

STRUCTURE AND MECHANICAL PROPERTIES OF (Zr,Nb)N, (Zr,Hf)N AND (Zr,Nb,Hf)N COATINGS

N.N. Cherenda, S.N. Grigoriev, A.V. Basalai, N.V. Bibik, A.A. Vereschaka, A.Yu. Isobello, D.P. Rusalsky, A.K. Kuleshov, V.V. Uglov, V.V. Chayuski, I.A. Saladukhin

Structure and mechanical properties of (Zr,Nb)N, (Zr,Hf)N, and (Zr,Nb,Hf)N vacuum arc coatings deposited on Ti-6Al-4V titanium alloy were investigated in this work. The coatings were single-phase solid solutions based on ZrN. The highest microhardness value (17 GPa) was observed for (Zr,Hf,Nb)N coating. (Zr,Hf)N coating possessed the highest critical force Lc3 during scratch tests. A decrease of the niobium concentration in the (Zr,Nb)N coating and an increase of the hafnium concentration in the (Zr,Hf)N coating led to the growth of the critical force Lc3.

Keywords: titanium alloy, medical implants, nitride coating, adhesion, microhardness.

INTRODUCTION

Titanium alloys being the most frequently used material for production of metal implants actively applied in various fields of medicine [1-4]. At the same time implants are foreign objects introduced into the human body and can cause a corresponding reaction of the immune and other systems [2]. For example, Ti-6Al-4V alloy that is widely used for implants production contains potentially toxic atoms of aluminum and vanadium which have the risk of releasing into the human body [1-3]. Vanadium has been associated with gastrointestinal discomfort and decreased body weight gain, carcinogenic effect [2]. Aluminium is also toxic in high doses and can be linked to a number of diseases: neurotoxicity, impairment of motor functions, reduction of spatial memory capacity and Alzheimer's disease [2].

Deposition of protective coatings is one of approaches most widely used to avoid this negative effect [5, 6]. Application of transition metals nitride PVD coatings in this direction attracts considerable attention [7]. Such coatings possess exceptional mechanical and tribological properties as well as good corrosion resistance [7]. ZrN coating is one of examples of such a kind [5,6,8]. In particular, ZrN coatings are commercially available coatings for orthopaedic implants, which are used for articulating surfaces in joint arthroplasty [5]. Besides binary nitride materials, ternary and higher order material systems are under development to ensure an optimal combination of properties [9]. Thus coatings of Zr-Nb-N and Zr-Hf-N compositions are of the interest in relation to this approach [9-17].

In a number of works it was reported that Zr-Nb-N PVD coatings and films possess high hardness, high elastic modulus and low wear rate [10-12]. In [10, 11] it was mentioned that Zr-Nb-N system has a high potential to provide scratch resistant coatings. In most of references fcc solid solution on the base of ZrN was mentioned as a single or a main phase constituent of the coating [11, 12]. At the same time change of Nb concentration led to the structural changes in coating influencing its mechanical properties [12, 13]. In [12] it was found that addition of niobium resulted in coating structure refinement. Similar effect was reported for Nb-Zr-N films [13]. Growth of the Zr/Nb stoichiometric ratio resulted in the average grain size and lattice parameter increase [13]. Zr-Hf-N coatings also had fcc crystalline lattice and is characterized by enhanced mechanical and tribological properties [14-16]. At the same time it was reported that increase of Hf concentration in coating did not change the hardness significantly [14-16]. Negligible solid solution hardening due to small atomic radius difference between Zr and Hf atoms can be the main reason of this effect [14]. Small difference in atomic radiuses also is a cause of insignificant influence of Hf atoms addition (up to 11.9 at.% Hf) on the level of ZrN films residual stress [17]. In contrast growth of Hf concentration considerably increases adhesion strength of coatings and wear resistance [14, 15].

Earlier conducted investigations of mechanical and corrosion properties of ZrN, (Zr,Ti)N, (Zr,Hf)N, (Zr,Nb)N, (Ti,Zr,Hf)N and (Ti,Zr,Nb)N coatings deposited on a Ti-6Al-4V titanium alloy revealed that presence of Hf atoms in the coating led to hardness and coating adhesion increase [18]. While addition of Nb atoms provided high corrosion resistance of (Ti,Zr,Nb)N coating [18]. Thus the investigation of Nb and Hf atoms concentration influence on the structure and mechanical properties of (Zr,Hf)N, (Zr,Nb)N and, (Zr,Nb,Hf)N coatings were the main aims of this work.

MATERIALS AND EXPERIMENTAL METHODS

The samples of Ti-6Al-4V titanium alloy (Grade 5) were used for investigations. Coatings were deposited by vacuum arc deposition technique with controlled movement of cathode spot in nitrogen atmosphere using a modernized VIT-2 PVD installation [19]. Cleaning of the surface by Zr ions was carried out before deposition resulting in formation of thin (~ 50 nm) metal sublayer. The coatings were deposited using two metal cathodes. The following pairs of cathodes were used: Zr and 50 at.% Zr - 50 at.% Nb, Zr and 50% at. Zr – 50 at.% Hf, 50 at.% Zr - 50 at.% Nb and 50% at. Zr – 50 at.% Hf. As a result, the following coatings were deposited: (Zr,Nb)N, (Zr,Hf)N and (Zr,Nb,Hf)N. Usage of second Zr cathode allows to diminish concentration of Nb and Hf in (Zr,Nb)N and (Zr,Hf)N coatings in contrast to the coatings investigated in [19]. During coating deposition, the arc current of the zirconium cathode was 80 A. The arc current of the Zr-Nb, Zr-Hf cathodes was, respectively, 85 and 90 A. Deposition was carried out under the following parameters, identical for all processes: nitrogen pressure was 0.42 Pa, bias voltage on substrate was -150 V, tool rotation speed was 0.7 rpm. The thickness of coatings was ~ 4.5 μm .

The structural-phase state of the coatings was studied by X-ray diffraction analysis using a Rigaku Ultima IV diffractometer (Rigaku Co., Tokyo, Japan) in Cu K α radiation focusing parallel beams. Analysis of elemental composition was carried out by energy dispersive X-ray analysis using LEO1455VP (Karl Zeiss, Germany) scanning electron microscope. The microhardness of the coatings was determined on 402MVD (Instron Wolpert Wilson Instruments) microhardness tester using a Vickers indenter. The normal load on the diamond indenter was 1 N, the holding time in the loaded state was 10 s. Scratch tests were carried out with 0.4 mm radius diamond indenter with a load linearly increasing from 0.05 to 98 N. The scratch tracks length was 15 mm (loading speed 0.17 kg/s, sample movement speed 0.19 mm/s). Three tests were carried out on each sample.

EXPERIMENTAL RESULTS

The results of coatings elemental composition analysis in the surface layer with the thickness of ~ 1 μm are presented in Table. From the data it is evident that zirconium was the predominant metallic element in the multicomponent coatings. The use of two cathodes (one of which is Zr) in the (Zr,Nb)N and (Zr,Hf)N coatings make it possible to reduce the concentration of niobium and hafnium in the ZrN-based solid solution up to 10.2 and 2.0 at.%, respectively. The use of one Zr-Nb or Zr-Hf cathode led to the formation of (Zr,Nb)N and (Zr,Hf)N coatings with a concentration of 23.5 and 5.7 at.% [19]. Combination of data received in this work with the data of earlier findings allow to investigate the effect of niobium and hafnium concentration on the coatings properties. The concentration of Nb and Hf in the (Zr,Nb,Hf)N coating was higher than for the case of (Zr,Nb)N and (Zr,Hf)N coatings. However, this difference is insignificant and is near the limit of error of concentration determination. For all types of coatings, the nitrogen concentration was close to stoichiometric one (47-49 at. %).

Table. Concentration of elements in (Zr,Nb)N, (Zr,Hf)N and (Zr,Nb,Hf)N coatings (energy dispersive X-ray analysis).

Coating	Concentration of elements, at. %			
	Zr	Nb	Hf	N
(Zr,Nb)N	41.1	10.2	-	48.7
(Zr,Hf)N	49.4	-	2.0	48.6
(Zr,Nb,Hf)N	38.5	11.5	3.3	46.7

Figure 1 shows the diffraction patterns of samples with (Zr,Hf)N, (Zr,Nb)N and (Zr,Nb,Hf)N coatings. As one can see from the figure, earlier obtained regularities are observed [19]. In particular, single-phase coatings based on a ZrN solid solution with fcc crystalline lattice containing additional alloying elements were formed during deposition. Diffraction lines of the solid solution based on ZrN had a larger width in the (Zr,Nb)N and (Zr,Nb,Hf)N coatings compared to that of (Zr,Hf)N coating. This effect can be associated with both a higher value of microstress in the coatings and a smaller size of crystallites. The latter effect was already found in [12, 13]. Beside that a change in the lattice parameter (calculated using (111) and (311) diffraction lines) of the solid solution based on ZrN is observed. The calculation results are shown in Figure 2.

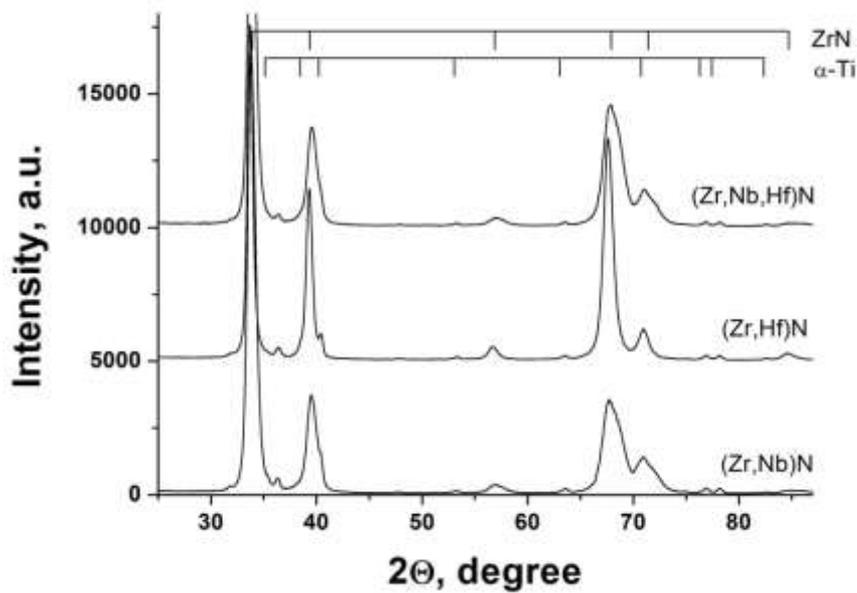


Fig. 1. Diffraction patterns of samples with (Zr,Nb)N, (Zr,Hf)N and (Zr,Nb,Hf)N coatings.

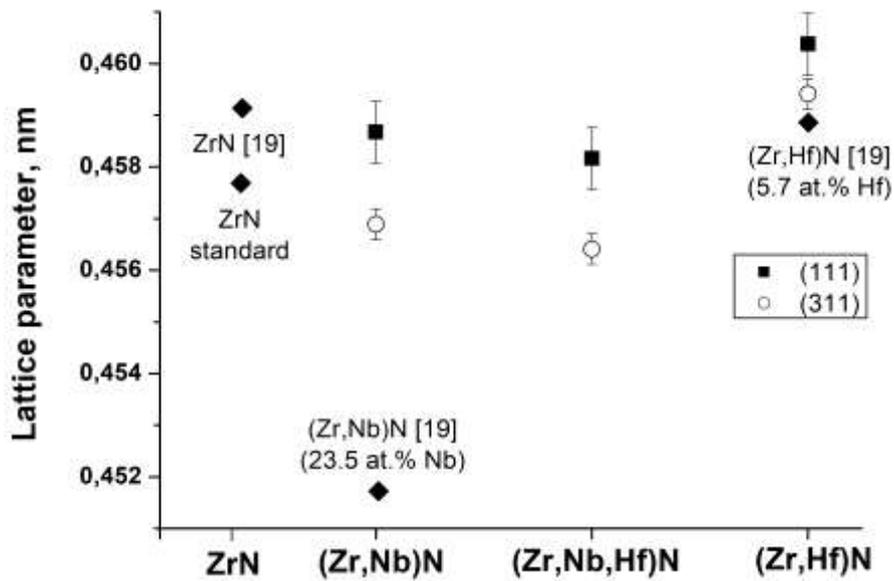


Fig. 2. Lattice parameter of ZrN solid solution in (Zr,Nb)N, (Zr,Hf)N and (Zr,Nb,Hf)N coatings. Lattice parameters taken from Ref. [19] were calculated using diffraction line (111) ZrN.

One can see that the use of the Zr-Nb cathode led to a decrease in the lattice parameter of the solid solution in the (Zr,Nb)N and (Zr,Nb, Hf)N coatings compared to the (Zr,Hf)N coating. Smaller radius of Nb atoms (0.164 nm) than that of Zr (0.175 nm) is the reason for this effect. Similar regularity was observed in [12]. The lattice parameter of the solid solutions corresponded (within the error limits) to the lattice parameter in the ZrN coating [19]. Comparison with the data of work [19] shows that a decrease in the hafnium concentration in the coating from 5.7 at.% to 2 at.% led to an insignificant decrease in the lattice parameter to a value corresponding to the lattice parameter in the ZrN coating. At the same time, a decrease of the niobium concentration from 23.5 at.% to 10.2 at.% resulted in significant increase of the lattice parameter up to the value of ZrN lattice parameter. In general, the decrease of niobium and hafnium concentration should lead to a decrease in micro- and macrostresses in the coatings and the corresponding response of mechanical characteristics. The lattice parameter of the solid solution in the (Zr,Nb,Hf)N coating does not differ within the error limits from the lattice parameter of the solid solution in the (Zr,Nb)N coating, which is associated with an insignificant change in the elemental composition of the coatings (Table).

The mechanical properties of (Zr,Nb)N, (Zr,Hf)N and (Zr,Nb,Hf)N were also investigated. In particular, Vickers microhardness measurements were carried out. The indenter penetration depth was 1.5-2 μm . Highest

microhardness values (15.8 ± 0.7 GPa and 16.9 ± 1.7 GPa) were observed for (Zr,Hf)N and (Zr,Nb,Hf)N coatings, which have close elemental composition (Table) and, probably, close macrostress values (Fig. 2). The microhardness of (Zr,Nb)N coating was less - 9.2 ± 0.6 GPa. The obtained data are consistent with the previously conducted research where it was found that (Zr,Nb)N coatings had lower microhardness compared to other types of coatings, which may be associated with the existence of tensile stresses in the coating [26].

In the work [18] the data on Knoop microhardness measurements of ZrN coating, (Zr,Nb)N coating with the Nb concentration of 23.5 at.% and (Zr,Hf)N coating with the Hf concentration of 5.7 at.% were presented. The microhardness values were 21.5, 12.0 and 28.3 GPa for the corresponding type of coating [18]. Direct comparison with the data received in this work is not correct because different types of indenters and different loads were used. However, it is possible to estimate the effect of the composition on the microhardness value through the ratio of the maximum microhardness (observed in the (Zr,Hf)N coating) to the minimum microhardness (that was obtained for (Zr,Nb)N coating). For the case presented in [18] this ratio was 2.4. At the same time, for the coatings under consideration, this ratio was decreased to 1.9. So diminishing of Nb and Hf concentration in the (Zr,Nb)N and (Zr,Hf)N coatings should obviously lead to decreasing of the concerned microhardnesses ratio to the value of 1 while microhardness value will be approached to the value of ZrN coating.

After coatings deposition on the titanium alloy tests were also conducted on their adhesive strength. All scratches were made along the direction of samples grinding. Investigations showed that the tracks were characterized by the appearance of chips on the sides of the track, and subsequent full delamination of the coating. It is known that three main critical loads are usually determined using scratch tests: Lc1 corresponding to initial cracking appearance, Lc2 – first chipping and Lc3 – full delamination of a coating [20]. In these experiments the critical force Lc3 was determined using optical microscopy basing on the distance at which full delamination occurred and basing on the dependence of the load applied on the diamond indenter sliding distance. Lc3 was equal 36 N for samples with (Zr,Nb)N coating, 50 N – for (Zr,Hf)N coating and 42 N – for (Zr,Nb,Hf)N coating.

Another criterion for full delamination of coating deposited on a relatively smooth surfaces may be a sharp change in the value of the friction coefficient of the diamond indenter during scratch tests [20]. The dependences of the indenter friction coefficient on its sliding distance are shown in Figure 3.

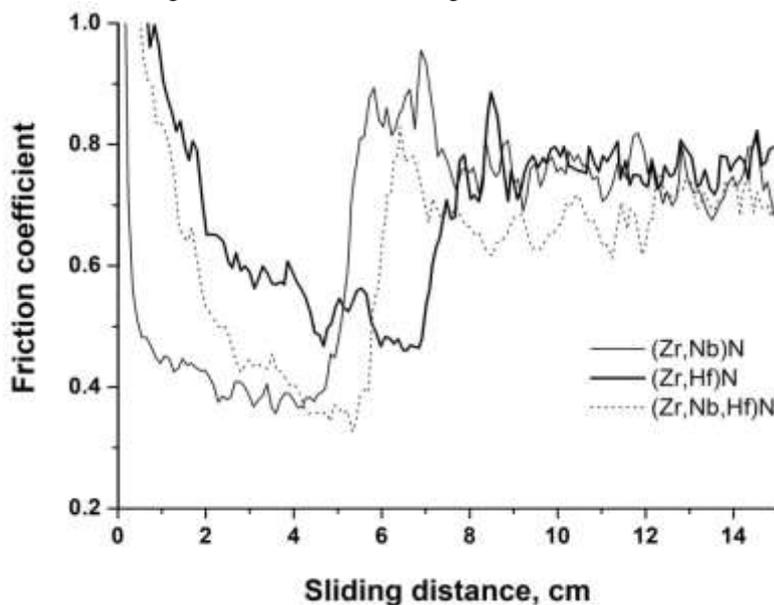


Fig. 3. Dependence of the (Zr,Nb)N, (Zr,Hf)N and (Zr,Nb,Hf)N coatings friction coefficient of a diamond indenter on its sliding distance

The dependences show a sharp increase in the friction coefficient indicating full delamination of the coating and penetration of indenter into Ti-6Al-4V alloy, that corresponds to the values of critical force Lc3 obtained using optical microscopy. The highest critical forces Lc3 were observed for samples with coatings containing hafnium. However, these coating were characterized by the largest chips along the entire length of the track, compared to the other coatings.

In the work [18] adhesion tests of ZrN, (Zr,Nb)N coatings with Nb concentration of 23.5 at.% and (Zr,Hf)N coatings with Hf concentration of 5.7 at.% were carried out under the same conditions as in the present case. The

critical force values for the corresponding coatings were 37.3, 33.4 and 54.0 N [18]. Comparison with the data obtained in the present work shows that a decrease in the niobium concentration in the (Zr,Nb)N coating and an increase in the hafnium concentration in the (Zr,Hf)N coating led to an increase of Lc3 critical force. These data correlate with previous findings [18] that the presence of Nb in the ZrN coating caused a decrease in the critical force in adhesion tests. The possible reason of this effect is the appearance of tensile residual stresses in the crystal lattice of the coating [19], which contribute to the destruction of the coating under mechanical loads. While the presence of Hf, on the contrary, leads to an increase in the adhesive strength and hardness of the coating. Positive influence of Hf atoms on adhesive strength of ZrN coatings was already found in [14, 15]. However, a large difference in the strength characteristics of the Ti alloy as a substrate and the hard coating in this case, resulted in increase of the area of coating chips along the scratch. The (Zr,Nb,Hf)N coating had a kind of "average" mechanical characteristics due to the "opposite" effect of Nb and Hf atoms on the mechanical properties of coatings based on ZrN solid solutions.

CONCLUSIONS

Structure, elemental composition, mechanical and corrosion properties of (Zr,Nb)N, (Zr,Hf)N and (Zr,Nb,Hf)N coatings which were deposited using two cathodes on a Ti-6Al-4V titanium alloy substrate by means of vacuum arc deposition were investigated this work. The coatings were single-phase solid solutions based on ZrN with fcc crystalline structure. The coatings containing Nb had a smaller lattice parameter compared to the ZrN standard, which is associated with a smaller atomic radius of niobium atoms. Comparison with previously conducted investigations showed that an increase of the niobium concentration led to a decrease of the lattice parameter of the solid solution based on ZrN.

Vickers microhardness measurements showed that (Zr,Hf)N and (Zr,Nb,Hf)N coatings had the highest microhardness value (16-17 GPa). The microhardness of the (Zr,Nb)N coating was lower ~ 9 GPa. During scratch testing the highest critical force Lc3 was observed for (Zr,Hf)N coating. However coatings containing Hf were characterized by the largest area of chips along the entire length of the track. (Zr,Nb)N coating showed relatively small value of critical load, which may be associated with the presence of tensile stresses in the ZrN solid solution. Comparison with the data obtained earlier showed that a decrease of the niobium concentration in the (Zr,Nb)N coating and an increase of the hafnium concentration in the (Zr,Hf)N coating led to an increase of the critical force Lc3.

FUNDING

This work was supported by the Belarusian Republican Foundation for Fundamental Research (project no. T23RNF-228) and the Russian Science Foundation (project no. 23-49-10038).

CONTRIBUTIONS

Conceptualization: N.N. Cherenda, S.N. Grigoriev, A.A. Vereschaka; Methodology: N.N. Cherenda, A.V. Basalai, N.V. Bibik, D.P. Rusalsky; Formal analysis and investigation: N.N. Cherenda, A.V. Basalai, N.V. Bibik, O.V. Reva, A.Yu. Isobello, D.P. Rusalsky, A.K. Kuleshov, V.V. Uglov, V.V. Chayeuski, I.A. Saladukhin; Writing: N.N. Cherenda, A.A. Vereschaka; Funding acquisition: N.N. Cherenda, S.N. Grigoriev, A.A. Vereschaka; Supervision: N.N. Cherenda, S.N. Grigoriev, A.A. Vereschaka

CONFLICT OF INTEREST

The authors declare no conflict of interest.

REFERENCES

1. Chen, Q., Thouas, G. A.: Metallic implant biomaterials. *Mater. Sci. Eng. R.* **87**, 1–57 (2015). <https://doi.org/10.1016/j.mser.2014.10.001>
2. Kaur, M., Singh, K.: Review on titanium and titanium based alloys as biomaterials for orthopaedic applications. *Materials Science and Engineering C* **102**, 844-862 (2019). <https://doi.org/10.1016/j.msec.2019.04.064>
3. Chen, H., Feng, R., Xia, T., Wen, Z., Li, Q., Qiu, X., Huang, B., Li, Y.: Progress in Surface Modification of Titanium Implants by Hydrogel Coatings. *Gels* **9**, 423 (2023). <https://doi.org/10.3390/gels9050423>

4. Grabovetskaya, G.P., Stepanova, E.N., Zabudchenko, O.V., I.P. Mishin: Formation of the Structure and Properties of the Near-Surface Layer in Alloys of the Ti–6Al–4V–H System Under Irradiation with a Pulsed Electron Beam. *Russ Phys J* **66**, 172–179 (2023). <https://doi.org/10.1007/s11182-023-02922-3>
5. Gabor, R., Cvrček, L., Kudrnová, M., Hlinka, J., Večeř, M., Buřil, M., Walter, J., Čekada, M., Drnovšek, A., Unucka, P., Mamulová Kutláková, K., Motyka, O., Seidlerová, J.: ZrN coating as a source for the synthesis of a new hybrid ceramic layer. *Applied Surface Science Advances* **22**, 100615 (2024). <https://doi.org/10.1016/j.apsadv.2024.100615>
6. Rabadzhyska, S., Dechev, D., Ivanov, N., Ivanova, T., Strijkova, V., Katrova, V., Rupetsov, V., Dimcheva, N., Valkov, S.: Wear and Corrosion Resistance of ZrN Coatings Deposited on Ti6Al4V Alloy for Biomedical Applications. *Coatings* **14**, 1434 (2024). <https://doi.org/10.3390/coatings14111434>
7. Wu, X., Han, H., Jiang, Y., Zhu, D., Zuo, B., Bian, S., Chen, C., Zhao, L., Xu, J., Yu, L.: Opportunities and challenges of the nitride coatings for artificial implants: A review. *Surface and Coatings Technology* **480**, 130587 (2024). <https://doi.org/10.1016/j.surfcoat.2024.130587>
8. Savostikov, V.M., Leonov, A.A., Denisov, V.V. et al. Formation of a Zr+Zr_xNy+(Zr+TiBSiNi)N+(TiBSiNi)N Gradient-Layered Coating Based on Physical and Tribotechnical Characteristics of Constituent Layers. *Russ Phys J* **67**, 1090–1099 (2024). <https://doi.org/10.1007/s11182-024-03220-2>
9. Kanoun, M., Goumri-Said, S.: Effect of alloying on elastic properties of ZrN based transition metal nitride alloys. *Surface and Coatings Technology* **255**, 140–145 (2014). <https://doi.org/10.1016/j.surfcoat.2014.03.048>
10. Zhang, S., Wang, N., Li, D.J., Dong, L., Gu, H.Q., Wan, R.X., Sun, X.: The synthesis of Zr–Nb–N nanocomposite coating prepared by multi-target magnetron co-sputtering. *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms* **307**, 119–122, (2013). <https://doi.org/10.1016/j.nimb.2012.12.067>
11. Wu, Z.T., Qi, Z.B., Jiang, W.F., Wang, Z.C., Liu, B.: Influence of niobium addition on microstructure, mechanical properties and oxidation resistance of ZrN coatings. *Thin Solid Films* **570**, 256–261 (2014). <https://doi.org/10.1016/j.tsf.2014.05.019>
12. Krysina O.V., Ivanov, Yu.F., Prokopenko, N.A., Shugurov, V.V., Petrikova, E.A., Denisova Yu.A., Tolkachev O.S.: Influence of Nb addition on the structure, composition and properties of single-layered ZrN-based coatings obtained by vacuum-arc deposition method. *Surface & Coatings Technology* **387**, 125555 (2020). <https://doi.org/10.1016/j.surfcoat.2020.125555>
13. Qian, J., Zhou, F., Li, K., Wang, Q., Kong, J., Zhou, Z.: Optimization of deposition parameters and performance analysis of Nb-Zr-N composite films. *Surface and Coatings Technology* **466**, 129641 (2023). <https://doi.org/10.1016/j.surfcoat.2023.129641>
14. Atar, E., Kayali, E.S., Cimenoglu, H.: Sliding wear behaviour of ZrN and (Zr, 12 wt% Hf)N coatings. *Tribology International* **39**, 297–302, (2006). <https://doi.org/10.1016/j.triboint.2005.01.038>
15. Atar, E., Kayali, E.S., Cimenoglu, H.: Reciprocating wear behaviour of (Zr, Hf)N coatings. *Wear* **257**, 633–639, (2004). <https://doi.org/10.1016/j.wear.2004.03.005>
16. Atar, E., Cimenoglu, H.C., Kayali, E.S.: Hardness characterisation of thin Zr(Hf,N) coatings. *Surface and Coatings Technology* **162**, 167–173, (2003). [https://doi.org/10.1016/S0257-8972\(02\)00558-3](https://doi.org/10.1016/S0257-8972(02)00558-3)
17. Atar, E., Sarioglu, C., Cimenoglu, H., Kayali, E.S.: Residual stresses in (Zr,Hf)N films (up to 11.9 at.% Hf) measured by X-ray diffraction using experimentally calculated XECs. *Surface & Coatings Technology* **191**, 188– 194 (2005). <https://doi.org/10.1016/j.surfcoat.2004.02.024>
18. Cherenda, N.N., Grigoriev, S.N., Basalai, A.V., Petukh, A.B., Vereschaka, A.A., Reva, O.V., Isobello, A.Yu., Rusalsky, D.P., Kuleshov, A.K., Uglov, V.V.: Comparative study of mechanical and corrosion properties of coating on the basis of ZrN and TiN solid solutions. *High Temperature Material Processes* **29**, in press (2025) DOI: 10.1615/HighTempMatProc.2024057613
19. Vereschaka, A., Cherenda, N., Sotova, C., Uglov, V., Reva, O., Basalai, A., Isobello, A., Baranova, N.: Development of Multicomponent Nanostructured Nitride Coatings to Protect against Corrosion Products from Titanium Alloy. *Coatings* **13**, 2028 (2023). <https://doi.org/10.3390/coatings13122028>
20. Cherenda, N.N., Petukh, A.B., Kuleshov, A.K., Rusalsky, D.P., Bibik, N.V., Uglov, V.V., Grigoriev, S.N., Vereschaka, A.A., Astashynski, V.M., Kuzmitski, A.M.: Scratch testing of ZrN coating on Ti-6Al-4V titanium alloy surface preliminary treated by compression plasma flows impact. *High Temperature Material Processes* **28**(3), 25–36 (2024). <https://doi.org/10.1615/HighTempMatProc.2023051420>