

Tribological properties of ZrN coatings deposited by magnetron sputtering in reactive and non-reactive mode

N. Giagkas^a, I. F. Micu^a, S. Vizireanu^b, N. Vasile^b, B. I. Biță^b, V. Sătulu^b, S. Mihai^a,
A. M. Manta^a, D. L. Cursaru^{a,*}

^a*Petroleum-Gas University of Ploiești, Romania*

^b*National Institute for Laser, Plasma and Radiation Physics, Romania*

Zirconium and zirconium nitride coatings were deposited via magnetron sputtering by using high-purity zirconium or zirconium nitride targets. As a particularity, the zirconium nitride coatings were deposited by using a ZrN target via non-reactive mode or by using a Zr target via reactive technique, in argon/nitrogen environment. Depending on the time deposition, coatings with different thicknesses (200, 500 and 1000 nm) have been obtained. Chemical and phase composition, thickness of the coating and morphology of the surfaces were investigated by highly sensitive X-ray photoelectron spectroscopy (XPS), energy dispersive X-ray spectroscopy (EDX), scanning electron microscopy (SEM) and X-Ray diffraction (XRD). The wear tests have been performed by High Frequency Reciprocating Rig (HFRR). The wear scar diameters decrease with an increase of coatings thickness, while the friction coefficient for the coatings with 500 nm thickness revealed the lowest values for friction coefficients, for all type of coatings.

(Received January 21, 2021; Accepted May 23, 2021)

Keywords: Zirconium coating, Zirconium nitride coating, Magnetron sputtering, Reactive deposition, Non-reactive deposition

1. Introduction

The introduction of PVD coatings for cutting tools is one of the most interesting applications in the use of modern coating technology in the last 30 years. The first commercial PVD-coating material used for cutting tools was titanium nitride (TiN) in the early 80's, and by the 90's most cutting tools were already PVD coated, especially in applications where sharp edges were required (e.g. threading, milling, fine milling, etc.) and cutting applications that have a high demand for a hard cutting edge (e.g. drilling). For many years, the most used type of coating was TiN. Due to its excellent mechanical properties and biocompatibility, it has also been successfully used in the medical industry [1].

Recently, many studies were focused on testing more suitable coatings for the same and even more special applications. It is already being a decade since zirconium, zirconium nitrides and zirconium carbonitrides coatings, started to become attractive due to their interesting properties such as hardness, corrosion resistance, tribological performance and optical properties [2-4].

Zirconium is a silver metal, hard, crystalline with a high melting temperature (1852 °C) and a very high boiling point (4377 °C). The high boiling point restricts the tendency of droplets to form during the evaporation of the "non-conducted" arc. Therefore, thin films of zirconium condensate and its chemical compounds, such as zirconium (ZrN), tend to be more fluid than those of less refractory metals or metalloids.

Many additional factors that influence droplet emissions, such as thermal conductivity, cooling efficiency (which influences the average temperature of the emission surface), the configuration of the deposition system, and the residual surface coating with oxides, nitrides, or carbides. This factor is defined by the ratio of the chemical reaction rates of the cathode material

* Corresponding author: dianapetre@yahoo.com

with the reactive gases present on the surface, compared to the pure cathode metal and the rate of removal of the reacted surface film ("surface poisoning").

The melting temperature of ZrN in bulk is 2980 °C, only slightly higher than that of TiN, which is 2930 °C, and the hardness in bulk is ~ 1500 HV, lower than that of TiN in bulk (~ 2000 HV). It has been shown that the hardness of ZrN films deposited by the PVD method tends to be higher than that of TiN films. For those reasons, zirconium nitride (ZrN) films manufactured by cathode deposition are usually finer than, for example, titanium nitride films deposited on tool surfaces under similar conditions and have a higher resistance to oxidation.

ZrN is a slightly more expensive coating than TiN or TiCrN, but this difference is often offset and justified by its higher cutting performance, especially in finishing operations. It is recommended in applications where superior lubrication is required. The most common application is aluminum processing, although wood processing and copper processing are among the applications in which it has demonstrated high performance.

Zirconium is a strongly reactive metal, as evidenced by its standard potential of 1.53 V compared to the normal hydrogen electrode (NHE) at 25 °C. For comparison, the potential for titanium, chromium, iron and nickel is 1.53; 0.74; 0.44 and 0.25 V. Zirconium owes its high corrosion resistance due to its strong affinity for oxygen. In a substance that contains oxygen from the environment, such as air, water or carbon dioxide, zirconium reacts spontaneously with oxygen at ambient temperature and forms a protective oxide layer on the surface. This layer protects the base metal from chemical and mechanical action at temperatures up to about 350 °C. As a result, zirconium resists the attacks of most acids, salt solutions, alkaline solutions and organic media. Zirconium is very suitable for handling reducing acids, in which most alloys have great difficulty in forming protective films. However, under extreme conditions, such as hydrofluoric acid, concentrated sulfuric acid and certain organic halides, no passive oxide could not easily form, therefore zirconium is not suitable for handling these media. Additionally, zirconium is susceptible to localized corrosion, and SCC (Stress Corrosion Cracking) in chlorine solutions, under oxidative conditions [5, 6].

Most of the studies reported the synthesis of zirconium compounds by CVD techniques [7-11] or by PVD techniques such as arc evaporation [12, 13], magnetron sputtering [14] or magnetron sputtering combined with ion implantation [15]. In our study, ZrN coatings have been synthesized by magnetron sputtering by using ZrN targets for the non-reactive deposition and Zr targets for the reactive deposition.

To investigate the tribological properties of the coatings, different friction experiments (ball on disk) were performed in the presence of a mineral base oil used as lubrication environment. The results of tribological tests performed by using disks coated with ZrN deposited in a reactive or non-reactive mode have been compared to those obtained for disks coated with Zr deposited in similar condition with zirconium nitrides.

2. Materials and experimental methods

For the tribological investigations, three types of coated disks have been used, Zr (obtained in a non-reactive technique) and ZrN deposited by a magnetron sputtering process at low pressure (obtained in a reactive and non-reactive technique). The tribological investigations consists of HFRR and Pin on Disk C.S.M tribometer procedures of various thicknesses of ZrN deposited on steel disks and the results were compared with those obtained for Zr coatings.

2.1. Materials

2.1.1. Synthesis and characterization of Zr and ZrN coatings

Disks of stainless-steel of AISI-E 52100/535A99 (with 10 mm diameter, roughness of $R_a=0.020 \mu\text{m}$ and a hardness of RC 76-79) were used as substrate for deposition of coatings. Before mounting in the deposition chamber, the samples were cleaned with acetone and isopropanol. The samples were positioned on a rotating substrate holder at 120 mm from the magnetron Zr and ZrN (2" in diameter, 99.99% purity) targets. Both targets of Zr and ZrN were

purchased from CRM MATERIAL CO from China (<http://www.china-raremetal.com>). The Zr coatings were deposited in non-reactive atmosphere (argon plasma), while ZrN was deposited in reactive environment (argon/nitrogen) from Zr target or in non-reactive plasma from Zr/N target.

Before the deposition of the non-reactive Zr or ZrN coatings, the vacuum chamber was pumped down to a base pressure of $2,75 \times 10^{-5}$ mbar and then was filled up with Ar up to $5,22 \times 10^{-3}$ mbar working pressure. The deposition parameters are the following: radiofrequency power 100 Watt, the Ar flow 50 sccm, the deposition time was varies in order to obtain coatings with different thicknesses (200, 500 and 1000 nm). After the end of the deposition, the sample was kept in a vacuum for 'relaxation' for 10 min, and the flow rate of Ar was increased to 100 sccm to accelerate cooling. For the reactive ZrN coatings, the deposition parameters were similar to the non-reactive procedure with the same Zr target, but the nitrogen is introduced from the Ar/N₂ magnetron plasma (in mass gas flow ratio 9:1 sccm).

3. Results and discussions

3.1. SEM investigations

The morphology of coatings was investigated by SEM (FEI S Inspect working at 20 kV) and the images are depicted in Fig. 1. For Zr coating with 500nm thickness, the surface of the disk is evenly covered without interruptions or gaps.

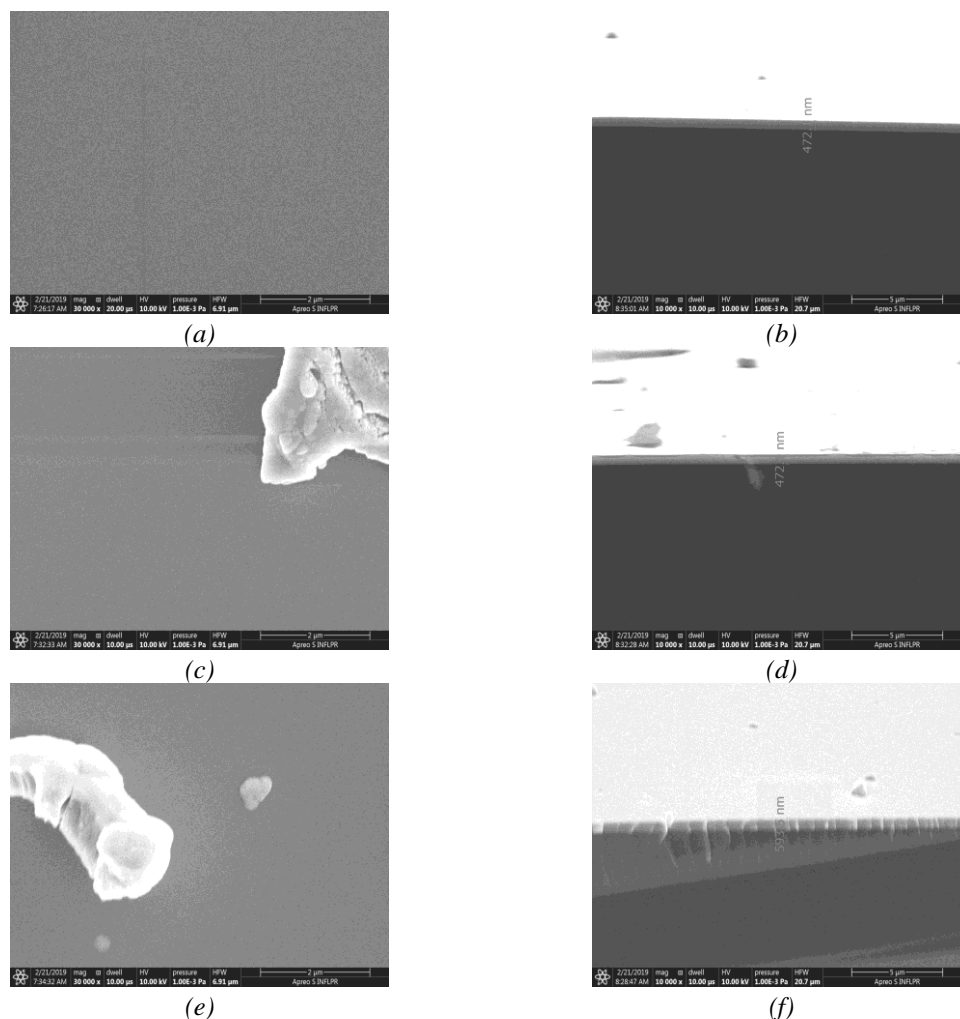


Fig. 1. Morphology of (a) Zr500, top view of the substrate (b) Zr500 cross section (c) ZrN500 non-reactive, top view of the substrate (d) ZrN 500 non-reactive cross section, (e) ZrN 500 reactive, top view of the substrate (f) ZrN reactive500 cross section,

In the image representing the cross-section (Fig. 1b) it can be noticed that the thickness of the Zr substrate is 472 nm which is very close to the desired thickness of 500 nm.

For the non-reactive ZrN 500 nm sample (Fig. 1c), the deposition test shows that the film is continuous and uniform, but some grains can also be observed. These may be the result of contamination of the sample during deposition in the magnetron or could be some scraps from the cleaning process of the samples. For the reactive ZrN coating, from the cross-sectional image (Fig. 1f), it is observed that the thickness of the layer deposited by ZrN is 593nm, which is substantially higher than the proposed thickness of 500nm. The most likely reason for this is that the sample was kept longer in the magnetron after the completion of the experiment, which resulted in the deposition of a thicker layer. Also, the coating shows few dirt particles on the surface.

3.2. EDX spectroscopy

The formation of Zr and ZrN substrates was confirmed by EDX investigations, performed on different areas of the coating surface.

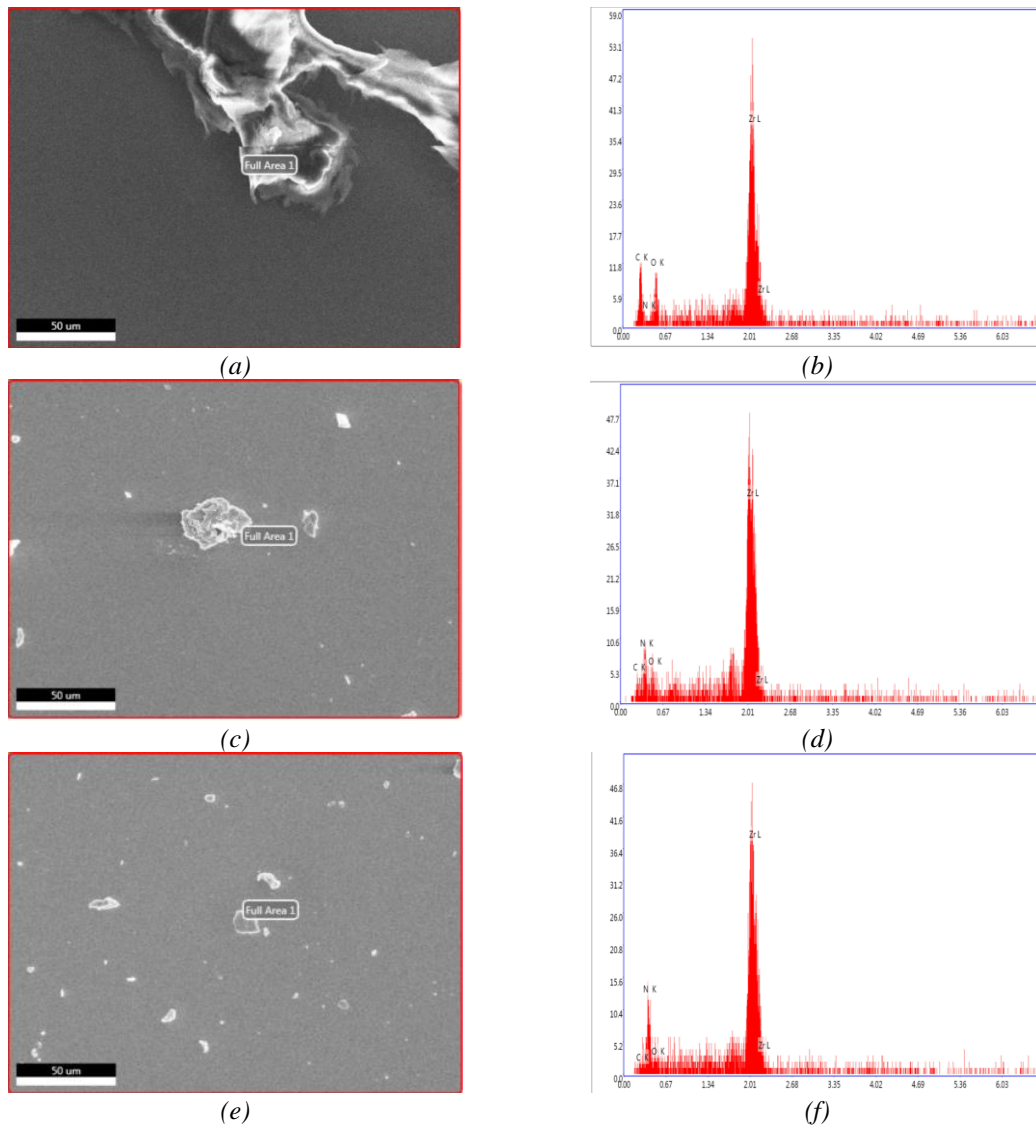


Fig.2. EDX spectroscopy of (a) Zr500, analysis area (b) Zr500 corresponding peaks (c) ZrN500 non-reactive, analysis area (d) ZrN 500 non-reactive corresponding peaks, (e) ZrN 500 reactive, analysis area (f) ZrN reactive500 corresponding peaks

Table 1. EDX results.

Element	Zr	C	N	O
Sample	% Atomic	% Atomic	% Atomic	% Atomic
Zr	42.88	40.68	0.64	15.8
ZrN non-reactive	54.15	7.43	28.86	9.56
ZrN reactive	44.95	7.86	40.57	6.62

The results depicted in Fig. 2 and in Table 1 prove the presence of Zr and N₂ on the coating. While the atomic percentage of zirconium varies within a tiny limit, from 42.88 atomic % corresponding to Zr coating, to 54.15 atomic % corresponding to ZrN non-reactive, the nitrogen atomic % varies in a wide range, from 0.64 (Zr coating) to 40.57 (ZrN reactive). A higher nitrogen content for ZrN coatings is explainable based on the nitrogen from the target and the nitrogen flow discharged in the vacuum chamber. The carbon content can be explained by contamination of the samples during deposition procedure. The carbon contaminant may lead to formation of zirconium carbonitride films, which can be evidenced by X-ray diffraction investigations.

3.3. XRD diffraction

XRD spectra for Zr and ZrN coatings are depicted in Fig. 3. The profiles of the specimens are dominated by the peak at 32° that indicate a polycrystalline structure with a (111) preferred orientation being specific to the monoclinic cubic phase of zirconium, as well as the peak at 45°.

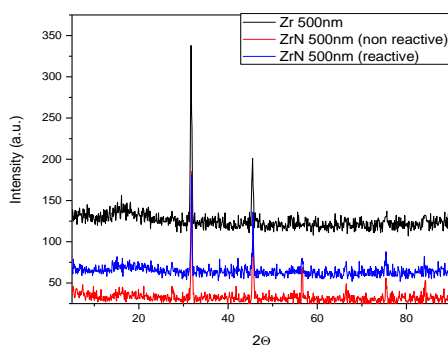


Fig. 3. XRD diffraction of Zr500, ZrN500 non-reactive and ZrN 500 reactive.

For zirconium nitrides spectra, it was noticed the presence of secondary peaks recorded at 57° that indicates the presence of Zr₃N₄ (220), while the peak at 75° indicates the presence of ZrN (222). X-ray diffractograms show that the film retains its epitaxial characteristics for the thicknesses of the coatings up to 1000 nm, without the appearance of other phases or orientations, and the network parameters do not show any clear evolution with increasing of the coating thickness.

3.4. XPS spectroscopy

Fig. 4 (a, b, c) presents an XPS survey (general) spectra of the Zr and ZrN coated samples.

These XPS spectra reveal zirconium, nitrogen, oxygen and few percentage of carbon (while carbon is missing in the depth profile).

For all XPS spectra, the binding energy data were referenced to the center after the aliphatic C1s peak at 284.8 eV. The relative concentration of Zr, N and O atoms were estimated using Advantage software XPS apparatus (Thermo Fisher Scientific) and the results for each sample and the results were given in Table 2.

Table 2. Chemical composition of the surface region of coatings in relative atomic percent (at.%).

Spectra	Samples		
	Zr	ZrN non-reactive	ZrN reactive
Zr 3d	27.0	28.8	28.4
O 1s	68.1	51.5	50.8
N 1s	4.9	19.7	20.8

The peak regions of zirconium Zr3d, N1s and O1s were investigated in detail and peak positions and intensities have been estimated from high resolution spectra. The deconvolution of the peaks (not presented in this paper) shows us the element species in different chemical bonding to their neighbours. The deconvoluted zirconium peak was taken with three groups of different chemical species: metallic zirconium (178 eV), zirconium in bonded to nitrogen environment ZrN (182 eV) and oxidic ZrO₂ (184 eV).

The N1s peak can be composed by two species due to the zirconium nitrides (396 eV for ZrN) and 399 eV for Zr₃N₄.

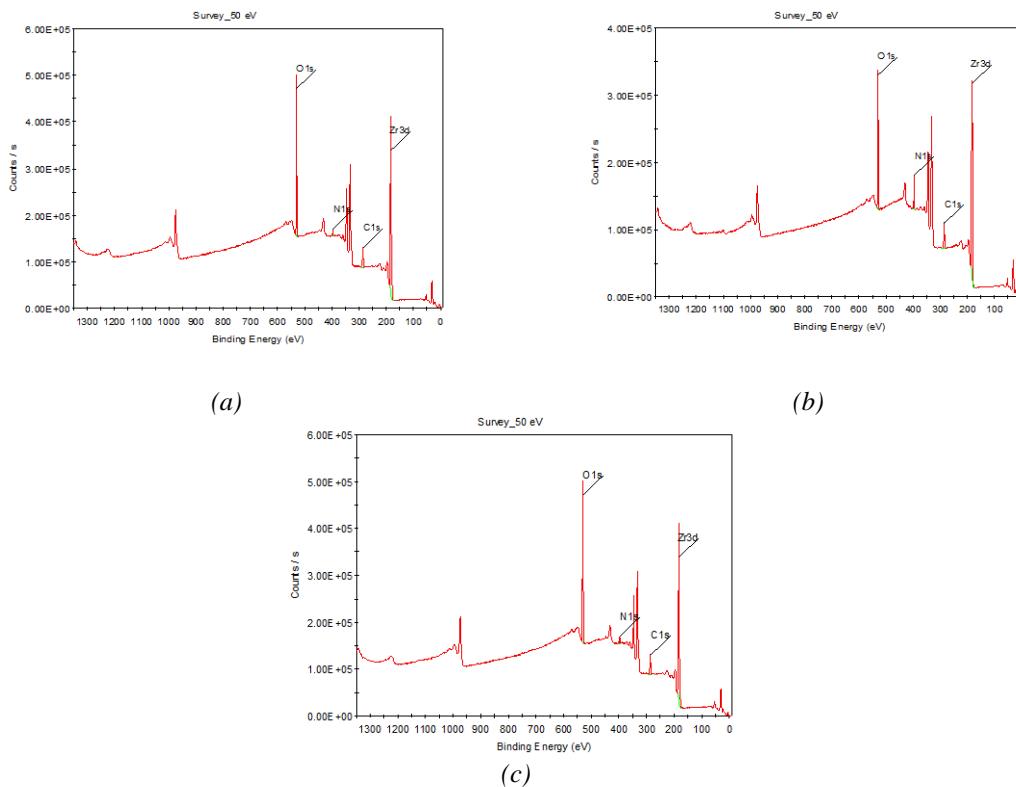


Fig. 4 . XPS spectra for Zr500, ZrN500 non-reactive and ZrN 500 reactive.

The high-resolution of O1s XPS peaks indicate that two Zr species are present: ZrO_2 and ZrO_xN_y at binding energies 530 eV respectively 531eV [16]. The results show that all three coatings contain zirconium metallic and almost zirconium oxide and zirconium nitride.

3.5. Tribological investigations

The tribological properties of coatings were investigated by using a High Frequency Reciprocating Rig (HFRR) equipment, which is a tribosystem from class 1, that contains triboelements such as a sliding steel ball AISI-E 52100/535A99 (with a roughness of $Ra=0.050\mu m$ and a hardness of RC 58-66) and steel disk AISI-E 52100/535A99 (with 10 mm diameter and a roughness of $Ra=0.020\mu m$ and a hardness of RC 76-79). The test consists of a steel ball rubbing against the steel coated/uncoated disk in the presence of 2 ± 0.2 ml lubricant. The lubricant selected for our investigations is a mineral base oil (SAE 20) [17]. Its physical-chemical characteristics are presented in table 3. The HFRR investigations were performed at a frequency of 50 ± 1 Hz, 1000 μm stroke, 200 ± 1 g load and $60\pm 2^\circ C$ (according to ASTM D-6079), while the relative humidity was kept between 40 and 60% and the ambient temperature between 24 and $26^\circ C$.

Table 3. Physical-chemical properties of mineral base oil (SAE 20).

Properties	SAE 20	Methods
Density ($20^\circ C$, kg/m^3)	880	ASTM D-1298
Kinematic viscosity ($40^\circ C$, cSt)	31.80	ASTM D-445
Kinematic viscosity ($100^\circ C$, cSt)	5.9	ASTM D-445
Viscosity index	130	ASTM D-2270
Flash point ($^\circ C$)	>210	ASTM D-92
Pour point, ($^\circ C$)	-15	ASTM D-97
Copper corrosion (at $100^\circ C$)	1a	ASTM D-130
Acid value (mg KOH/g)	0.12	ASTM D-974

During ball on disk friction experiments in the presence of lubricant, a tribofilm is formed to protect the surfaces. By using a lubricant with inferior lubricating properties, the tribofilm can be destroyed much faster and the surfaces are no longer protected against the effect of friction, the wear. There are two possibilities to avoid this undesirable situation: one is to improve the antiwear properties of lubricant by adding specific antiwear additives, while the second possibility is the enhancement of the surfaces. Our investigations, were focused on improving the surfaces of the tribological system by deposition of zirconium and zirconium nitride coatings.

By tribological investigation it was possible to evaluate the effect of thickness of the coating and the type of coating on the wear, quantified as wear scar diameter imprinted on the steel ball, and friction coefficient. The effect of the wear scar diameter is shown in table 4, while the effect on the friction coefficient is presented in Fig. 5.

Table 4. Influence of the coating thickness on the wear scar diameter imprinted on the ball.

Coating thickness, nm	Wear scar diameter, μm		
	Zr	ZrN non-reactive	ZrN reactive
0	165	165	165
200	161	137	146
500	148	134	143
1000	143	124	140

By increasing the thickness of the coatings, it was observed a decreasing of the wear scar diameter for all three type of coatings, but the zirconium nitrate coating obtained via non-reactive

approach, was the most promising, while the wear scar diameters were the smallest for all 3 thicknesses. These results are in agreement to SEM investigations (Fig. 1), the wear being more pronounced for ZrN coating obtained via reactive mode, while this coating presented discontinuities on the surface.

Although, there are small differences between friction coefficients recorded for different thicknesses and different coatings, the coating with a thickness of 500 nm, presented the lowest values for friction coefficients, for all type of coatings.

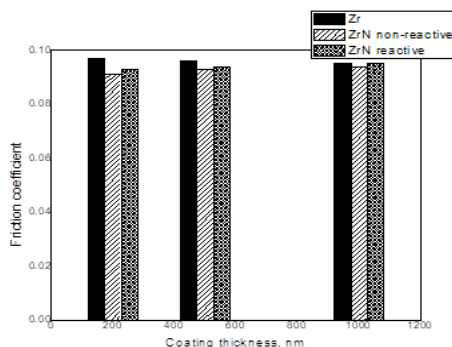


Fig. 5. Friction coefficients vs. thickness of the coatings.

4. Conclusions

Zirconium and zirconium nitride coatings with a thickness between 200-1000 nm, have been obtained by magnetron sputtering. The zirconium nitride coatings were obtained via reactive and non-reactive techniques. During the friction that occurred in a tribosystem, some conditions could favor the interruption of the tribofilm between the surfaces of the friction couple. By improving the surfaces, it is possible to overcome this undesired situation. In our study we investigate the influence of the synthesis method and the thickness of the coatings on the tribological properties, quantified as wear scar diameter and friction coefficient.

By increasing the thickness of the coatings, it was observed a decreasing of the wear scar diameter for all three type of coatings, but the zirconium nitride coating obtained via non-reactive approach, was the most promising, while the wear scar diameters were the smallest for all 3 thicknesses. For zirconium nitride coatings, the deposition method seems to have a strong influence on the tribological properties, as by the reactive technique, the surface of the coatings presented discontinuities that can amplify the wear effects. From the friction coefficient perspective, it was observed small differences between values recorded for different thicknesses and different coatings, but the optimum thickness seems to be 500 nm, because it demonstrated the lowest values for all type of coatings.

Acknowledgements

This work was supported by grants of the Romanian Ministry of Research and Innovation, CCCDI - UEFISCDI, in the frame of Nucleus Program INFLPR LAPLAS VI 16N/2021 and projects: no 80 PCCDI/2018 PN-III-P1-1.2-PCCDI-2017-0387 Emerging technologies for industrial valorization of 2D structures (graphene and non-graphene)-EMERG2Ind and no 271 PED/2020 PN-III-P2-2.1-PED-2019-4569 Cold plasma for fluoride retention improvement and biofilm modulation in dental application-PlasmaDent, within PNCDI III.

References

- [1] <https://www.pvd-coatings.co.uk/applications/>
- [2] S. Heinrich, S. Schirmer, D. Hirsch, J. W. Gerlach, D. Manova, W. Assmann, S. Mändl, *Surface & Coatings Tehnology* **202**, 2310 (2008)
- [3] A. Rizzo, M. A. Signore, L. Mirengi, D. Dimaio, *Thin Solid Films* **515**, 1486 (2006)
- [4] D. Jianxin, L. Jianhua, Z. Jinlong, S. Wenlong, N. Ming, *Wear* **264**, 298 (2008)
- [5] H. G. Rickover, L. D., Geiger, B., Lustman, U. S. Energy Research and Development Administration, Division of Naval Reactors; TID-26740 U.S. GPO Washington, DC, (1975)
- [6] T. L. Yau, R. C. Sutherlin, *Corrosion: Materials. ASM Handbook* **13 B**, Materials Park, OH: ASM International, 300 (2005).
- [7] J. Wöhle, A. Gebauer-Teichmann, K. T. Rie, *Surface & Coatings Technology* **661**, 142 (2001)
- [8] D. L. Cursaru, S. Vizireanu, S. Mihai, D. Ghiță, D. S. Stoica, Gh. Dinescu, *Digest Journal of Nanomaterials and Biostructures* **9**(3), 1105 (2014).
- [9] K. T. Rie, J. Wöhle, *Surface & Coatings Technology* **112**, 226 (1999)
- [10] D. L. Cursaru, D. Ghiță, S. Mihai, *Digest Journal of Nanomaterials and Biostructures* **9**(4), 1379 (2014).
- [11] L. Alberts, D. Boscarino, A. Patelli, V. Rigato, H. Ahn, K. T. Rie, *Surface & Coatings Technology* **169**, 388 (2003)
- [12] F. Hollstein, D. Kitta, P. Louda, F. Pacal, J. Meinhardt, *Surface & Coatings Technology* **142**, 1063 (2001).
- [13] M. Bălăceanu, M. Braic, V. Braic, G. Pavelescu, *Surface & Coatings Technology* **200**, 1084 (2005).
- [14] S. H. Yao, Y. L. Su, W. H. Kao, K. W. Cheng, *Material Letters* **59**, 3230 (2005).
- [15] E. Grigore, C. Rușeț, X. Li, H. Dong, *Surface & Coatings Tehnology* **204**, 1889 (2010)
- [16] Y. Yuan, J. Wang, S. Adimi, H. Shen, T. Thomas, R. Ma, J. P. Attfield, M. Yang, *Nature Materials* **19**, 282 (2020).
- [17] D. L. Cursaru, N. Giagkas, S. Vizireanu, S. Mihai, D. Matei, B. Biță, C. Stancu, A. M. Manta, I. Ramadan, *Digest Journal of Nanomaterials and Biostructures* **14**(4), 907 (2019).