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Deposition of carbonitride titanium coatings by magnetron sputtering and its effect on tribo-mechanical properties

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ABSTRACT
Metal parts in machinery often fail as a result of damage caused by wear and tear, resulting in the loss of functionality of the products. Thin film solid nitride coatings are used to improve the wear resistance and service life of parts and are considered to be effective. The article presents a brief overview of modern literature in the field of obtaining wear resistant coatings of titanium carbonitride by using magnetron sputtering. The review presents a detailed assessment of the scientific results obtained depending on the deposition parameters and the conditions for obtaining coatings. The results of the coefficient of friction, wear rate of the coating and counterbody, nanohardness and adhesion force of coatings obtained by magnetron sputtering and its modifications are shown. The influence of alloying elements on the mechanical and tribological properties of titanium carbonitride coatings is considered. Recent advances in the production of titanium carbonitride coatings with improved wear characteristics are discussed.
Keywords: titanium carbonitride, magnetron sputtering, coating, wear resistance, coefficient of friction.

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Introduction

Hard and ultra-hard protective coatings are increasingly being used in various technical fields, including the automotive, aerospace, and manufacturing industries. Today, the use of wear resistant coatings in harsh working conditions is becoming more and more important [[1], [2], [3]]. For this reason, a number of studies have been devoted to the problems of creating thin hard coatings and their application in the production of machine parts and tools [[4], [5], [6], [7]]. Transition metal nitrides are widely used as functional coatings, which is justified by a set of their properties, such as good conductivity, hardness, high melting point, chemical resistance, and wear resistance [[8], [9]]. Titanium carbonitride (TiCN) coating is one of the most attractive among them. The tribological properties of such coatings have been studied in the following works [[10], [11]].

Such coatings have found application in cutting tools, in the details of the instrument, and mechanical engineering to increase the duration of their service life. They are biocompatible [[12], [13]], which, combined with their relatively high ductility and hardness, makes this material promising for medical applications.

Currently, a wide range of developed and tested techniques is used to form TiCN coatings. These include physical vapor deposition (PVD), chemical vapor deposition (CVD), spray techniques, and others. Each of these methods has advantages and disadvantages. Disadvantages common to many methods include poor adhesion of the coatings to the substrate, the inability to regulate their elemental composition, and the limited choice of substrate material [14]. Physical deposition methods are devoid of some disadvantages. Thus, the widespread use of PVD technologies for industrial applications is associated with the possibility of obtaining hard and durable coatings that can be applied to organic or inorganic substrates [15]. For example, magnetron sputtering (MS), cathodic arc, and pulsed laser spraying methods can be used to apply TiCN coatings with high tribotechnical properties to parts that are exposed to aggressive environments or extreme operating conditions.

The MS method allows the deposition of hard TiCN coatings with a low level of impurities at a controlled rate [16]. Depending on the sputtering conditions, this method makes it possible to obtain coatings of various morphologies and structures.

Since the chemical composition and structure of coatings are interrelated with their mechanical properties and, in particular, tribological characteristics, it is important to know how the parameters of magnetron sputtering affect them. Therefore, the purpose of this review is to show a rief, modern scientific and technical literature analysis on the preparation of wear resistant coatings based on TiCN, obtained using MS under different conditions of their deposition.

Research on obtaining titanium carbonitride coatings

Magnetron sputtering is a vacuum coating process using a specially formed magnetic field applied to a target. A typical MS scheme for TiCN coating deposition is shown in Figure 1. A typical deposition system includes a vacuum chamber, magnetron, cooling system, power supply, evacuation pumps, and other additional instrumentation for measurement.

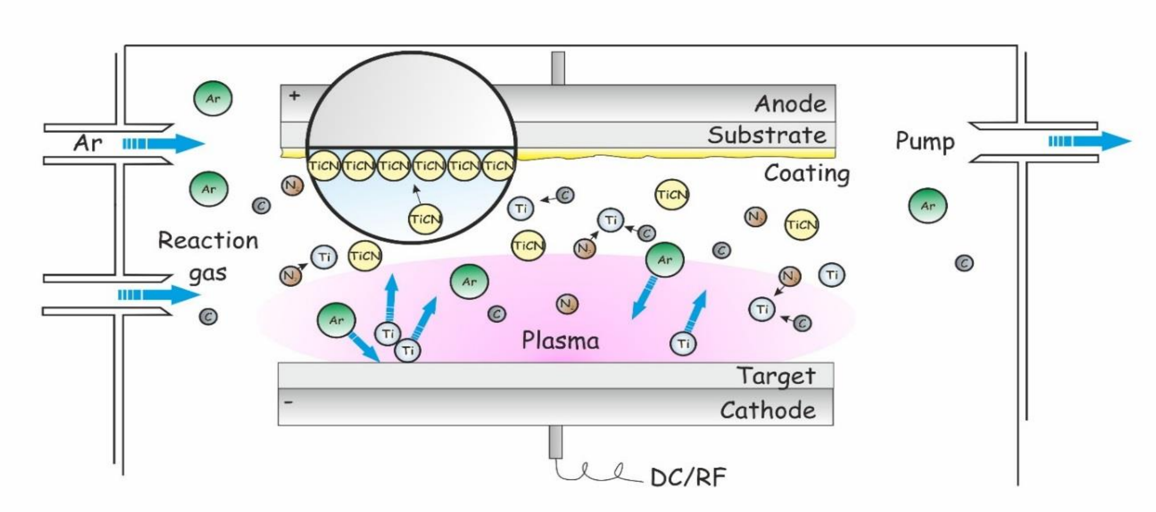

Figure 1 - Typical MS scheme and coating deposition process

TiCN coatings are obtained by MS at direct current (DCMS) [[17], [18], [19], [20], [21], [22], [23]] and radio frequency (RFMS) [[15], [25], [26], [27]] under balanced and unbalanced magnetron operating conditions [[28][29]]. The deposition process of TiCN hard coatings is directly influenced by parameters such as working atmosphere pressure, composition and ratio of reaction gases, current power supplied to the magnetron, bias potential and substrate temperature, target composition, and more. Let us consider the influence of these parameters on the structure, composition, and properties of TiCN coatings.

Numerous studies [[11], [30]] are aimed at obtaining and improving tribological properties of TiCN nanocomposite coatings. The formation of nanocrystals in the amorphous matrix of the deposited compound is an effective way to improve the tribological properties of TiN and TiC coatings, which leads to increased hardness and reduced friction [[31], [32]].

The carbon content of TiCN coatings significantly affects the final coating properties. From the results of the following studies, it has been determined that the presence of amorphous carbon and carbon sp2 in composite films significantly reduces the coefficient of friction (CoF) and wear rate (WR) [[17], [22]], increasing carbon content gives results similar to decreasing substrate displacement stress [20] and reduces corrosion resistance [21]. In the paper [20], detailed X-ray diffraction studies of TiCN coatings are given depending on the carbon content. The following conclusions were drawn from the results: 1) the adatomic mobility decreased with increasing carbon content in the coating; 2) the measured lattice parameter is in agreement with published literature data for stoichiometric TiN coatings; 3) the observed micro deformation as a function of carbon content in the coating, increased with increasing carbon content. The results of electrochemical experiments described in [21] showed that the corrosion resistance of TiCN coatings decreases with an increase in the carbon content in them. The authors explain this by an increase in the density of defects in such coatings, despite their high hardness and adhesion to substrates. The film structure was directly affected by its thickness, and the residual stress values were higher for thinner coatings (1 μm).

When TiCN coatings are deposited, a titanium target or a combined target is used. In the latter case, the target can be made from titanium and carbon powders in different ratios or by assembling the target from individual segments, disks. For example, in [22], TiN/(a-C) composite coatings were deposited with different ratios of graphite to Ti (G/Ti) in a single target on steel at 200 °C. The G/Ti ratio in the target was 0.5, 1.0, 2.0. The obtained coatings showed an orientation (222) and a columnar structure at a lower G/Ti ratio. The tribological properties of the coatings were tested on a ball-on-disc tribometer under dry conditions, at 60 % relative humidity, using a hardened steel ball HRC62 as a counterbody at a normal load of 1.0 N. The results showed that the presence of amorphous carbon in composite films significantly reduces the CoF and WR [22]. The authors of [17] conducted a similar study where TiCN nanocomposite coatings were obtained by DC from a combined Ti/C target at different nitrogen flow rates. When nitrogen flow is increased from 0 to 30 sccm at an operating pressure of 0.3 Pa, both the crystallinity and the carbon sp2 content of the coatings are increased. CoF and WR can be significantly reduced by increasing the carbon sp2 content. Figure 2 shows the CoF and WR of the coatings obtained at different nitrogen flow rates. Based on the results of [17] it can be said that at a nitrogen flow rate of 30 sccm the TiCN coating can provide a combination of high hardness, toughness, and wear resistance.

Among the works studied, the relatively lowest coefficient of friction of the TiCN coating with low WR (~10^{-6} mm^3/Nm) was achieved in our experimental work [23]. Sample rotation speed, 1 cm/s; load, 1 N; wear track radius, 7 mm; friction path, 100 m; data collection speed: 50 Hz, a Si_3N_4 ball with a diameter of 6 mm was used as a counter body.

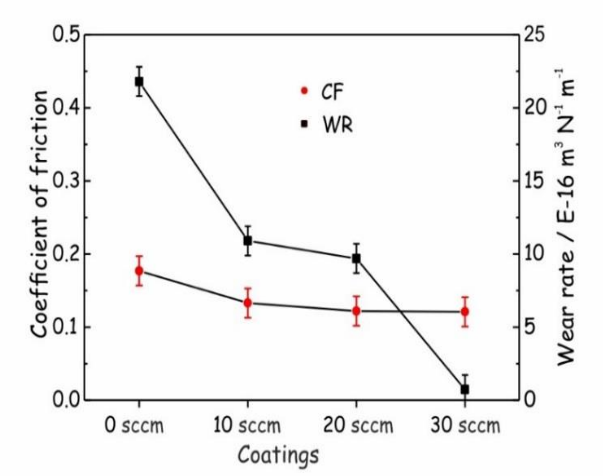

Figure 2 - Results of CoF and WR of coating obtained at different nitrogen flow rates [17]

The magnetron sputtering deposition condition at a substrate bias -70 V made it possible to obtain a coating with a CoF of 0.06 (figure 3). This was due to the formation of third bodies in contact and the subsequent formation of a lubricating transition layer. Also, it should be noted that during the test, no sharp jumps in CoF were observed, which indicates a high adhesion of the coating to the substrate [24].

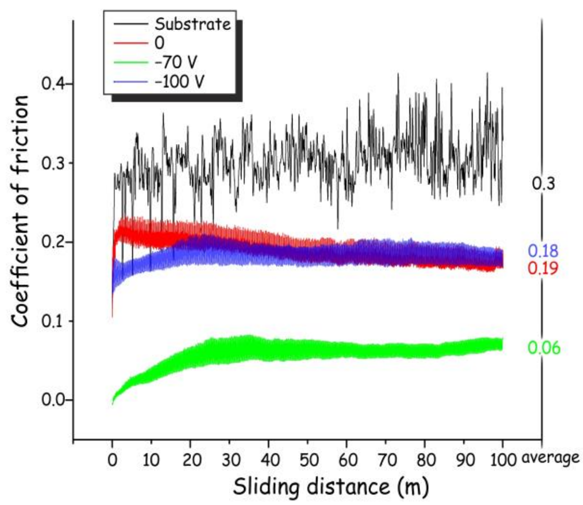

Figure 3 - CoF for titanium VT6 substrate and TiCN coatings [23]

The sputtering of a pure titanium layer is considered necessary by some researchers to improve the adhesion properties between the carbonitride coating and the substrate. According to the authors [[15], [17], [33], [34]] this helps to increase the nucleation density and reduce the surface roughness of the coating.

In the works considered above the coatings were deposited by MS method at direct current. The authors of works [[15], [25]] have shown, that the coatings deposited in conditions of RFMS are not inferior in tribomechanical properties to the coatings received at direct current. Saoula N. and colleagues [15] investigated the effect of substrate potential displacement on the structure and properties of TiCN coatings. TiCN coatings were grown on silicon and steel substrates by RFMS method by sputtering a pure titanium target in Ar-CH_4-N_2 gas mixture.

The tribotechnical properties of the coatings were investigated by testing them together with an alumina ball in the air. The experimental results showed a decrease in the deposition rate from 31 to 9 nm/min with an increase in the bias voltage of the substrate from Us = 0 to -100 V, respectively. The coating deposited at 0 V was amorphous, while the coatings deposited when a bias voltage was applied to the substrate had a facecentered cubic structure with a predominant growth orientation (111). The results also show that TiCN coatings deposited at a substrate voltage of -70 V had a maximum hardness of 39 GPa and showed better wear resistance at a minimum WR and lower CoF of 0.13, this tendency showed also in [23].

As the bias voltage was increased from 0 to -70 V, the hardness increased from 16 to 39 GPa, and then slightly decreased to 38 GPa, while it was further increased to -100 V, as shown in Figure 4. In [24], the mechanical properties of TiN, TiC, and TiCN coatings deposited by the RFMS method were compared. Plasma power during deposition was maintained at 200 W. The hardness of TiN, TiC, and TiCN coatings was evaluated using the nanoindentation test. All thin film samples showed increased hardness with an increase in the applied negative bias voltage to -75 V. The increase in hardness was explained by a change in surface morphology. The hardness of the TiN, TiCN and TiC films ranged from 4.9 to 34.1 GPa, from 16 to 39 GPa, and from 9.8 to 26.97 GPa, respectively.

The tribological properties of coatings depend significantly on the test conditions. Wang Q. and others [35] showed significant dependence of WR and CoF on friction speed and load value on the results of tests of TiCN coatings on WC-based hard alloy substrates on a ball-on-disk tribometer. The measurements were performed concerning balls made of SiC, SUJ2 and SUS440C steels at normal load from 3 to 12 N and sliding speed from 0.1 to 0.4 m/s.

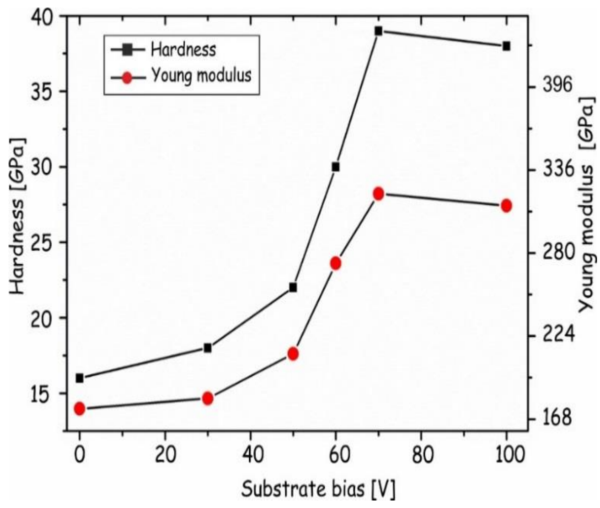

Figure 4 - Hardness and Young's modulus of the TiCN coating depending on the applied bias potential of the substrate [15]

It was shown that the tribological properties of the TiCN/SiC pair are better under friction in water than in air [[35], [36]]. Temperature is also one of the important parameters in studies of coating wear resistance. Polcar T. and others performed the work in this direction [18]. They investigated the tribological characteristics of the TiCN coating at elevated temperatures. The tests were performed according to the “pin-on-disc” scheme using balls made of bearing steel 100Cr6, Al_2O_3, and Si_3N_4 as a counter body. The results of testing specimens at temperatures below 200 ºC and up to 500 ºC are shown in Figure 5. All wear tests were performed at a normal load of 5 N at linear velocities from 0.04 m/s to 0.3 m/s for up to 30,000 cycles. The results showed that raising the temperature increased the CoF and WR of TiCN coating when sliding on 100Cr6 balls. In contrast, for Si_3N_4 balls, friction and wear were independent of temperature[[18], [35]]. In [19] the same authors showed results comparing the tribological behavior of TiN, TiCN, and CrN coatings under similar test conditions at temperatures up to 500 ºC, at a linear velocity of 4 cm/s, for 5000 cycles. These results indicate that the TiCN coating can perform as a wear resistant coating at high temperatures [19].

Thus, the wide range of studies on the preparation and study of the mechanical properties of TiCN coatings indicate a great interest in the scientific community for them as promising wear-resistant coatings.

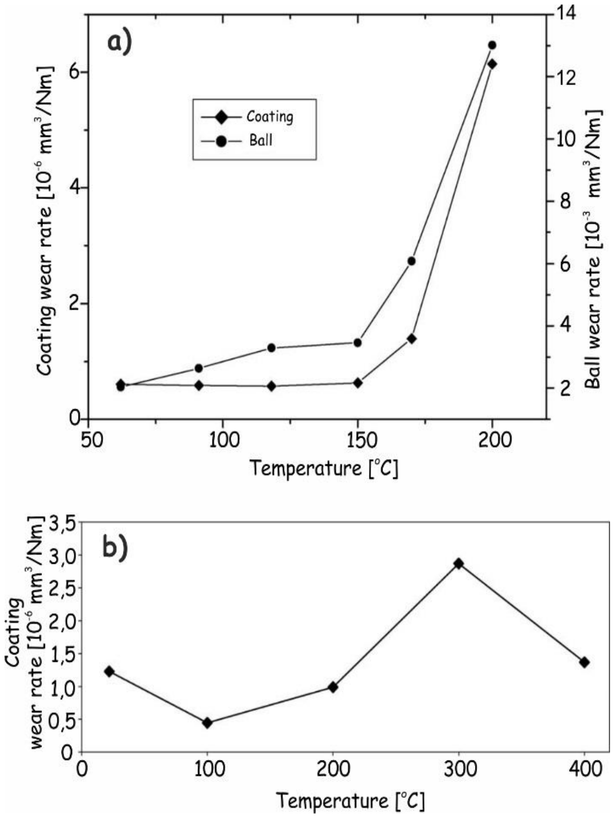

Figure 5 - The dependency of coating wear rate on temperature using 100Cr6 ball (a) and Si_3N_4 ball [18]

Research on obtaining multilayer and alloyed TiCN coatings

Recently, coatings of a new generation based on TiCN have appeared, such as multi-component (TiAlCN, TiNCO) [[39] [40]], multilayer (TiN/TiCN/TiC) [41], gradient (Ti/TiN/TiCN) [42] and composite [17], [22] coatings. The authors of these studies believe that the properties of these new TiCN-based coatings are better than those of traditional TiCN coatings. Typically, the thickness of the TiCN coating varies from a few nanometers [17] to 4-5 microns [15]. In the case of multilayer coatings, this indicator can be higher and exceed several times, while they show good chemical stability, excellent mechanical properties, as well as excellent wear resistance and corrosion resistance. For example, Su Y.L. and his colleagues [43] found that multilayer TiN/TiCN/TiN coatings with a thickness of 7 µm, containing a two-layer TiN (2 µm) and TiCN (2 µm) with an upper TiN layer (3 µm), had high wear resistance, but coatings with a thickness of about 9 µm showed low wear resistance due to poor adhesion. A similar TiN/TiCN/TiC coating was obtained by the authors of [44]. The results of tests for scratching and nanoindentation showed the best mechanical properties for a coating on a Ti6Al4V substrate with a hardness of 19.96 GPa and a critical load of 25 N.

It is known that increasing the thickness of the coating not only contributes to the prolongation of the service life but also seriously affects the adhesion between the coating and the substrate. The authors of [45] argue that a possible solution to this problem is the formation of a gradient structure and the composition of a multilayer coating. They deposited a 23.5 µm thick TiN/TiCN multilayer coating on silicon and steel (Figure 6a). It was found that the inner TiCN layers consisted of a mixture of the nanocrystalline TiCN phase and amorphous carbon, while the TiN layers had a nanocolumnar structure. According to the results of scratching and nanoindentation tests, the coating showed high adhesion and satisfactory hardness even at a thickness of 23.5 µm (29.0 N and 21.4 GPa), as can be seen from the sclerometric result in Figure 6b. The results of tribological tests showed that the wear resistance of such a coating did not decrease in comparison with other thin hard films, but its service life was extended due to its large thickness (> 11 hours). Figure 6c shows the friction curve of a TiN/TiCN multilayer coating. It is noticeable that the CoF of such a coating exhibits good performance and has some variation due to the composition of the transition layer and the friction surface [45].

Alloying TiCN coatings with different elements, such as O, Al, Si, Cr, Zr, Ag, etc., makes it possible to influence their mechanical properties. The introduction of oxygen into the TiCN coating increases their resistance to friction and corrosion, which is justified by the inertness of the oxide and the small atomic size of oxygen, which creates high hardness and compressive stress [46]. In [[47], [48], [49]], the authors studied the effect of the oxygen fraction in the reaction atmosphere during MS on the properties of the TiCN coating. The results seen in Table 1 show that the TiCNO coating obtained at an oxygen consumption of 4 sccm is characterized by the lowest WR and the highest nanohardness. A further increase in oxygen consumption led to a decrease in hardness, adhesion, and wear resistance. Olteanu C. and her colleagues [49] deposited a TiCNO coating in an Ar, $C_2H_2/(O_2 + N_2)$ atmosphere. During deposition, the working pressure was kept constant at about 0.4 Pa, and the bias voltage of the substrate was -70 V. In all cases, the deposition time was 1 hour. The maximum CoF values were recorded for coatings deposited at a $C_2H_2/(O_2 + N_2)$ flux ratio of about 2.5.

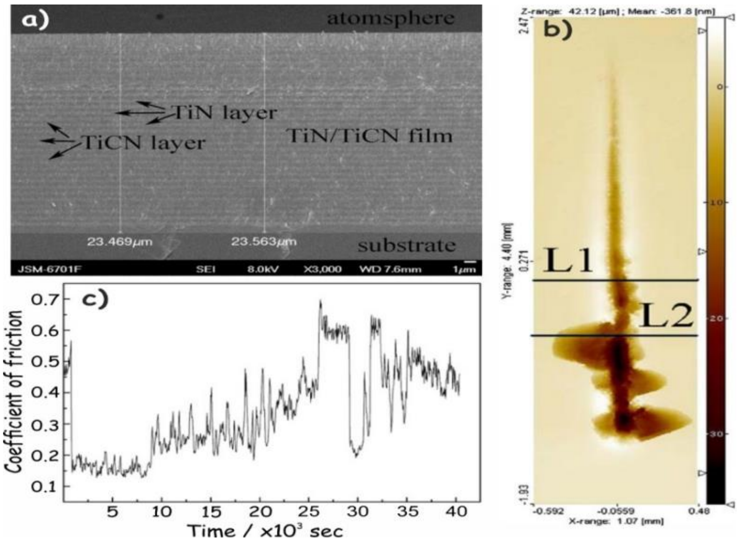

Figure 6 - SEM images of a cross-section (a), micrograph of a scratch (b) and a friction curve (c) of a multilayer TiN/TiCN coating [45]

The authors [50] obtained (Zr, Ti)CN coatings for medical applications by MS of two targets of Zr and Ti (purity 99.99 %). The substrates were placed at a distance of 17 cm from the targets, rotating them at a speed of 30 rpm. The reactive atmosphere was a mixture of N_2, CH_4, and Ar gases. It was found that the coatings have a composite structure in which the crystalline phase (Zr, Ti)CN coexists with the amorphous phase C. The measured thickness and hardness of the coating were in the ranges of 1.8-2.1 µm and 25-29 GPa, respectively.

Works [[51], [52], [53]] have focused on the study of TiSiCN nanocomposite coatings due to their excellent mechanical and tribological properties. Thus, the aim of work [51] was to compare the microstructural, mechanical, and tribological properties of TiSiCN coatings obtained by MS and plasma enhanced magnetron sputtering (PEMS) under practically identical conditions on Custom-450 and Ti-6Al-4V stainless steel for gas and steam turbines. During the deposition of both MS and PEMS, two Ti target magnetrons were used in an argon-nitrogen-trimethyl silane gas mixture. The results showed that the surface microhardness of the PEMS coating (24.65 GPa) is twice as high as that of the MS coating (11.77 GPa), which provided a much lower WR during the sliding and erosion rate of the TiSiCN coating (Figure 7a). In a study [52], TiSiCN coatings were deposited by PEMS in an Ar + N_2 + C_2H_2 atmosphere with the addition of two types of silicon precursors: gaseous trimethylsilane (TMS - $(CH_3)_3SiH$) and hexamethyldisilazane liquid (HMDSN - $(CH_3)6Si_2NH$). The flow rate for TMS was 0, 1.5, 3, 6, and 9 sccm, and for HDMSN it was maintained at 3 g/h. TiSiCN coatings obtained at a TMS flow rate of 6 and 9 sccm and for an HMDSN liquid of 3 g/h showed high wear resistance (Figure 7b).

A comparative study of the structure and properties of Al- and Cr-doped TiSiCN coatings was performed by the authors of [53]. The deposition of coatings was performed in a gas mixture of argon and nitrogen at a pressure of 0.1 Pa using targets made of TiAlSiCN and TiCrSiCN. The current and voltage supplied to the magnetron were 2 A and 500 V, respectively. The bias voltage of the substrate was -50 V, and the substrate temperature was kept constant at 300 °C (for TiCrSiCN coating) and 500 °C (for TiAlSiCN coating). To assess the thermal stability and resistance to oxidation, the coatings were annealed in vacuum at 1000, 1100, 1200, and 1300 °C or in the air at 1000 °C for 1 h. The results obtained show that the hardness of TiAlSiCN coatings increased from 41 to 46 GPa, reaching a maximum at 1000 °C, and then slightly decreased to 38 GPa at 1300 °C. TiCrSiCN coatings have demonstrated high thermal stability up to 1100 °C at a hardness above 34 GPa. TiAlSiCN coatings were more resistant to oxidation than TiCrSiCN coatings.

Tillmann W. et al. [54] compared TiAlCN coatings obtained by MS and high-power impulse magnetron sputtering (HiPIMS). The results showed that all MS coatings showed better adhesion than their HiPIMS counterparts. After that, the same authors presented the following study [55], where TiAlCN coatings were deposited using hybrid (MS/HiPIMS) technology with increasing acetylene flow. The results of tribological studies have shown that CoF does not depend as much on the carbon content as on the sliding speed and normal load.

Table 1 - Gas flow rate and some properties of TiCNO coatings [47]

N_2 flow rate (sccm)	O_2 flow rate (sccm)	Hardness (GPa)	Adhesion (load, N)	C:N:O	Coating color
22	0	26	54	1:2:0	Pink brown
20	2	30	60	1:3.8:0.2	Pink purple
18	4	32	65	1:3.5:0.4	Red brown
16	6	30	45	1:5:0.4	Yellow brown
14	8	29	40	1:3.5:0.5	Red brown
12	10	24	38	1:3.5:0.6	Gray brown

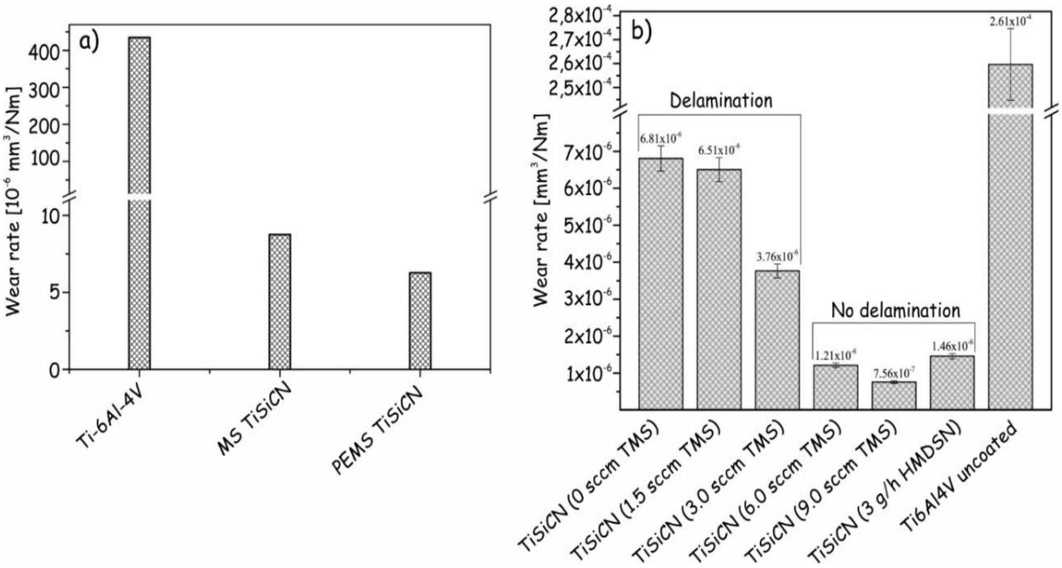

Figure 7 - Wear rate of TiSiCN coating depending on: (a) deposition method [42], (b) silicon precursor flow [52]

It is known about alloying TiCN coating with silver [56] and deposition of the surface layer of hydroxyapatite (HA) [57] for use in biomedicine. In [56], the characteristics of thin coatings based on silver-containing carbonitrides (Ag-TiCN) obtained by DCMS were studied. The Ag content in the coatings was varied from 0 to 26.7 at. % by changing the targets and the proportion of C_2H_2 and N_2 in the gas mixture with Ar. As a result, when the Ag/Ti ratio was below 0.20, coatings were obtained with high mechanical properties (hardness ~ 18 GPa, WR ~ 10^{-6} mm^3/Nm, CoF ~ 0.3) and good biocompatibility. Thampi A. and her colleagues [57] deposited a HA layer on top of TiCN coatings, which were obtained using DCMS by deposition on substrates of medical grade 316 L SS. This study proves that HA-TiCN can provide better surface properties when used as a biocompatible coating on implant material.

Table 2 lists the target and substrate materials, deposition parameters, and tribological characteristics of some TiCN-based coatings published in the literature. The table shows the best selective tribological characteristics of the coating in the results of one work, regardless of the sample. From the data, it can be said that TiCN coatings deposited by sputtering a combined C/Ti target (~10^{-14} mm^3/Nm) have the best wear resistance [[17], [21]]. The best wear characteristics in terms of CoF were 0.06 [23].

Thus, studies on TiCN coatings indicate that their properties can be significantly affected by alloying them with different elements.

Table 2 - Deposition parameters of a TiCN-based coating by the MS method and its influence on the coating results

Coating	Deposition materials and parameters				Coating results			Reference
	Target material and	Target material and subject to the impact	Working gas atmosphere and flow	Working pressure, Pa	Coating thickness, µm	Coefficient of friction of the coating	Wear rate of the coating, mm^3/Nm	

	sputtering type							
TiCN	Ti RF	Steel XC38 and Si (100) U = 0,-30, -70, -100 B	Ar : 8 sccm N_2 : 4 sccm CH_4 : 4 sccm	1.33	2-4	0.13 and higher	1.12×10^{-4}	[15]
TiCN	C/Ti DC	Si (100) T = 200 °C U = -100 B	Ar/N_2 = 30 sccm N_2 = 0, 10, 20, 30 sccm	0.3	0.5	0.13 and higher	7.3×10^{-14}	[17]
TiCN	Ti DC	Steel T = 450 °C	Ar/N_2 = 50%/50% C_2H_2	10^{-3}	1.7	0.14 and higher	0.5×10^{-3}	[18]
TiCN	Ti DC	Steel T = 450 °C	Ar/N_2 = 50%/50% C_2H_2	0.1	–	0.14 and higher	0.8×10^{-6}	[19]
TiCN	C/Ti DC	Steel W6Mo5Cr4V2 T = 200 °C U = -80 B	Ar :4 sccm N_2 : 4 sccm	0.4	1.2	0.12 and higher	0.67×10^{-14}	[21]
TiCN	Ti DC	Titanium VT6 U = 0, -70, -100 B	Ar : 18 sccm N_2 : 2.6 sccm C_2H_2 : 4.6 sccm	0.4	0.8-1.4	0.06 (average)	1.4×10^{-6}	[23]
TiCN	Ti RF	Carbide-grade H-21 U = -90 B	Ar/N_2/C_2H_2	–	2.3	0.14	1.83×10^{-12}	[26]
TiCN	Ti RF	Steel XC38 U = 0-100 B	Ar: 8 sccm N_2: 4 sccm CH_4: 4 sccm	–	–	0.13	–	[27]
TiCN	Ti	WC	Ar/N_2/CH_4	0.8	3	0.2 (average)	–	[35]
TiCN	Ti, Al RF/DC	Ti6Al4V U = -80 B	Ar: 15 sccm N_2	0.6	~2	0.16	–	[37]
TiCN	TiC	Si (100), steel AISI 1045 T = 250 °C	Ar: 50 sccm N_2: 16 sccm	1.4	–	0.75 and higher	$0.125\ x10^{-12}$	[38]
TiN/TiCN/TiC	Ti DC	Ti and Ti6Al4V, Si U = -60 B	Ar/N_2/C_2H_2	0.3	1.7	0.1 and higher	–	[44]
TiN/TiCN	Ti DC	Steel 2520-310S and Si (100) T = 40-100 °C U = -100 B	Ar : 20 sccm N_2 : 0-6 sccm CH_4 : 0-10 sccm	0.4	23.5	0.15 and higher	–	[45]
TiCNO	Ti	Steel AISI 316 T = 260 °C	CO_2/N_2	0.1	~1	0.1 and higher	–	[46]
TiCNO	Ti DC	Steel M2 T = 300 ºC U = - 60 B	O/N_2 = 22 sccm N_2 = 22, 20, 18, 16, 14, 12 sccm, C_4H_{10}	0.44	3	0.2 and higher	1×10^{-9}	[47]
TiCNO	Ti DC	Steel M2 T = 200 °C U = - 70 B	Ar/N_2+O_2 /C_2H_2	0.4	–	0.2 and higher	2.47×10^{-6}	[49]
TiSiCN	Ti PEMS	Ti-6Al-4V and steel Custom-450 T = 400 °C U = - 40 B	Ar/N_2/TMS N_2 : 45 sccm TMS : 6 sccm	10^{-4}	29.8	0.2 and higher	6.26×10^{-6}	[51]
TiSiCN	Ti PEMS	Ti-6Al-4V T = 200 °C U = - 60 B	Ar :190 sccm, N_2 : 45 sccm C_2H_2 : 30 sccm TMS : 0-9 sccm	0.4	8-10	0.15 and higher	7.5×10^{-7}	[52]
TiSiCN	Ti, Si, C	Si (100)	Ar/N_2=70%/30%	0.53	0.4-2.0	0.4 and higher	–	[60]

	DC	T = 500 °C						
TiCrSiCN	TiCrSiCN DC	WC, Si (100), Ni foil, Al_2O_3 T = 500 °C U = - 50 B	Ar	0.1	1	0.4-0.45	1.5×10^{-6}	[53]
TiAlSiCN	TiAlSiCN DC	WC, Si (100), Ni foil, Al_2O_3 T = 300 °C U = - 50 B	Ar	0.1	1.7	0.5 and higher	6×10^{-6}	[53]
TiAlSiCN	TiAlSiCN DC	Si and Ni T = 500 °C U = - 250 B	Ar + 15% N_2	0.2	–	0.5 and higher	2.9×10^{-6}	[62]
TiAlCN	Ti DC	Steel AISI H11 T = 425 °C U = - 100 B	Ar: 295 sccm Kr: 200 sccm C_2H_2 : 20 sccm N_2	5×10^{-2}	3	~ 0.78	3.1×10^{-6}	[54]
TiAlCN	Ti HiPIMS	Steel AISI H11 U = - 80 B	Ar: 295 sccm Kr: 200 sccm C_2H_2 : 15 sccm N_2	5×10^{-2}	3	~ 0.4	1.5×10^{-6}	[54]
TiAlCN	Ti, Al, C DC	Steel AISI 316 and Si (111)	Ar/N_2=70%/30%	0.4	–	0.25 and higher	8×10^{-6}	[61]
TiAlN/ TiAlCN	Ti, TiAl48-12 MS/HiPIMS	Steel AISI H11 U = - 80 B	Ar: 295 sccm Kr: 200 sccm C_2H_2 : 5 и 10 sccm N_2	5×10^{-2}	–	0.5 and higher	1.42×10^{-6}	[55]
TiBCN	TiBC DC	Steel AISI 304 and Si (100) U = - 50 B	Ar+N_2: 20 sccm N_2: 0-7 sccm	0.27	2-3	0.54 and higher	2×10^{-6}	[58]
WTiCoCN	Ti (DC) WC (RF)	Steel H13 and Si (100) U = - 50 B	Ar/N_2	0.13	–	0.2 (average)	5×10^{-7}	[59]

Conclusions

Titanium carbonitride coatings are characterized by high wear resistance, relatively low coefficient of friction in various media, and corrosion resistance. This makes them promising for a wider application on the working surfaces of parts in the friction units of various mechanisms, on the surfaces of implants, as protective coatings providing corrosion protection at different temperatures.

Magnetron sputtering is a well established technique for the deposition of thin TiCN coatings, which is flexible, has a wide range of possibilities, and ensures a high level of adhesion of the coatings on the substrate. If you vary the ratio and composition of the reaction gases, the composition of the atomized target, the bias voltage on the substrate, the parameters of the current fed to the magnetron, and the number of magnetrons, you can vary the composition of the deposited coatings in a wide range, introduce alloying elements and deposit multilayer coatings. Such coatings are characterized by different levels of properties, including mechanical and tribological.

Further developments in the method of magnetron sputtering can relate to the upgrades of the method (HiPIMS, PEMS, RF and DC combined MS and others), which open up new possibilities for designing the microstructure and tuning the mechanical properties of TiCN-based coatings.

In addition, the elemental inclusion during alloying of TiCN coatings makes it possible to increase the tribological and mechanical properties. In the future, a number of elements such as O, Al, Cr, Si will be promising alloying elements that provide high wear resistance. However, to date, there is no universal TiCN coating that meets all the requirements and is characterized by high tribotechnical characteristics in various environments. This indicates the need for further studies and, in particular, to investigate the effect of alloying with various elements on the properties of such coatings.

Conflict of interest. On behalf of all authors, the correspondent author declares that there is no conflict of interest.

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Магнетронды тозаңдату әдісімен титан карбонитридті жабындарын отырғызу және оның трибо-механикалық қасиеттеріне әсері

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ТҮЙІНДЕМЕ

Техникадағы металл бөлшектер көбінесе тозудан туындаған зақымдардың салдарынан сәтсіздікке ұшырайды, бұл өнімнің функционалдығын жоғалтуға әкеледі. Бөлшектердің тозуға төзімділігі мен қызмет ету мерзімін арттыру үшін тиімді деп саналатын нитридті жұқа қатты жабындар қолданылады. Мақалада магнетронды тозаңдандыру әдісімен титан карбонитридінің тозуға төзімді жабындарын алу саласындағы қазіргі заманғы әдебиеттерге қысқаша шолу жасалды. Әдеби шолуда тозаңдандыру параметрлері мен жабындарды алу шарттарына байланысты алынған ғылыми нәтижелерді егжей-тегжейлі бағалау ұсынылды. Магнетронды тозаңдату әдісімен және оның модификацияларымен алынған жабындардың үйкеліс коэффициенті, жабынды мен контртелдің тозу жылдамдығы, наноқаттылық және адгезия күші нәтижелері көрсетілген. Легирленген элементтердің титан карбонитриді жабындарының механикалық және трибологиялық қасиеттеріне әсері қарастырылады. Жақсартылған тозу сипаттамалары бар титан карбонитридті жабындарды алу саласындағы соңғы жетістіктер талқыланды.

Түйін сөздер: титан карбонитриді, магнетрондық тозаңдандыру, жабынды, тозуға төзімділік, үйкеліс коэффициенті.

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Осаждение покрытий карбонитрида титана методом магнетронного распыления и его влияние на трибо-механические свойства

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АННОТАЦИЯ
Металлические детали в технике часто выходят из строя в результате повреждений, вызванных износом, что приводит к потере функциональности изделий. С целью повышения износостойкости и срока службы деталей используют тонкопленочные твердые нитридные покрытия, считающиеся эффективными. В статье представлен краткий обзор современной литературы в области получения износостойких покрытий карбонитрида титана методом магнетронного распыления. В обзоре представляется детальная оценка полученных научных результатов в зависимости от параметров напыления и условий получения покрытий. Показаны результаты коэффициента трения, скорости износа покрытия и контртела, нанотвердости и силы адгезий покрытий, полученные методом магнетронного распыления и его модификациями. Рассматривается влияние легирующих элементов на механические и трибологические свойства покрытий карбонитрида титана. Обсуждаются последние достижения в области получения покрытий из карбонитрида титана с улучшенными характеристиками износа.

Ключевые слова: карбонитрид титана, магнетронное распыление, покрытие, износостойкость, коэффициент трения.

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References

[1] Ceschini L, Lanzoni E, Palombarini G, Sambogna G. Frictional behaviour and wear resistance of TiN-based PVD coatings dry sliding against a TiN coated tool steel. Metallurgia Italiana. 1999;91:45-51.

[2] Rodriguez RJ, Garcia JA, Medrano A, Rico M, Sanchez R, Martinez R, Labrugere C, Lahaye M, Guette A. Tribological behaviour of hard coatings deposited by arc-evaporation PVD. Vacuum 2002;67:559-566. https://doi.org/10.1016/s0042-207x(02)00248-8

[3] Yeshmanova GB, Smagulov DU, Blawert C. Plasma electrolytic oxidation technology for producing protective coatings of aluminum alloys. Complex Use of Mineral Resources. 2021;2(317):78-93. https://doi.org/10.31643/2021/6445.21

[4] Ramazanova JM, Zamalitdinova MG. Physical and mechanical properties investigation of oxide coatings on titanium. Complex Use of Mineral Resources 2019;2:34-41. https://doi.org/10.31643/2019/6445.14

[5] Kozyreva LV, Fadeev OV, Yudin AO. The algorithm of development safe methods for depositing metallic coatings by CVD-method of organometallic compounds. Complex Use of Mineral Resources 2020;1(312):5-10. https://doi.org/10.31643/2020/6445.01

[6] Uskenbayeva AM, Aubakirova RK, Panickin AV, Dzhumabekov DM. Polucheniye misheney na osnove alyuminidnykh sistem dlya magnetronnogo osazhdeniya zharostoykikh pokrytiy [Preparation of targets based on aluminide systems for magnetron deposition of heat-resistant coatings]. Kompleksnoe Ispol’zovanie Mineral’nogo Syr’a = Complex Use of Mineral Resources 2017;4:49-56. (in Russ.).

[7] Kapsalamova FR, Kenzhaliyev BK, Mironov VG, Krasikov SA. Structural and phase transformations in wear resistant Fe-Ni-Cr-Cu-Si-B-C coatings. Journal of the Balkan Tribological Association 2019;25:95-103.

[8] Arndt M, Westphal H. Influence of residual stresses and nanostructure on the properties and applications of PVD coatings. In: Institute of Production Engineering and Machine Tools, organizer. Proceedings of the 7th International Conference "THE Coatings" in Manufacturing Engineering and EUREKA partnering event; 2008 October 1-3; Kallithea of Chalkidiki, Greece. p. 151-155.

[9] Sagdoldina Zh, Skakov M, Rahadilov B, Zhadyranova A. Struktura poverkhnosti bystrorezhushchey stali R6M5 posle elektronno-luchevoy obrabotki [Preparation of TiN/Al2O3 coatings by mechanical fusion]. Kompleksnoe Ispol’zovanie Mineral’nogo Syr’a = Complex Use of Mineral Resources 2017;3:47-53. (in Russ.).

[10] Zhang GJ, Li B, Jiang BL, Chen DC, Yan FX. Microstructure and mechanical properties of multilayer Ti(C,N) films by closed-field unbalanced magnetron sputtering ion plating. Material Science Technology 2010;26:119-124.

https://doi.org/10.1016/s1005-0302(10)60019-9
[11] Martinez-Martinez D, Sanchez-Lopez JC, Rojas TC, Fernandez A, Eaton P, Belin M. Structural and microtribological studies of Ti-C-N based nanocomposite coatings prepared by reactive sputtering. Thin Solid Films 2005;472:64-70. https://doi.org/10.1016/j.tsf.2004.06.140
[12] Sedira S, Achour S, Avci A, Eskizeybek V. Physical deposition of carbon doped titanium nitride film by DC magnetron sputtering for metallic implant coating use. Applied Surface Science 2014;29515:81-85. https://doi.org/10.1016/j.apsusc.2014.01.010
[13] Anusha TVV, Subramanian B. Enhancement of bioactivity of pulsed magnetron sputtered TiCxNy with bioactive glass (BAG) incorporated polycaprolactone (PCL) composite scaffold. Journal of Alloys and Compounds 2015;649:1210-1219. https://doi.org/10.1016/j.jallcom.2015.06.250
[14] Bunshah RF. Handbook of Hard Coatings Deposition Technologies, Properties and Applications, Norwich: Noyes Publications / William Andrew Publishing LLC;2001.
[15] Saoula N, Madaoui N, Tadjine R, Erasmus RM, Shrivastava S, Comins JD. Influence of substrate bias on the structure and properties of TiCN films deposited by radio-frequency magnetron sputtering. Thin Solid Films 2016;616:521-529. https://doi.org/10.1016/j.tsf.2016.08.047
[16] Auciello O, Engemann J. Multicomponent and multilayered thin films for advanced microtechnologies: techniques, fundamentals and devices, Bad Windsheim: NATO ASI Series, Springer;1993.
[17] Chen R, Tu JP, et al. Microstructure, mechanical and tribological properties of TiCN nanocomposite films deposited by DC magnetron sputtering. Surface & Coatings Technology 2011;205:5228-5234. https://doi.org/10.1016/j.surfcoat.2011.05.034
[18] Polcar TR, Novak P, Siroky P. The tribological characteristics of TiCN coating at elevated temperatures. Wear. 2006;260:40-49. https://doi.org/10.1016/j.wear.2004.12.031
[19] Polcar T, Kubart T, Novak R, Kopecky L, Siroky P. Comparison of tribological behaviour of TiN, TiCN and CrN at elevated temperatures. Surface & Coatings Technology 2005;193:192- 199. https://doi.org/10.1016/j.surfcoat.2004.07.098
[20] Schneider JM et al. X-Ray diffraction investigations of magnetron sputtered TiCN coatings. Surface and Coatings Technology 1995;74:312-319. https://doi.org/10.1016/0257-8972(95)08238-7
[21] Senna LF et al. Structural, chemical, mechanical and corrosion resistance characterization of TiCN coatings prepared by magnetron sputtering. Surface and Coatings Technology 1997;94-95:390-397. https://doi.org/10.1016/s0257-8972(97)00447-7
[22] Zheng XH, Tu JP, Gu B, Hu SB. Preparation and tribological behavior of TiN/a-C composite films deposited by DC magnetron sputtering. Wear 2008;26:261-265. https://doi.org/10.1016/j.wear.2007.10.007
[23] Mamaeva A, Kenzhegulov A, Panichkin A, Alibekov Z, Wieleba W. Effect of Magnetron Sputtering Deposition Conditions on the Mechanical and Tribological Properties of Wear-Resistant Titanium Carbonitride Coatings. Coatings 2022;12(2):193. https://doi.org/10.3390/coatings12020193
[24] Kenzhegulov, A.K.; Mamayeva, A.A.; Panichkin, A.V. Adgezionnyye svoystva kaltsiy-fosfatnykh pokrytiy na titane [Adhesion properties of calcium phosphate coatings on titanium]. Kompleksnoe Ispol'zovanie Mineral'nogo Syr'a = Complex Use of Mineral Resources 2017;3:35-41. (in Russ.).
[25] Saoula N, Madaoui N, Ait Djafer AZ, Annou K, Tadjine R, Shrivastava S, Erasmus RM, Comins JD. Mechanical proprieties of TiN, TiC and TiCN coatings deposited by magnetron sputtering deposition technique. In: Tampere University of Technology, organizer. Surface modification technologies XXVIII proceedings of the Twenty Eighth International Conference on Surface Modification Technologies; 2014 June 16-18; Tampere, Finland. p. 521-530.
[26] Bull SJ, Bhat DG, Staia MH. Properties and performance of commercial TiCN coatings. Part 2: tribological performance. Surface and Coatings Technology 2003;163-164:507-514. https://doi.org/10.1016/s0257-8972(02)00651-5
[27] Mechri H, Saoula N, Madaoui N. Friction and wear behaviors of TiCN coating treated by R.F magnetron sputtering. In: Research Center in Industrial Technologies CRTI, organizer. 7th African Conference on Non Destructive Testing ACNDT 2016 & the 5th International Conference on NDT and Materials Industry and Alloys (IC-WNDT-MI); 2016 July 31; Algiers, Algeria p. 16-20.
[28] Alfonso E, Olaya J, Cubillos G. Crystallization – Science and Technology. Rijeka:InTech, 2012.
[29] Sarakinos K, Alami J, Konstantinidis S. High power pulsed magnetron sputtering: A review on scientific and engineering state of the art. Surf Coat Technol 2010;204:1661-1684. https://doi.org/10.1016/j.surfcoat.2009.11.013
[30] Zhang GJ, Li B, Jiang BL, Yan FX, Chen DC. Microstructure and tribological properties of TiN, TiC and Ti (C, N) thin films prepared by closed-field unbalanced magnetron sputtering ion plating. Appl Surf Sci 2009;255:8788-8793. https://doi.org/10.1016/j.apsusc.2009.06.090
[31] Martinez-Martinez D, Lopez-Cartes C, Justo A, Fernandez A, Sanchez-Lopez JC, Garcia-Luis A, Brizuela M, Onate JI. Tailored synthesis of TiC⁄a-CTiC⁄a-C nanocomposite tribological coatings. Vac Sci Technol A 2005;23:1732-1736. https://doi.org/10.1116/1.2101810
[32] Sanchez-Lopez JC, Martinez-Martinez D, Abad M.D, Fernandez A. Metal carbide/amorphous C-based nanocomposite

coatings for tribological applications. Surf Coat Technol 2009;204:947-954. https://doi.org/10.1016/j.surfcoat.2009.05.038

[33] Saoula N, Henda K, Kesri R, Shrivastava S, Erasmus RM, Comins JD. Effect of the plasma deposition parameters on the properties of Ti/TiC multilayers for hard coatings applications. Acta Physica Polonica A 2012;121:172-174. https://doi.org/10.1063/1.2999950

[34] Saoula N, Djerourou S, Yahiaoui K, Henda K, Kesri R, Erasmus RM, Comins J.D. Study of the deposition of Ti/TiN multilayers by magnetron sputtering. Surf. Interface Anal 2010;42:1176-1179. https://doi.org/10.1002/sia.3299

[35] Wang Q, Zhou F, Chen K, Wang M, Qian T. Friction and wear properties of TiCN coatings sliding against SiC and steel balls in air and water. Thin Solid Films 2011;519:4830-4841. https://doi.org/10.1016/j.tsf.2011.01.038

[36] Santecchia E, Zalnezhad E, Hamouda AMS, Musharavati F, Cabibbo M, Spigarelli S. Wear resistance investigation of titanium nitride-based coatings. Ceramics International 2015;41:10349-10379. https://doi.org/10.1016/j.ceramint.2015.04.152

[37] Danısman S, Odabas D, Teber M. The Effect of Coatings on the Wear Behavior of Ti6Al4V Alloy Used in Biomedical Applications, In: IOP Publishing, organizer. 9th International Conference on Tribology; 2017 September 13-15, Nevsehir, Turkey, p. 1-12.

[38] Correa JF, Aperador W, Caicedo JC, Alba NC, Amaya C. Structural, mechanical and tribological behavior of TiCN, CrAlN and BCN coatings in lubricated and nonlubricated environments in manufactured devices. Materials Chemistry and Physics 2020;252:123164. https://doi.org/10.1016/j.matchemphys.2020.123164

[39] Shi Y, Peng H, Xie Y, Xie G, Zhao Ch, Li S. Plasma CVD of hard coatings Ti(CNO) using metallo-organic compound Ti(OC3H7)4. Surface and Coatings Technology 2000;132:26-30. https://doi.org/10.1016/s0257-8972(00)00743-x

[40] Endler I, Hohn M, Herrmann M, Holzschuh H, Pitonak R, Ruppi S, van den Berg H, Westphal H, Wilde L. Aluminium-rich TiAlCN coatings by low pressure CVD. Surface & Coatings Technology 2010;205:1307-1312. https://doi.org/10.1016/j.surfcoat.2010.09.002

[41] Behrens BA, Huskic A. Reduction of wear on dies for precision forging of gears through multi-layer hard material coating (TiN-TiCN-TiC). Materialwiss Werkst 2005;36:218-225.

[42] Agudelo LC, Ospina R, Castillo HA, Devia A. Synthesis of Ti/TiN/TiCN coatings grown in graded form by sputtering DC. Phys Scr 2008;T131:1-3. https://doi.org/10.1088/0031-8949/2008/t131/014006

[43] Su YL, Kao WH. Tribological behavior and wear mechanisms of TiN/TiCN/TiN multilayer coatings. Mater Eng Perform 1998;7:601-612. https://doi.org/10.1361/105994998770347440

[44] Razmi A, Yeşildal R. Microstructure and mechanical properties of TiN/TiCN/TiC multilayer thin films deposited by magnetron sputtering. International Journal of Innovative Research and Reviews 2018;5(1):15-20. https://doi.org/10.20944/preprints201807.0127.v1

[45] Zheng J, Hao J, Liu X, Gong Q, Liu W. A thick TiN/TiCN multilayer film by DC magnetron sputtering. Surface & Coatings Technology 2012;209:110-116. https://doi.org/10.1016/j.surfcoat.2012.08.045

[46] Stanishevsky A, Lappalainen R. Tribological properties of composite Ti(N,O,C) coatings containing hard amorphous carbon layers. Surf Coat Technol 2000;123:101-105. https://doi.org/10.1016/s0257-8972(99)00514-9

[47] Hsieh JH, Wu W, Li C, Yu CH, Tan BH. Deposition and characterization of Ti(C,N,O) coatings by unbalanced magnetron sputtering. Surface and Coatings Technology 2003;163:233-237. https://doi.org/10.1016/s0257-8972(02)00494-2

[48] Hsieh JH, Tan ALK, Zeng XT. Oxidation and wear behaviors of Ti-based thin films. Surf Coat Technol 2006;201:4094-4098. https://doi.org/10.1016/j.surfcoat.2006.08.026

[49] Olteanu C, Munteanu D, Ionescu C, Munteanu A. Tribological characterisation of magnetron sputtered Ti(C, O, N) thin films. Int J Materials and Product Technology 2010;39:186-194. https://doi.org/10.1504/ijmpt.2010.034270

[50] Braic V, Braic M, Balaceanu M, Vladescu A, Zoita CN, Titorencu I, Jinga V. (Zr,Ti)CN coatings as potential candidates for biomedical applications. Surface & Coatings Technology 2011;206:604-609. https://doi.org/10.1016/j.surfcoat.2011.03.074

[51] Abd El-Rahman AM, Wei R. A comparative study of conventional magnetron sputter deposited and plasma enhanced magnetron sputter deposited Ti–Si–C–N nanocomposite coatings. Surface & Coatings Technology 2014;241:74-79. https://doi.org/10.1016/j.surfcoat.2013.08.049

[52] Hatem A, Lin J, Wei R, Torres RD, Laurindo C, Biscaia de Souza G, Soares P. Tribocorrosion behavior of low friction TiSiCN nanocomposite coatings deposited on titanium alloy for biomedical applications. Surface & Coatings Technology 2018;347:1-12. https://doi.org/10.1016/j.surfcoat.2018.04.049

[53] Shtansky DV, Kuptsov KA, Kiryukhantsev-Korneev PhV, Sheveiko AN, Fernandez A, Petrzhik MI. Comparative investigation of Al- and Cr-doped TiSiCN coatings. Surface & Coatings Technology 2011;205:4640-4648. https://doi.org/10.1016/j.surfcoat.2011.04.012

[54] Tillmann W, Grisales D, Stangier D, et al. Residual stresses and tribomechanical behaviour of TiAlN and TiAlCN monolayer and multilayer coatings by DCMS and HiPIMS. Surface & Coatings Technology 2021;406:126664. https://doi.org/10.1016/j.surfcoat.2020.126664

[55] Tillmann W, Grisales D, Tovar CM, Contreras E, Apel D, Nienhaus A, Stangier D, Lopes Dias NF. Tribological behaviour of low carbon-containing TiAlCN coatings deposited by hybrid (DCMS/HiPIMS) technique. Tribology International

2020;151:106528. https://doi.org/10.1016/j.triboint.2020.106528
[56] Sanchez-Lopez JC, Abad MD, Carvalho I, Escobar GR, et. all. Influence of silver content on the tribomechanical behavior on Ag-TiCN bioactive coatings. Surface & Coatings Technology 2012;206:2192-2198. https://doi.org/doi:10.1016/j.surfcoat.2011.09.059
[57] Thampi VVA, Dhandapani P, Manivasagam G, Subramanian B. Enhancement of bioactivity of titanium carbonitride nanocomposite thin films on steels with biosynthesized hydroxyapatite. International Journal of Nanomedicine 2015;10:107-118. https://doi.org/10.2147/IJN.S79976
[58] Lin J, Moore JJ, Mishra B, Pinkas M, Sproul W.D. The structure and mechanical and tribological properties of TiBCN nanocomposite coatings. Acta Materialia 2010;58:1554-1564. https://doi.org/10.1016/j.actamat.2009.10.063
[59] Ataie SA, Soltanieh M, Naghizadeh R, Ahmadi M, Ghanaatshoar M. Effects of substrate temperature and reactive gas flow rate on the crystalline ceramic phases formation and tribological properties of W–Ti–Co–C–N thin films produced by co-sputtering. Ceramics International 2020;46:29137-29149. https://doi.org/10.1016/j.ceramint.2020.08.087
[60] Onoprienko AA, Ivashchenko VI, Dub SN, Khyzhun OYu, Timofeeva II. Microstructure and mechanical properties of hard Ti–Si–C–N films deposited by dc magnetron sputtering of multicomponent Ti/C/Si target. Surface & Coatings Technology 2011;205:5068-5072. https://doi.org/10.1016/j.surfcoat.2011.05.009
[61] Zhang X, Qiu Y, Tan Zh, Lin J, Xu A, Zeng Y, Moore JJ, Jiang J. Effect of Al content on structure and properties of TiAlCN coatings prepared by magnetron sputtering. Journal of Alloys and Compounds 2014;617:81-85. https://doi.org/10.1016/j.jallcom.2014.08.009
[62] Kiryukhantsev-Korneev FV, Kuptsov KA, Sheveiko AN, Levashov EA, Shtansky DV. Wear Resistant Ti–Al–Si–C–N coatings produced by magnetron sputtering of SHS targets. Russian Journal of NonFerrous Metals 2013;54:330-335. https://doi.org/10.3103/s106782121304007x