

Evaluation of scratch resistance of nitride coatings on Ti grade 2

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Abstract. Hard coatings limiting direct contact of material susceptible to wear are applied in order to improve resistance to abrasive wear. The key importance in using anti-wear coatings has their adhesion to substrate and differences in mechanical properties of the coating and substrate, particularly their Young's module. Studies have analyzed merits of applying nitride coatings TiAlN, AlTiN and hybrid coating TiAlN/TiSiN on titanium substrate ASTM grade 2. For that purpose, nanohardness and scratch tests for each coating were conducted. Apparatus of Anton Paar Company was used in these studies – ultra-high resolution nanoindenter and micro combi tester. Due to the fact, that surface roughness is a significant parameter affecting properties of the surface layer, the first appointed parameters were Sa roughness with a use of optical profilometer Bruker Contour GT. Obtained results suggest the best adhesive grip of hybrid coating TiAlN/TiSiN compared with other tested. The weakest adhesion to titanium grade 2 has TiAlN coating, on which in scratch test has been observed significantly faster total damage, in comparison with other tested. Research results will provide the input data for numerical analysis, enabling fast receiving effects of applying tested coatings without the need to carry out time-consuming research.

1 Introduction

Titanium and titanium alloys, especially Ti6Al4V, found application not only in the aerospace or petrochemical industries, but also in biomedical industry. They have several beneficial features, which must be fulfilled by the materials used in such conditions. These features are: high load resistance factors, low degrees of corrosion and oxidation, low toxicity and beneficial biocompatibility [1]. In addition, a relatively small Young's module causes that titanium and titanium alloys are very good materials for bone implants. However, their low abrasion resistance and metallosis effect caused by alloys, poses a challenge. The most commonly used alloy in medicine – Ti6Al4V – can cause side effects due to formation of cytotoxic vanadium oxides [2]. For this reason, researchers are looking for solutions by applying appropriate coatings, such as nitrides. This is very important, because medical implants are used to improve the quality of patients' lives by reducing the pain and restoring a function of infected structures [3]. In recent years, TiN, TiO₂ and N-TiO₂ were successfully used as protective coatings against wear and corrosion. It was observed, that this increases the life span of surgical implants and prostheses. Coatings, among others with PVD method, enable to obtain a gradient diffusion layer of sufficient thickness and adhesion, which ensures long-lasting abrasion-resistant surface [4].

In this research, it was decided to study the usefulness of AlTiN TiAlN coatings and TiAlN/TiSiN applied on titanium ASTM grade 2 to improve its abrasion resistance. For that purpose, applied coatings should have high hardness, as well as a good connection

with substrate. Only two conditions allow for their use in mentioned above medical applications. Comparison of properties of three tested coatings enables to assess, which one is the best to protect titanium substrate against wear. Comparison with other similar tested coatings allows for general evaluation of merits of their application. Appointed hardness values of coatings and Young's module enable their use as the input in computer modelling of coatings and simulating their behaviors, as well as cooperation with the substrate.

2 Studied materials

TiAlN, AlTiN and hybrid coating TiSiN/TiAlN were the subject of research. The substrate material was technically pure titanium – ASTM grade 2. The sample in a form of discs \varnothing 25 mm and thickness of 6 mm were prepared in the industrial technological line. At first, studied surface were polished mechanically to achieve surface roughness below Ra 0.5 μ m. Pre-cleaning and degreasing in biological parts washer machine was followed by blasting in water corundum suspension of 300 μ m gradation at a pressure of 0.4 MPa through 10 seconds. The last preparation stage of samples was a bath in washing line in the water subjected to reverse osmosis process with ultrasounds and gas bubbles flowing through the liquid. Coatings were placed physically from the gas phase PVD in the magnetron sputtering process. Targets placed on the cathode in appropriate proportions, as described in Table 1, were the source of coating material. After placing the samples

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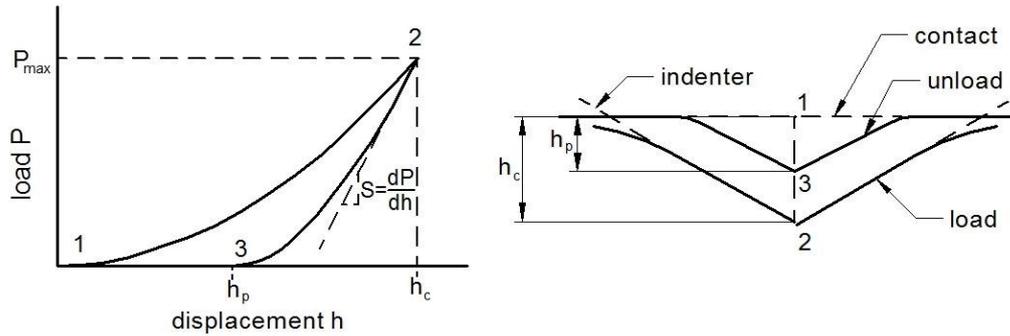


Fig. 1. Scheme of loading relation – offloading in nanohardness studies with Olivier Phar method; 1 – contact with studied surface; 2 – maximum deflection h_c with P_{max} loading and maintenance of the force for 5 seconds; 3 – residual deflection h_p after removal of the load.

in working chamber, the sputtering process was preceded by preliminary heating to 400° C, ion etching with direct current of 100 V with intensity 20 A, and then with modulated current with frequency of 240 kHz. Sputtering process was carried out in vacuum below 10^{-7} Pa in argon and krypton atmosphere.

Table 1. Proportion of coating materials and predicted thickness

Pos.	Coating	Coating thickness	Proportion of targets with coating material
1	AlTiN	3.0 - 4.0 μ m	3 x TiAl70 (70 points Al) 1 x Ti
2	TiAlN	2.0 - 3.0 μ m	3 x TiAl60 (60 points Al) 1 x Ti
3	TiAlN/TiSiN	4.0 - 5.0 μ m	2 x TiSi23 (23 points Si) 2 x TiAl60 (60 points Al)

3 Surface characteristics

Geometrical measurements of surface roughness parameters were conducted in the first research stage with a use of optical profilometer Bruker Contour GT, with parameters using white light interference. Samples without coating were measured up before washing in industrial washing line and right after that coating was applied. Measured values of roughness parameters S_a from the surface with dimension 1 mm x 1 mm were described in Table 2. Measured surfaces were characterized by a uniform geometrical structure with local defects in a form of scratches.

Table 2. Parameters of surface roughness S_a .

Sample	S_a [μ m]
Ti grade 2 without coating	0.209
AlTiN	0.217
TiAlN	0.234
TiAlN/TiSiN	0.223

4 Nanohardness studies

Nanohardness study of coatings was conducted in the next research stage using Olivier Phar method [5].

Berkovich diamond indenter of angle cut cube shape was pressed on ultra-high resolution nanoindenter of Anton Paar Company into tested surface with small P_{max} load (Figure 1) with value 2 mN and 5 mN. Sample surface was loaded gradually from the moment of contact to maximum adopted load in time 2 mN/min. Before the surface was loaded with the same velocity, P_{max} force maintained at a constant level for 5 seconds. At that time, indenter reached the maximum deflection h_c . After total removal of load, the indenter remained at residual deflection h_p , dependent on the quantity of plastic strain. 30 attempts were conducted for each coating with maximum load of 5 mN and 2 mN. Only the smallest load enabled to carry out study without excessive deformation of coatings. Hardness (H) was set from the relation:

$$H = \frac{P_{max}}{A(h_c)} \quad (1)$$

where A is a contact area of indenter with tested surface resulting from measured h_c values and applied indenter geometry. The effective Young's E_{eff} module was appointed considering stiffness S, which is tangent to the initial load curve. Both the deformation of studied material and indenter deformation according to the relation are affecting E_{eff} [5].

$$\frac{1}{E_{eff}} = \frac{1-\nu^2}{E} + \frac{1-\nu_i^2}{E_i} \quad (2)$$

The study was conducted with assumption that Young's module of indenter was $E_i = 1140$ GPa and its Poisson number $\nu_i = 0.07$. Poisson's rate of coating was assumed as $\nu_i = 0.031$. Measurement results of hardness and appointed effective Young's module were presented in Table 3. The use of tested nitride-coatings clearly increased the hardness of surface layer by approximately 7 times compared with substrate material. The largest hardness showed AlTiN coating, and the smallest layered TiAlN/TiSiN coating, however given the overlapping confidence intervals of results it is possible to state that coatings have similar properties in this respect. Similarly appointed values of the effective Young's module did not show major differences and

analyzing all received load curves – it will not be possible to state, which of all coatings is more elastic-plastic. Clearly, we can see that study of technically pure titanium shows properties characteristic of plastic material (Figure 2a), and after applying the coating of studied nitrides, curves take a form of more elastic materials (Figure 2b). The surface of crosshatch area on Figures 2a and 2b indicates plastic strain, and it is clearly greater for pure titanium.

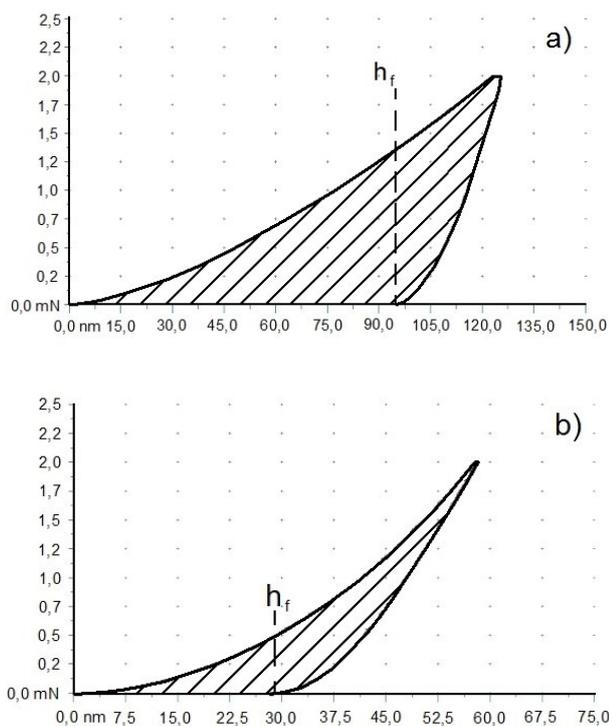


Fig. 2. Load curves – displacement in nanohardness studies; a – titanium grade 2; b – AlTiN.

Table 3. Results of measurements carried out with nanohardness.

Sample	Nanohardness [GPa]	Young's modulus E_{eff} [GPa]	Friction coefficient μ
Ti grade 2 without coating	4.99 ± 0.42	186 ± 13	–
TiAlN / TiSiN	33.91 ± 10.55	515 ± 175	0.16
TiAlN	36.08 ± 7.84	622 ± 185	0.10
AlTiN	36.49 ± 8.06	610 ± 162	0.29

5 Scratching tests

Scratching tests of coatings were carried out using Rockwell's indenter with a radius of 100 μ m with a growing load of 0.5 N up to 30 N on 6 mm. The velocity of normal forces to the surface was 10 N/min. There were analyzed damages of coatings on scratches signs with a use of the optical microscope built-in micro combi tester presented in Figure 3a, b, c. In each test, three distinctive limits were indicated i.e. Lc_1 , Lc_2 and Lc_3 , which corresponded to the normal indenter forces respectively described in Table 4. Lc_1 was accepted as the normal force by which first damage of coating was visible usually with

fracture along direction of the test. These fractures were peculiarly visible on hybrid coating TiAlN/TiSiN and provided cohesiveness of coating material [6]. AlTiN and TiAlN films presented more plastic initial deformations without distinct fractures (Fig. 3f, j). As Lc_2 limit adopted forces by which first wear of adhesion connection of the coating with substrate with crosswise fractures (Figure 3 e, i, l) and chips in the lateral parts of scratch sign. With Lc_3 limit, places of total coating rupture were indicated (Figure 3d, g, k). On TiAlN coatings, spreads of coating chips were often visible much earlier than clear limit of total coating destruction (Figure 3h). In carried-out scratching tests, the best adhesive properties to the substrate had hybrid coating TiAlN/TiSiN. Figure 3n presents visible transition between TiAlN and TiSiN coating. It is not possible to explicitly highlight the place of first coating wiping off. Noticeable fluent color change of scratch sign provides very good connection of both coatings.

Table 4. Results obtained in scratching tests.

Sample	Lc_1 [N]	Lc_2 [N]	Lc_3 [N]
TiAlN / TiSiN	0.68 ± 0.31	9.90 ± 3.29	23.90 ± 4.23
TiAlN	0.91 ± 0.54	7.23 ± 1.19	15.38 ± 3.43
AlTiN	0.91 ± 0.61	8.87 ± 2.40	18.93 ± 4.76

6 Discussion

Scratching tests were conducted to evaluate the adhesion. This method was often used by other researchers – among others [6, 7]. The following limits, appropriately indicating indenter load in marked places, were adopted in the evaluation [7]: Lc_1 : cohesive failure to indicate edge or parallel cracking, Lc_2 : adhesive failure to indicate delamination of film from its substrate, and Lc_3 : total coating failure by the total exposure of the substrate surface. In the current work, Lc_2 was identified to mark the critical load that was required to break the bonding between the film and its substrate. As it is known from [7] and own studies, the results of scratching tests depend largely on such parameters as load rate, maximum test force and its duration. Other factors, determining the different test results, are associated with the same sample. It can be a different thickness of coating, local defects, different surface roughness and surface defects, such as scratches. In studies of this work, despite preserving identical test conditions, discrepancies were obtained in results of total destroying of coating presented in Table 4. What is interesting, on each sample conducted, 5 identical scratching tests and their results were often different. This indicates the stochastic nature of the phenomenon of adhesion breaking the coatings, and it is impossible to accurately determine this limit. Successfully, it is possible to relate above statements to the research on nanohardness where indenter enters the material on a very small depth of 50 – 150 nm while the average surface irregularities in analyzed samples were more than 200 nm.

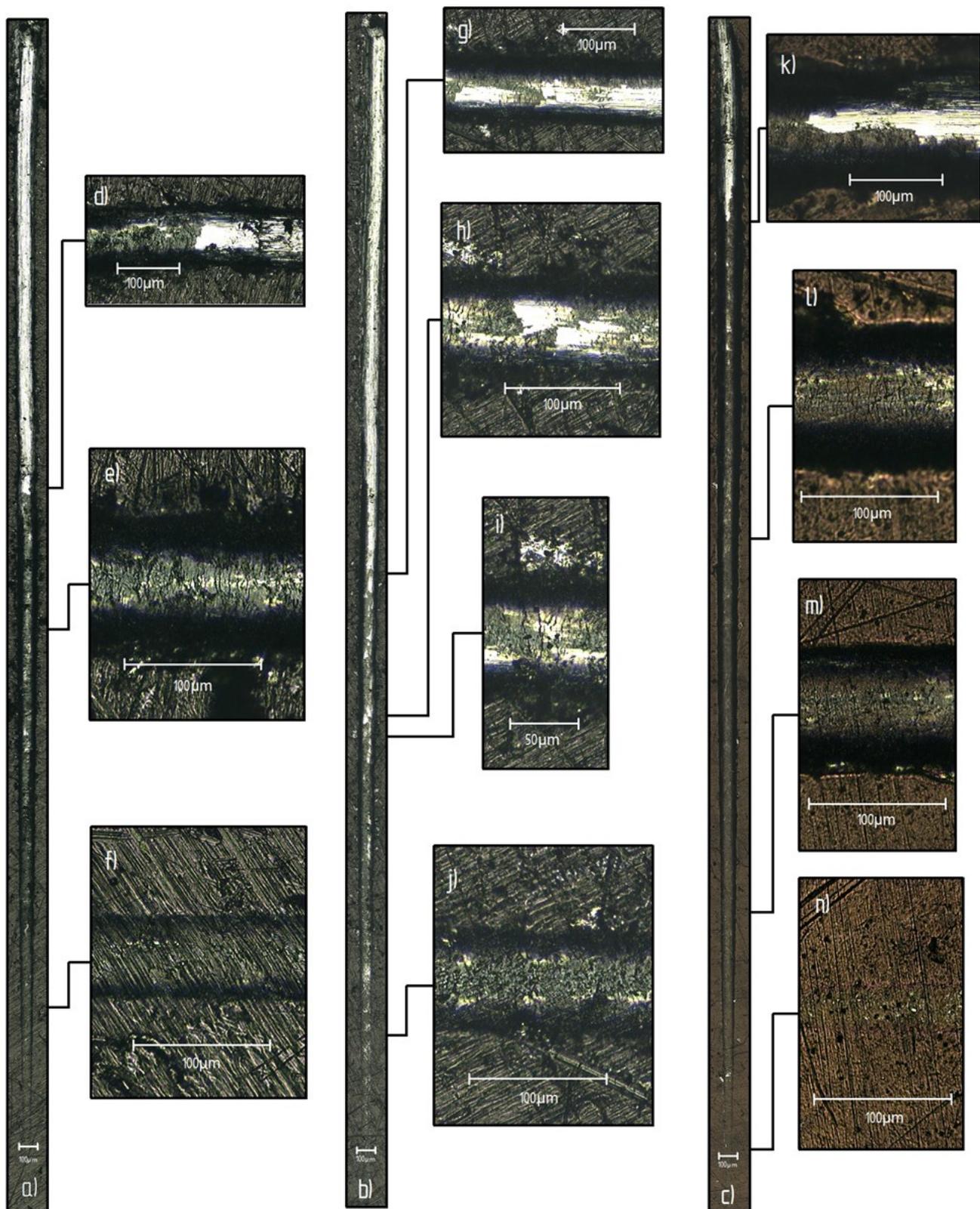


Fig. 3. Scratching test with Rockwell's indenter; a – scratching sign of AlTiN coating; b – scratching sign of TiAlN coating; c – scratching sign of TiAlN/TiSiN coating; d, g, h, k – surface of total coating rupture; e, i, l – surface of transverse fracturing caused by adhesive wear of coating; f, j, n – initial decohesion surface of coating material; m – transition from TiAlN to TiSiN coating.

7 Conclusions

In this study, AlTiN, TiAlN and TiSiN coatings were deposited on titanium grade 2. The surface roughness, nanohardness, as well as adhesion of the coatings were evaluated. According to the results provided, the following conclusions can be drawn:

- Modification of the surface layer of titanium materials using PVD magnetron sputtering, with studied nitride materials, allows for application in biomedical implants. Studies have shown that their use significantly improves exploitation properties, such as hardness and abrasion resistance compared with pure technical titanium grade 2.
- Application of analyzed coatings on titanium grade 2 increased the hardness of substrate surface layer by about 7 times, and the effective Young's module by 3 times.
- Based on conducted studies, similar hardness of analyzed coatings on titanic substrate was observed. Relatively great dispersion of test results on nanohardness does not enable explicitly to assess which coating is the hardest. Large disparity in results can be caused by too big surface roughness on tested samples. It is necessary to consider further research on more precisely polished samples.
- Hybrid coating TiAlN/TiSiN presented much better adhesion properties to the substrate as compared to the TiAlN and AlTiN.
- Friction coefficients in scratching tests are presented in the following order: AlTiN > TiAlN/TiSiN > TiAlN.

References

1. Q. Yao, J. Sun and others, *Vacuum*. **142**, 45-51 (2017)
2. M. Tarnowski, K. Kulikowski and others, *Diam. Relat. Mater.* **75**, 123-130 (2017)
3. P. Yi, L. Peng and others, *Mater. Sci. Eng. C*. **59**, 669-676 (2016)
4. H. Wang, R. Zhang, *Ceram. Int.* **41**, 11844-11851 (2015)
5. W.C. Oliver, G.M. Pharr, *J. Mater. Res.* **19**, 3-20 (2004)
6. M. Łępicka, M. Grądzka-Dahlke, D. Pieniak, K. Pasierbiewicz, A. Niewczas, *Wear*. **382-383**, 62-70 (2017)
7. A.R. Bushroa, H.H. Masjuki and others, *Surf. Coat. Tech.* **206**, 1837-1844 (2011)
8. Wo P.C., Munroe P.R. and others, *Mater. Sci. Eng. A*. **527**, 4447-4457 (2010)
9. Deng Y., Tan Ch. And others, *Ceram. Int.* **43**, 8721-8729 (2017)
10. Chen J., Li H. and others, *Surf. Coat. Tech.* **308**, 289-297 (2016)
11. B. Surowska, J. Bieniaś, M. Walczak, K. Sangwal, A. Stoch, *App. Surf. Sci.*, **238**, 288-294 (2004)
12. J. Bieniaś, B. Surowska, A. Stoch, H. Matraszek, M. Walczak, *Dent. Mater.* **25**, 1128-1135 (2009)