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The influence of the zirconium sublayer thickness on the surface microstructure of the magnetron ZrN coatings

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Abstract. The results of investigations the microstructure of ZrN coating with a thickness of about 3 μm obtained magnetron sputtering, are presented. The difference of the coatings is in the thickness of the zirconium underlayer: 250, 560 and 750 nm. The surface microstructure was investigated by profilometry, scanning electron microscopy (SEM) and atomic force microscopy (AFM). The dependences in a grain size, a roughness, the number and size of microparticles of the coating on the underlayer thickness are established. The mechanical characteristics of the coatings (microhardness and elasticity modulus) are determined.

1. Introduction

Modern materials science is actively using processes that provide the required microstructure of structural materials, including the formation of nanostructures, the use of modifiers and additives [1–3]. Hard coatings are one of the effective ways to improve the mechanical and tribological properties of the surface of machine parts [4–6]. ZrN PVD coatings occupy a special place among the protective coatings from transition metal nitrides because of a favorable combination of mechanical properties under conditions that require high heat resistance [7–9]. ZrN is a biologically inert compound and can be applied for a medical instruments. The coatings applied in the modern technology should be characterized by a complex of different properties. For protective coatings deposited on parts of machines or tools, these are most often tribological characteristics that largely depend on the surface microstructure: the size of microparticles (or the microdroplet phase), grains, the size of phases on the surface [4]. The main structural features of arc deposited nitride coatings are microparticles ranging in size from 0.5 to several μm [5, 6] and grains (crystallites) of the coating. Together, they affect the surface roughness, which is important both for tribocontact and for medical applications of the coatings. Microparticles can be very important for tribological coatings because they can involved in the formation of a surface modified layer that is actively working in friction processes, especially under the conditions of the so-called “green” treatment without the use of coolant. On the other hand the reduced surface roughness of the coating helps it not to overgrow with biological cells upon contact with tissues [10]. It is rather for description of cathodic arc evaporation. Here we have other deposition technology – magnetron sputtering, which is characterized by smooth surface without surface defects. Due to it I crossed above sentences. In addition to the numerous deposition parameters, the thickness of the underlayer is a factor capable of influencing the morphology of the surface of the working coating under other equal conditions. The microstructure of the under layer of multilayer coatings largely determines the morphology of the subsequent layer and affects its mechanical properties [11–14]. The surface of the underlayer is important for the formation of the coating since it creates additional nucleation centers during the formation of the subsequent working layer.

The method for versatile characterization of the coating surface is an AFM. AFM is the technique to simultaneous examination the different surface phenomena, such as roughness [10, 15], morphological surfaces after mechanical or chemical treatment [3, 16, 17], friction test [18], phases distribution [1, 2]. AFM provides a multi-scale (from scanning areas of 100 x100 μm to 100x100 nm and less) surface visualization, allowing micron-sized microparticles, submicron and nanometer grains of a smooth surface to be studied, and various phases can be identified among them by the properties contrast. AFM allows to determine not only the diameter of the particles, but also their height. The aim of the work is the investigation of the influence of the zirconium underlayer thickness on the height and diameter of surface defects, roughness and the grain size of ZrN magnetron sputtered coatings. The thickness of the zirconium underlayes is 250, 560 and 750 nm.

2. Experimental details

The ZrN coatings with a thickness of about 3 μm were deposited on the hardened HS6-5-2 steel substrates with a diameter of 32 mm, polished to Ra = 0.02 μm, using a reactive magnetron sputtering system with a 100 mm in diameter Zr targets. The time of the Zr sublayer deposition was 1.5, 3 and 4.5 min, which made it possible to obtain the sublayer thicknesses of 250, 560, and 750 nm. The flow rate of nitrogen in the vacuum chamber was 4 cm^3/min at a bias voltage on the substrate of –10 V.

A Mitutoyo profilometer was applied to determine the roughness of the coatings. The test was performed five times for one sample.

The surface investigation of the coatings was carried out using Dimension FastScan atomic-force microscope (Bruker, USA) in the PeakForce Tapping QNM (Quantitative Nanoscale Mechanical Mapping) mode using standard silicon cantilevers of MPP-12120-10 type (Bruker, USA). The particles distribution by diameter with the specification of the height boundary conditions of the particles was performed using the NanoScope Analysis software via the application function Particle Analysis. The images of three points were obtained and analyzed on each sample. Every point consisted the fields of 60x60, 30x30 and 10x10 μm. When analyzing a field of 30 μm, the largest particles, which already participated in the calculation of the average height in the field of 60 μm, were excluded. Similarly, particles on the 10 μm field, which participated in the calculation of 30 and 60 μm fields, were excluded.

The microhardness (H) and the elasticity modulus (E) were measured by Hysitron 750 Ubi nanoindenter (US) via the indentation of a diamond Berkovich indenter with a curvature radius of 200 nm and load of 10 mN into the coating surface. The tip radius was calibrated via indentation into a calibration melted-quartz sample. H and E were calculated using Oliver–Pharr formula from the 60 experimental curves of continuous recording of the applied load – indentation depth.

3. Results and discussion

The SEM images (figure 1) enable the comparative microstructural characterization of ZrN coatings deposited at different sublayer thickness. The surface of all coating is very smooth even for magnetron sputtered coatings. The roughness determined by the profilometer on the distance of 3 mm is 46–85 nm (figure 2(a)). The small number of macroparticles are embedded on the surface of all coatings (figure 2(b)). The size of the most microparticles is less than 1 μm. On the SEM images of ZrN coatings the smooth surface is visible. The particle diameter on the coating surface determined by the AFM ranged from 410 nm to 2.6 μm, the height from 21 nm to 275 nm. The size of individual grains in coatings is from 90 to 120 nm (figure 3). It has been established that most of the characteristics have a parabolic dependence on the thickness of the zirconium underlayer, while the lateral characteristics – the diameter of microparticles and grains – have a minimum at an underlayer thickness of 560 nm, and the height parameters – roughness, the height of particles – a maximum at the same thickness of the underlayer (figure 4). It is shown that measurements made in fields of different sizes are sensitive to varying degrees to changes in the thickness of the sublayer. The most sensitive to the changes in the microstructure due to the sublayer thickness is the size of the scanning field 10x10 microns. In addition, the height of the microparticles changes more strongly with an increase in the thickness of the sublayer than the diameter. The microstructure of the smooth surface of ZrN coatings obtained at different thicknesses of the sublayer were examined, and the differences in their morphology were revealed. The coating obtained on the 250 nm sublayer had the rounded grains of 130–190 nm in diameter in the surface structure, dominant in height, and grains of 45–75 nm in diameter, forming fragments of lines and chains. The average grain size in the coating obtained on the 250 nm sublayer was 100 ± 55 nm. With an increase in the thickness of the sublayer to 560 nm, in the structure, not separate grains, but entire chains and lines are already distinguished in height. The average grain size in the coating obtained on the 560 nm sublayer was 90 ± 40 nm. An increase in the thickness of the sublayer to 750 nm led to the formation of a different relief type – the grain size increased significantly. The average grain size in the coating obtained with the 750 nm sublayer was 120 ± 50 nm. The surface roughness of samples with sublayers 250, 560 and 750 nm thick on the area 2x2 μm^2 was 6.3, 7.3, and 7.7 nm, respectively.

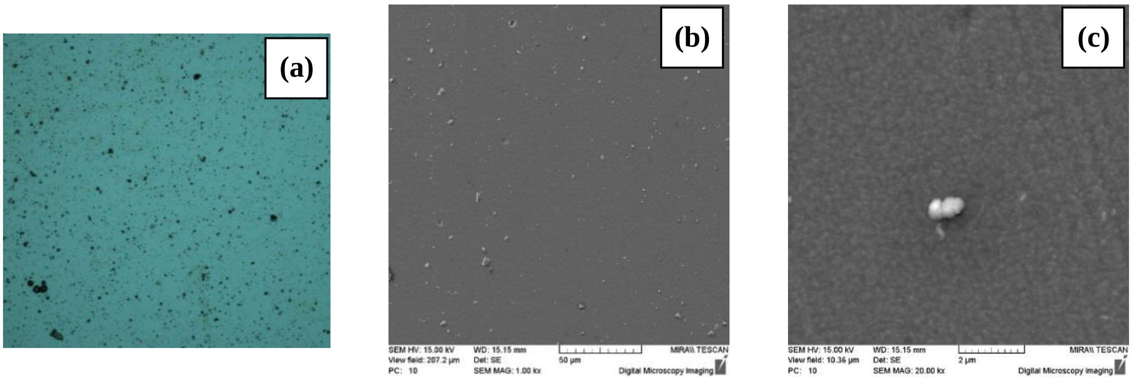

Figure 1. Micrograph of ZrN coating morphology deposited with the 560 nm underlayer thickness: **(a)** – optical image 700x700 μm; **(b)** – SEM, magnification of 1000x; **(c)** – SEM, magnification of 20000x.

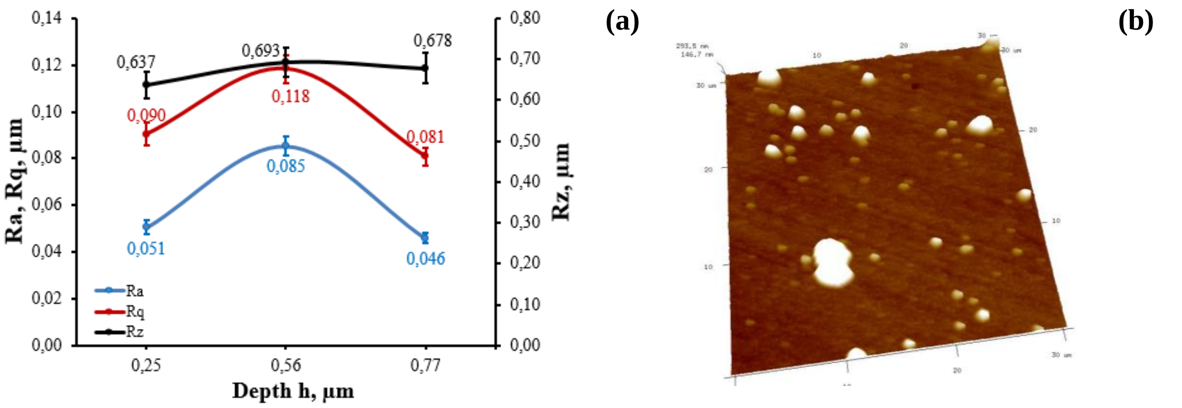

Figure 2. The roughness Ra, Rq and Rz determined on the distance of 3 mm of ZrN coatings deposited on the sublayer of different thickness **(a)** and AFM-topography of ZrN coatings, deposited on 250 nm Zr sublayer, scanned area 30x30 μm^2 **(b)**.

The values of the elasticity modulus E, defined by nanoindentation, were 314±14 GPa for coating with 250 nm sublayer, 310±21 GPa for coating with 560 nm sublayer, and 321±21GPa for coating with 770 nm sublayer. The values of microhardness were 29.3±2.4 GPa for coating with 250 nm sublayer, 27.7±3.5 GPa for coating with 560 nm sublayer, and 29.3±3.3 GPa for coating with 770 nm sublayer. Due to the standard deviation, these values are very close, however, both for E and H there is a minimum of values for the sublayer thickness of 560 nm. The change in the mechanical characteristics of the ZrN coating with the sublayer thickness correlates with the dependences of grains and microparticles on the sublayer thickness and does not obey the Hall–Petch relationship, in which lower crystallite sizes in the material correspond to higher properties.

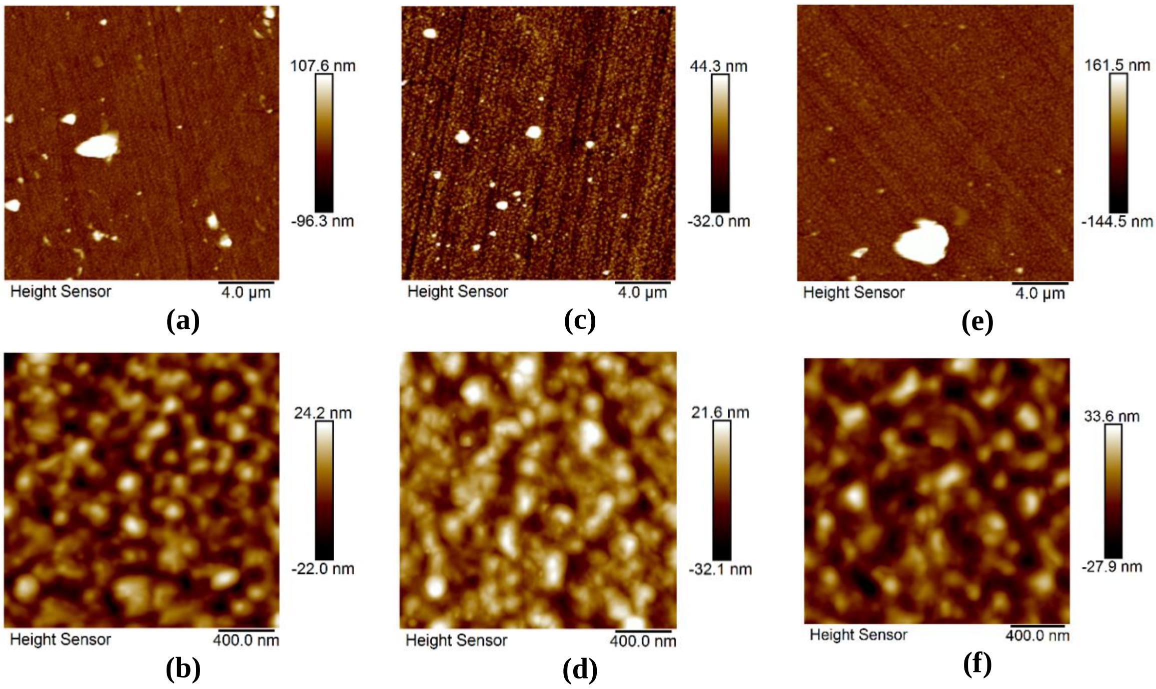

Figure 3. The AFM images of the surface of ZrN coatings, obtained by magnetron sputtering on the sublayer of different thickness: **(a)**, **(c)**, **(e)** – scanned area 20x20 μm^2, **(a)**, **(b)** – 250 nm, **(c)**, **(d)** – 560 nm, **(e)**, **(f)** – 750 nm.

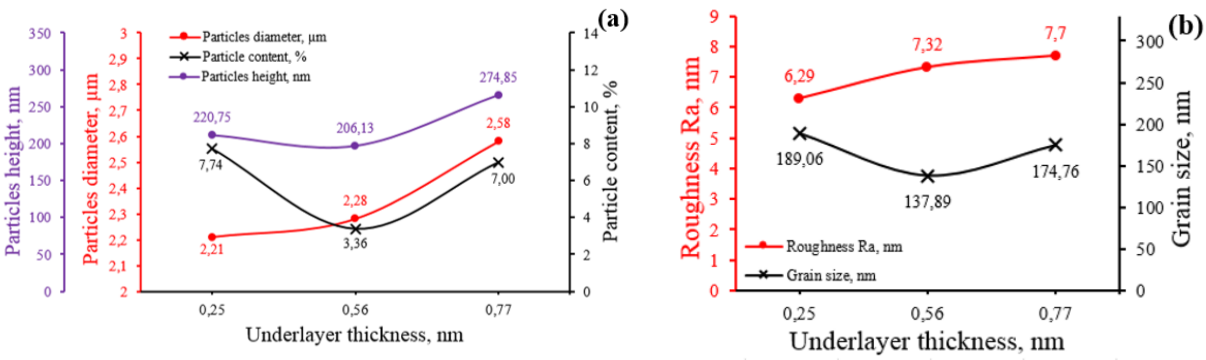

Figure 4. Influence of sublayer thickness of ZrN coatings on: **(a)** – diameter, hight and content of microparticles, **(b)** – surface grain size and roughness Ra on scanning area 2x2 μm^2.

4. Conclusions

The ZrN coatings with a thickness of about 3 μm with various sublayer thicknesses were obtained by the magnetron sputtering. Using AFM method the microstructure was revealed and the dependence of the surface roughness, diameter and height of microparticles, the content of microparticles and the grain size of the ZrN coating on the thickness of the zirconium sublayer were determined. It was found that the dependences of the microparticle diameter and roughness on the field of 2x2 μm are increasing, the dependence of the roughness at the distance of 3 mm with a maximum at 560 nm sublayer thickness, and the dependence of the microparticles content in %, the height of microparticles and crystallite sizes (grains) in the coating with a minimum at same thickness of underlayer. Thus, the surface roughness of the ZrN magnetron sputtered coating can be controlled by varying the thickness of the zirconium sublayer. The values of the elasticity modulus E of the coatings, determined by

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nanoindentation, were 310–321 GPa, microhardness H 27.7–29.3 GPa. The dependences of the mechanical characteristics on the thickness of the underlayer correlate with the dependences of the grain size, of the content of microparticles in % and the height of the microparticles on the thickness of the underlayer.

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References
[1] Chizhik S A, Kuznetsova T A, Khudolei A L, Komarova V I and Vasilenko M S 2013 *Journal of Engineering Physics and Thermophysics* **86**(5) 1008–19
[2] Zhdanok S A, Sviridenok A I, Ignatovskii M I, Krauklis A V, Kuznetsova T A, Chizhik S A and Borisevich K O 2010 *Journal of Engineering Physics and Thermophysics* **83**(1) 1–5
[3] Vityaz P A, Komarov A I, Komarova V I and Kuznetsova T A 2011 *Journal of Friction and Wear* **32**(4) 231–41
[4] Musil J 2000 *Surface and Coating Technology* **125** 322–30
[5] Warcholinski B, Gilewicz A, Kuprin A S, Tolmachova G N, Ovcharenko V D, Kuznetsova T A, Zubar T I, Khudoley A L and Chizhik 2018 *Vacuum* **156** 97–107
[6] Warcholinski B and Gilewicz A 2011 *Wear* **271**(11–12) 2812–20
[7] Warcholinski B, Kuznetsova T A, Gilewicz A, Zubar T I, Lapitskaya V A, Chizhik S A, Komarov A I, Komarova V I, Kuprin A S, Ovcharenko V D and Goltvyanytsya V S 2018 *Journal of Materials Engineering and Performance* **27**(8) 3940–50
[8] Kuznetsova, T A, Lapitskaya, V A, Chizhik, S A, Warcholinski B, Gilewicz A and Kuprin A S 2018 *IOP Conference Series: Materials Science and Engineering* **443** 012017
[9] Warcholinski B, Gilewicz A, Kuprin A S, Tolmachova G N, Ovcharenko V D, Kuznetsova T A, Lapitskaya V A and Chizhik S A 2019 *Journal of Friction and Wear* **40**(2) 163–70
[10] Melnikova G B, Petrovskaya A S, Kuznetsova T A, Chizhik S A, Zykova A, Safonov V and Yakovin S 2019 *International Journal of Nanoscience* https://doi.org/10.1142/S0219581X19400787
[11] Kuznetsova T A, Lapitskaya V A, Chizhik S A, Uglov V V, Shimanskii V I and Kvasov N T 2018 *IOP Conference Series: Materials Science and Engineering* **443** 012018
[12] Kuznetsova T A, Zubar T I, Lapitskaya V A, Sudilovskaya K A, Chizhik S A, Uglov V V, Shimanskii V I and Kvasov N T 2019 *Journal of Surface Investigation* **13**(3) 408–11
[13] Lapitskaya V A, Kuznetsova T A, Chizhik S A and Rogachev A A 2018 *IOP Conference Series: Materials Science and Engineering* **443** 012020
[14] Lapina P A, Mitrin B I, Kuznetsova T A and Lapitskaya V A 2018 *MATEC Web of Conf.* **226** 03031
[15] Ulyanova T M, Titova L V, Medichenko S V, Zonov Yu G, Konstantinova T E, Glazunova V A, Doroshkevich A S and Kuznetsova T A 2006 *Crystallography Reports* **51**(Suppl 1) S144–49
[16] Kuznetsova T A, Chizhik S A and Khudoley A L 2014 *Journal of Surface Investigation* **8**(6) 1275–85
[17] Lapitskaya V A, Kuznetsova T A, Chizhik S A, Sudzilouskaya K A, Kotov D A, Nikitiuk S A and Zaparozhchanka Y V 2018 *IOP Conference Series: Materials Science and Engineering* **443** 012019
[18] Kuznetsova T A, Zubar T I, Lapitskaya V A, Sudzilouskaya K A, Chizhik S A, Didenko A L, Svetlichnyi V M, Vylegzhanina M E, Kudryavtsev V V and Sukhanova T E 2017 *IOP Conference Series: Materials Science and Engineering* **256** 012022