good combination of properties, both in the substrate–adhesive layer system and in the adhesive layer–wear-resistant layer system.

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