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RESEARCH ARTICLE

Microstructure and Mechanical Properties of TiN/TiCN/TiC Multilayer Thin Films Deposited by Magnetron Sputtering

Abbas RAZMİ[1, *], Ruhi YEŞİLDAL[1]

[1] *Faculty of Engineering, Department of Mechanical Engineering, Construction and Manufacturing Division, Atatürk University, 25240 Erzurum, Turkey*

**Corresponding author E-mail: abbasrazmi@hotmail.com*

HIGHLIGHTS

> The mechanical properties of Cp-Ti substrate, such as nanohardness and scratch resistance, was significantly improved by the application of TiN/TiCN/TiC multilayer thin films.

> TiCN (1 1 1) phase was observed as the most dominant peak in the XRD spectrum and it indicates good crystallization which results in improved tribological and mechanical properties.

> Nanohardness of Cp-Ti substrate material increased from 3.15 GPa to 19.75 GPa after TiN/TiCN/TiC multilayer coating and the critical load for scuffing of the coating was found to be as high as 21 N in the scratch test.

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ABSTRACT

Enhancement of scratch and hardness mechanical properties of TiN/TiCN/TiC multilayer thin films deposited on commercially pure Titanium (Cp-Ti) and silicon (Si) substrates via magnetron sputtering technique were investigated in this study. The structural, chemical and mechanical properties of the coatings were characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), nanoindentation and scratch tests. Results of the XRD analysis showed reflections corresponded to cubic and polycrystalline structure for TiN/TiCN/TiC films. XPS analysis of the uppermost layer of TiN/TiCN/TiC film revealed that titanium nitride and titanium carbide were formed in the coatings. According to SEM cross-sectional images, the coatings demonstrated dense structure as well as good adhesion to the substrate with a thickness of 3.035 µm. Nanoindentation hardness and critical load value of scratch test results of TiN/TiCN/TiC multilayer film coated on Cp-Ti substrate materials obtained 19.75 GPa and 21 N, respectively.

Contents

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1. Introduction

Titanium and alloys have good mechanical properties such as low density and elastic modulus, high corrosion resistance, biocompatibility and long fatigue life, and therefore they find a wide range of application area in industries including, but not limited to, aerospace, automotive, medical, orthopedic, and dental [1–4]. Various deposition techniques such as chemical vapor deposition (CVD) [5], plasma enhanced chemical vapor deposition (PECVD) [6], magnetron sputtering [7], and thermal spraying [8, 9] have been used to improve surface properties of titanium and its alloys.

TiN, TiC, CrN, ZrN, NbN, TiCN, ZrCN, WC, WC–Co and WC–Ni, as the early examples of hard film layers, outperformed high-speed steel and cementite carbide thanks to greater hardness, toughness and lower friction coefficient. TiN, TiC and TiCN films have become highly preferable in fabrication of cutting tools, load bearings as well as in various tribological and biomedical applications as they offer excellent wear resistance, high hardness, good corrosion resistance, and biocompatibility [10–15].

TiN films, a hard ceramic layer, are usually deposited on hard steel substrates [16]. On the other hand, for many tribological applications, TiC has become the prominent coating material [17]. TiCN is another hard coating that offers outstanding wear resistance, hardness and corrosion resistance. Accompanied with non-cytotoxic character, TiCN films come forth as the ideal solution for biomedical applications [18]. Furthermore, a multilayer coating comprising of TiN/TiCN exhibits excellent mechanical properties such as higher hardness, wear and corrosion resistance than those of TiN and TiCN single layer films [19]. In this study, the microstructure and mechanical properties of TiN/TiCN/TiC multilayer thin films deposited on Cp-Ti substrates by magnetron sputtering technique were investigated.

2. Materials and Methods

Table 1 Chemical composition of Cp-Ti samples provided by supplier.

Element (%)	Cp- Ti
Ti	99.8
Si	< 0.0100
Mn	< 0.0100
Cr	< 0.0100
Mo	< 0.0100
Al	< 0.0050
Cu	< 0.0100
Fe	0.0926
V	< 0.0500
Zr	< 0.0100
Sn	0.0997
Nb	< 0.0100

Cp-Ti (grade 4) samples were used as substrate material. These samples were cut in 25×25×3 mm dimensions by using abrasive water jet method. Chemical composition of used substrate provided by supplier is given in Table 1.

Samples were ultrasonically cleaned with ethanol for 10 min. TiN/TiCN/TiC multilayered films were deposited on silicon and Cp-Ti substrates by using a DC closed field unbalanced magnetron sputtering system (CFUBMS) produced by Teer Coatings Ltd. The position of substrates and used targets in coating device is given in Figure 1.

Two rectangular titanium targets with the size of 380×175 ×10 mm and purity of 99.9% for both targets have been used for synthesizing the films. The sputtering gas was a mixture of Ar and N_2. The C_2H_2 gas was used to prepare the carbon content of the coatings.

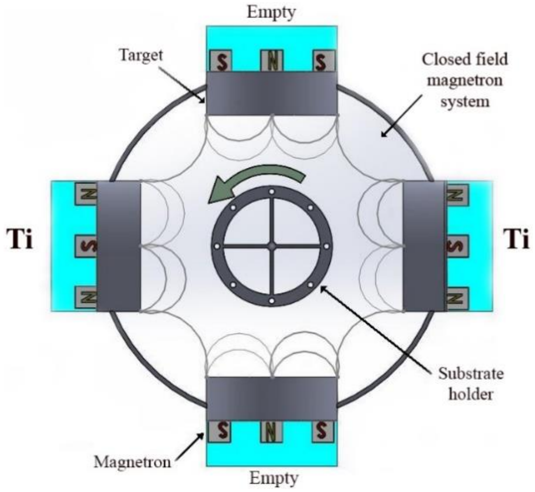

Figure 1 The position of substrates and targets in the magnetron sputtering system.

The substrates were rotated at speed of 2 rpm by substrate holder to obtain homogenous film structure. The deposition was carried out at a bias voltage of -60 V, a target current of 6 A, a distance from substrate to target of 90 mm and working pressure of 0.27 Pa. After putting samples into chamber, it was pumped down to a base pressure below 2.66×10^{-3} Pa. Afterwards, substrate materials were cleaned by ion cleaning in vacuum chamber for 20 min to remove oxide layers and surface contaminations. Before deposition of the TiN/TiCN/TiC multilayer film, Ti interlayer film was grown for 2 min, which could be beneficial to good adhesion properties [20]. Experimental parameters of TiN/TiCN/TiC coating are shown in Table 2.

Table 2 The TiN/TiCN/TiC multilayer thin film obtained by variation of N_2 and CH_4 flow rate.

Flow rate (%)			Ti target current (A)	Treatment time (min)	Phase
Ar	N_2	C_2H_2			
100	0	0	0	20	Ion cleaning
100	0	0	6	2	Ti (interlayer)
40	60	0	6	10	TiN
25	5	70	6	45	TiCN
75	0	25	6	15	TiC

Cross-section SEM image of the multilayer TiN/TiCN/TiC thin film deposited on Cp-Ti substrate was observed by

Quanta 250 FEG model scanning electron microscope. The crystalline structure of the multilayer film was investigated by the GNR X-Ray Explorer diffractometer using CuKα radiation (λ=1.5406 Å) with a Bragg-Brentano configuration (θ/2θ) and the scan range was from 20° to 90° at a scan speed of 2°/min. The composition of various compounds of the uppermost TiC layer of coating was performed by XPS (PHI-5000 versaprobe) with monochromatized Al Kα X-ray source at pass energy of 58.75 eV. In order to obtain the composition of the TiC layer, Ti2p, N1s and C1s spectra of the film were examined at pass energy of 187.85 eV and samples were sputtered by argon to remove the probable contaminations and or oxidations from the film surfaces.

The adhesion force of the TiN/TiCN/TiC film was measured by means of scratch test. The test was conducted by CSM Revetest Scratch Tester in dry atmosphere condition with a progressive load sliding between 0-30 N over the coating surfaces using Rockwell-C indenter tip with radius of 0.2 mm. The loading rate and track length were 100 N/min and 3 mm, respectively. Instron hardness tester was used to measure the nano-hardness values occurring on the top of the surface of the thin film. The applied load was 10 mN, with the loading time, waiting time, discharging time and thermal sliding time being, in the respective order, 15 s, 10 s, 15 s, and 45 s.

3. Results and discussion

3.1. Microstructure and composition examination

The XRD pattern of TiN/TiCN/TiC multilayer film deposited on silicon is given in Fig. 2. According to XRD pattern all peaks related to the (111), (220) and (222) plane of the cubic TiCN phases, (111) and (200) planes of the TiC phases and TiN (311) phase have been found in TiN/TiCN/TiC multilayer coating. The Ti peak (101) which has been applied as Ti interlayer for increase in adhesive properties between coating and substrate also has been found in multilayer coating [11, 21, 22]. The most dominant peak of the XRD pattern belongs to the TiCN (1 1 1) phase as a result of good crystallization which could result in improving tribological and mechanical properties of the film. On the other hand, TiC (111) phase which has high hardness and good resistance properties with weak diffraction was observed in coating [23–25].

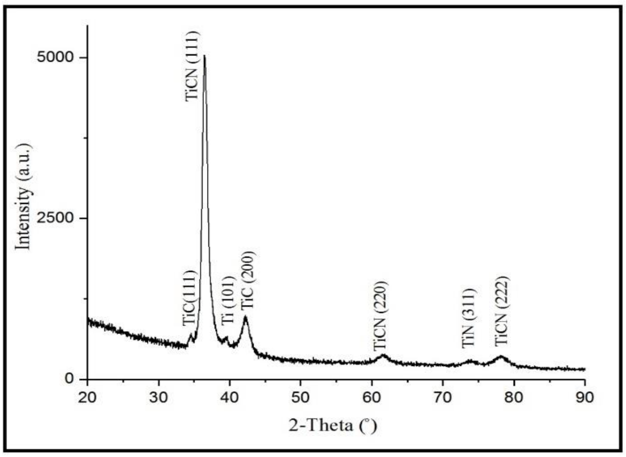

Figure 2 XRD patterns of the TiN/TiCN/TiC coating deposited on the silicon.

The XPS was used to determine the composition of the uppermost layer of the TiN/TiCN/TiC multilayer film. XPS spectra of Ti2p, N1S and C1s of the film are shown in Fig. 3. In order to obtain the composition of uppermost layer of film, spectra lines were deconvoluted with Gaussian function. According to the XPS results, Ti2p had three peaks at binding energy of 454.4 eV and 460.6 eV binding energy corresponds to TiC and the peak at 456.2 eV corresponds to TiN. The N1s spectrum had a peak in 397.2 eV corresponds to the TiN. In the case of C1s spectrum, one peak was found at 281.9 eV corresponds to TiC bonds. These results showed that nitrogen had diffused into the TiC layer of coating [26].

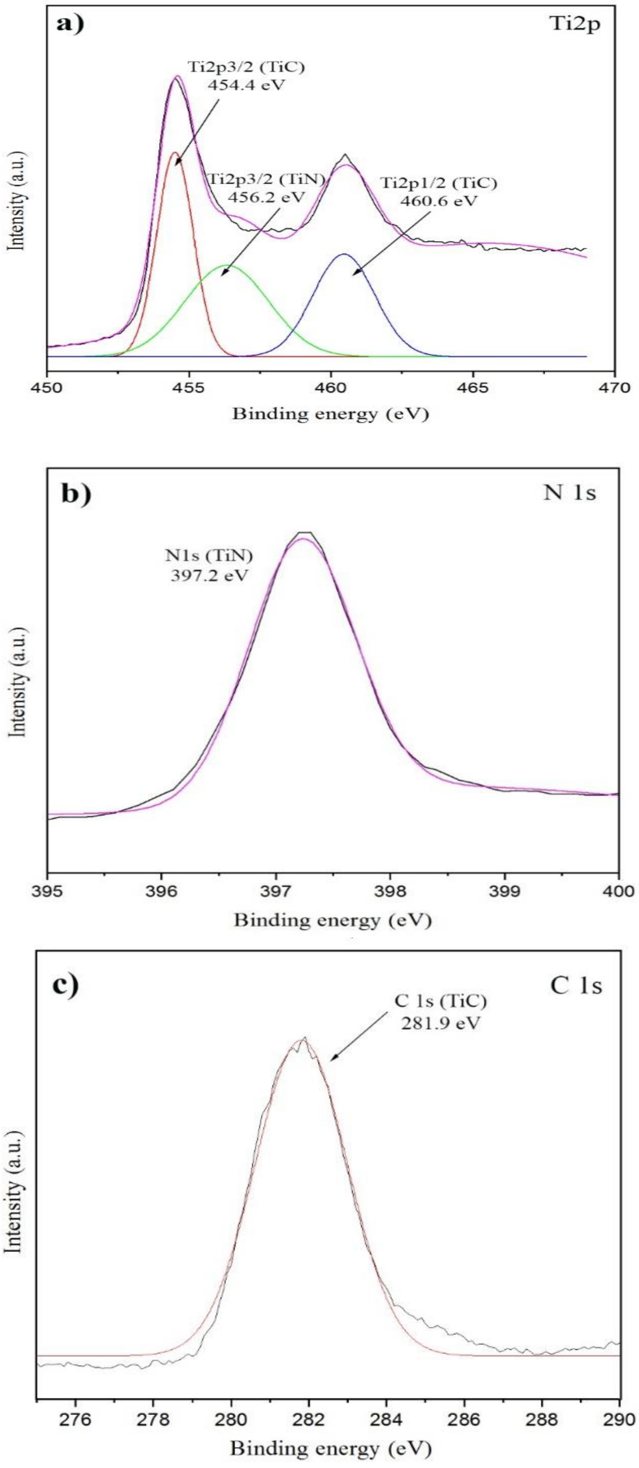

Figure 3 XPS spectra of; **(a)** Ti2p **(b)** N 1s and **(c)** C 1s of the TiN/TiCN/TiC coating.

Fig. 4 shows the cross-section SEM image of the TiN/TiCN/TiC films deposited on Cp-Ti substrate. To observe the cross-section view of the films, coated substrate was frozen in liquid nitrogen to give a brittle behavior to the ductile substrates and then fractured immediately. After that fractured substrate washed with ethanol several times and then dried. As can be seen from the SEM image, the thicknesses of films deposited on Cp-Ti substrate is 3.035 µm. The film-substrate interface for TiN/TiCN/TiC films are observed to be quite smooth and there is no apparent delamination between the substrate and the films.

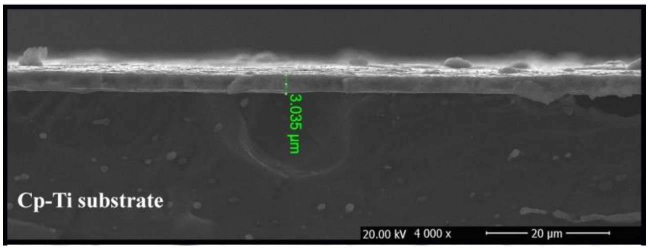

Figure 4 SEM cross-sectional image of TiN/TiCN/TiC films deposited on Cp-Ti substrate.

3.2. Mechanical properties

3.2.1. Scratch test

The value changes chart of coated Cp-Ti substrate of friction force, coefficient of friction and normal force values graph and optic microscope images obtained from the scratch test is given in Fig. 5. When the load value reached to 6 N, initial small cohesive fractures (Lc_1) began to show and followed up to 14 N. These cohesive cracks were widely formed on coating surface and present ductile fracture. First adhesive fractures occurred at 14 N (Lc_2), where coating started to separate from the substrate in the form of brittle fracture and coating is completely removed from the substrate at 21 N (Lc_3).

SEM images of scratch test of coated Cp-Ti sample are given in Fig. 6. When the SEM images were examined it was seen that first cohesive cracks were started in the vertical direction of the scratch path and were defined as Lc_1 critical load [27]. By increasing the normal load value, the coating began to separate from the substrate material and cause adhesive fractures (Lc_2) [28]. The critical load value (Lc_3) of TiN/TiCN/TiC coating deposited on Cp-Ti substrate was 21 N. Properties and performance of coating during the scratch test are related to the thickness of film. As coating thickness increased, more load is required to remove the coating and strength of scratch to delamination increased due to the lower stress concentration in the interface and more load support by the coating [29, 30]. When we consider our coatings thickness (3.035 µm), the film presents good adhesion force in comparison with the result of other authors [11, 31].

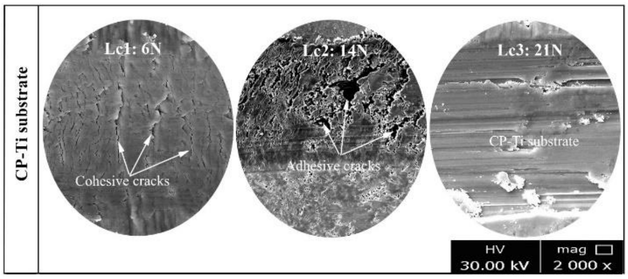

Figure 5 SEM images of scratch tracks of coated Cp-Ti substrate.

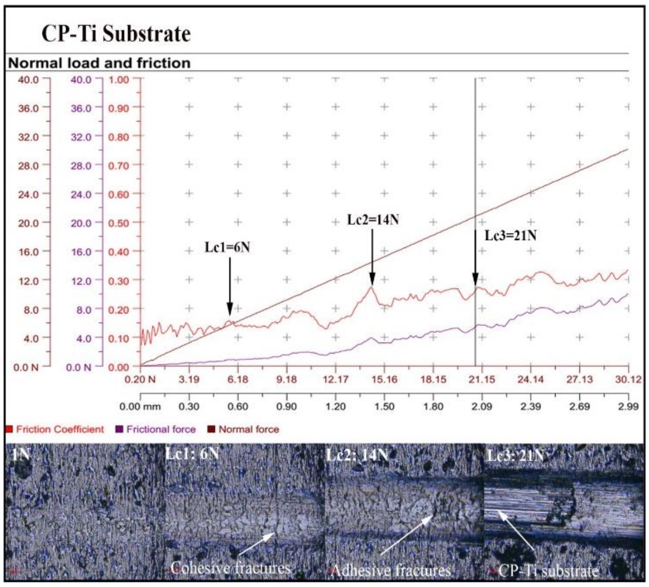

Figure 6 Frictional force, friction coefficient, normal force values graph and optic microscope images of Cp-Ti substrate.

3.2.2. Nano-Hardness measurements

Fig. 7 gives a typical loading-unloading indentation curves of TiN/TiCN/TiC film coated on Cp-Ti substrate material. The initial loading part involved of an elastic-plastic displacement while the unloading section released the elastic energy. Table 3 presents the results of nanoindentation and elastic modulus measurements for coated and uncoated substrates of TiN/TiCN/TiC multilayer films. The mean values of nanohardness and elastic modulus of the film deposited on Cp-Ti substrate were 19.75 GPa and 162.81 GPa, respectively. Some authors have reported hardness of TiN, TiCN and TiN/TiCN multilayer film with the thickness of 0.5-6 µm which ranges from 8.2 GPa to 27.3 GPa [2, 32–34]. Multilayer films could improve mechanical properties of films like hardness compared to every single-layered films. This improvement leads to high hardness and density. It can be explained that strong interface bonding of multilayered films results in hindering dislocation movement and dislocation glide over the TiN, TiCN and TiC layers which could be justified by the differences in the elastic shear modulus of the individual layer materials [35].

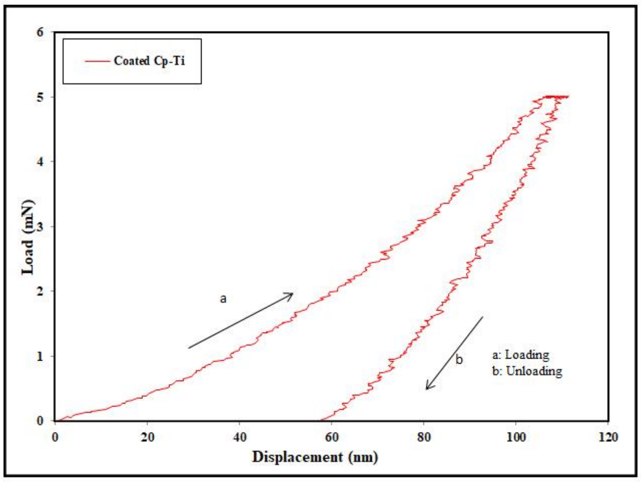

Figure 7 The typical loading-unloading curves of the Ti/TiN/TiCN/TiC multilayer film.

Table 3 Details of nanoindentation hardness and elastic modulus measurements of uncoated and TiN/TiCN/TiC coated Cp-Ti substrates.

Samples	Nanoindentation Hardness (GPa)	Elastic modulus (GPa)
Uncoated Cp-Ti	3.15	93.71
Coated Cp-Ti	19.75	162.81

4. Conclusions

The TiN/TiCN/TiC multilayered coatings were successfully deposited by CFUBMS technique on silicon, and Cp-Ti substrates. Results obtained are given below;

The thickness of films reached 3.035 μm on Cp-Ti substrate.

According to the XRD spectrum of the TiN/TiCN/TiC coating, Ti, TiN, TiC and TiCN diffractions were detected in the coating and the most prominent crystallographic reflection was in TiCN (111) plane.

XPS peaks corresponding to TiN and TiC bonds were found in the coating and showed that nitrogen had diffused into TiC layer, the top layer of the coating.

Nanoindentation tests indicate that, by applying of TiN/TiCN/TiC multilayer coating, nanohardness of Cp-Ti substrate material increased from 3.15 GPa to 19.75 GPa.

Scratch results showed that the critical load value (Lc_3) of TiN/TiCN/TiC coating deposited on Cp-Ti substrate was 21 N.

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Author Contributions

Yeşildal conceptualized the study, and participated in its design and coordination. Razmi carried out the validation of the data and participated in the discussions. Drafting, writing, and editing were also carried out by Razmi. All authors read and approved the final manuscript.

Conflicts of Interest

The authors declare that they have no competing interests.

References

[1] Kolli M, Kumar A. Effect of dielectric fluid with surfactant and graphite powder on Electrical Discharge Machining of titanium alloy using Taguchi method. *Engineering Science and Technology, an International Journal* (2015) **18**(4):524–535.

[2] Sivaprakasam P, Hariharan P, Gowri S. Modeling and analysis of micro-WEDM process of titanium alloy (Ti–6Al–4V) using response surface approach. *Engineering Science and Technology, an International Journal* (2014) **17**(4):227–235.

[3] Ataibis V, Taktak S. Characteristics and growth kinetics of plasma paste borided Cp–Ti and Ti6Al4V alloy. *Surface and Coatings Technology* (2015) **279**:65–71.

[4] Lautenschlager EP, Monaghan P. Titanium and titanium alloys as dental materials. *Int Dent J* (1993) **43**(3):245–253.

[5] Bao M, Xu X, Zhang H, Liu X, Tian L, Zeng Z, et al. Tribological behavior at elevated temperature of multilayer TiCN/TiC/TiN hard coatings produced by chemical vapor deposition. *Thin Solid Films* (2011) **520**(2):833–836.

[6] Wang HL, He JL, Hon MH. Sliding wear resistance of TiCN coatings on tool steel made by plasma-enhanced chemical vapour deposition. *Wear* (1993) **169**(2):195–200.

[7] 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.

[8] Zhu L, He J, Yan D, Xiao L, Dong Y, Zhang J, et al. Synthesis and microstructure observation of titanium carbonitride nanostructured coatings using reactive plasma spraying in atmosphere. *Applied Surface Science* (2011) **257**(20):8722–8727.

[9] Mi P, He J, Qin Y, Chen K. Nanostructure reactive plasma sprayed TiCN coating. *Surface and Coatings Technology* (2017) **309**:1–5.

[10] Devia DM, Restrepo-Parra E, Arango PJ. Comparative study of titanium carbide and nitride coatings grown by cathodic vacuum arc technique. *Applied Surface Science* (2011) **258**(3):1164–1174.

[11] Zheng J, Hao J, Liu X, Gong Q, Liu W. A thick TiN/TiCN multilayer film by DC magnetron sputtering. *Surface and Coatings Technology* (2012) **209**:110–116.

[12] Wang S-S, Xia Y, Zhang L-B, Guang H-B, Shen M, Zhang F-M. Effect of NbN and ZrN films formed by magnetron sputtering on Ti and porcelain bonding. *Surface and Coatings Technology* (2010) **205**(7):1886–1891.

[13] Zambrano G, Prieto P, Perez F, Rincon C, Galindo H, Cota-Araiza L, et al. Hardness and morphological characterization of tungsten carbide thin films. *Surface and Coatings Technology* (1998) **108-109**:323–327.

[14] Yao SH, Su YL, Kao WH, Cheng KW. Wear behavior of DC unbalanced magnetron sputter deposited ZrCN films. *Materials Letters* (2005) **59**(26):3230–3233.

[15] Rie KT, Wöhle J. Plasma-CVD of TiCN and ZrCN films on light metals. *Surface and Coatings Technology* (1999) **112**(1):226–229.

[16] Latella BA, Gan BK, Davies KE, McKenzie DR, McCulloch DG. Titanium nitride/vanadium nitride alloy coatings: mechanical properties and adhesion characteristics. *Surface and Coatings Technology* (2006) **200**(11):3605–3611.

[17] Radhakrishnan G, Adams PM. Pulsed-laser deposition of particulate-free TiC coatings for tribological applications. *Applied Physics A* (1999) **69**(1):S33-S38. doi:10.1007/s003399900163.

[18] Antunes RA, Rodas ACD, Lima NB, Higa OZ, Costa I. Study of the corrosion resistance and in vitro biocompatibility of PVD TiCN-coated AISI 316L austenitic stainless steel for orthopedic applications. *Surface and Coatings Technology* (2010) **205**(7):2074–2081.

[19] Su YL, Kao WH. Tribological Behavior and Wear Mechanisms of TiN/TiCN/TiN Multilayer Coatings. *Journal of Materials Engineering and Performance* (1998) **7**(5):601–612.

[20] Behrens BA, Huskic A. Wear reduction on dies for precision forging of gear wheels by means of multi-layer coating (TiN-TiCN-TiC). *Materialwissenschaft und Werkstofftechnik* (2005) **36**(5):218–225.

[21] Zhang G, Li B, Jiang B, Yan F, Chen D. Microstructure and tribological properties of TiN, TiC and Ti(C, N) thin films prepared by closed-field unbalanced magnetron sputtering ion plating. *Applied Surface Science* (2009) **255**(21):8788–8793.

[22] Natarajan G, Kumar N, Pandian R, Amirthapandian S. Grain boundary modification of TiC ultrananocrystalline thin films: Improvement in tribo-physical properties. *Materials Chemistry and Physics* (2018) **217**:468–476.

[23] Levi G, Kaplan WD, Bamberger M. Structure refinement of titanium carbonitride (TiCN). *Materials Letters* (1998) **35**(5):344–350.

[24] Meng J, Lu J, Wang J, Yang S. Tribological behavior of TiCN-based cermets at elevated temperatures. *Materials Science and Engineering: A* (2006) **418**(1):68–76.

[25] Siow PC, A. Ghani J, Ghazali MJ, Jaafar TR, Selamat MA, Che Haron CH. Characterization of TiCN and TiCN/ZrN coatings for cutting tool application. *Ceramics International* (2013) **39**(2):1293–1298.

[26] Restrepo Parra E, Arango PJ, Benavides V. *XPS structure analysis of TiN/TiC bilayers produced by pulsed vacuum arc discharge* (2010).

[27] Bhushan B, Ko PL. Introduction to tribology. *Appl. Mech. Rev.* (2003) **56**(1):B6-B7.

[28] Bull SJ. Failure mode maps in the thin film scratch adhesion test. *Tribology International* (1997) **30**(7):491–498.

[29] Zeng XT, Liu Y, Wei J, Holiday P. *Influence of Substrate Hardness on the Properties of PVD Hard Coatings* (2008). 156-161.

[30] Wirasate S, Boerio FJ. Effect of Adhesion, Film Thickness, and Substrate Hardness on the Scratch Behavior of Poly(carbonate) Films. *The Journal of Adhesion* (2005) **81**(5):509–528. doi:10.1080/00218460590944954.

[31] Guruvenket S, Li D, Klemberg-Sapieha JE, Martinu L, Szpunar J. Mechanical and tribological properties of duplex treated TiN, nc-TiN/a-SiNx and nc-TiCN/a-SiCN coatings deposited on 410 low alloy stainless steel. *Surface and Coatings Technology* (2009) **203**(19):2905–2911.

[32] Bemporad E, Pecchio C, Rossi S de, Carassiti F. Characterization and hardness modelling of alternate TIN/TICN multilayer cathodic arc PVD coating on tool steel. *Surface and Coatings Technology* (2001) **146-147**:363–370.

[33] Kim G-H, Rand AG, Letcher SV. Impedance characterization of a piezoelectric immunosensor: Part I: Antibody coating and buffer solution. *Biosensors and Bioelectronics* (2003) **18**(1):83–89.

[34] Peters AM, Nastasi M. Effect of carrier gas on the deposition of titanium carbo-nitride coatings by a novel organo-metallic plasma immersion ion processing technique. *Vacuum* (2002) **67**(2):169–175.

[35] Caicedo JC, Amaya C, Yate L, Gómez ME, Zambrano G, Alvarado-Rivera J, et al. TiCN/TiNbCN multilayer coatings with enhanced mechanical properties. *Applied Surface Science* (2010) **256**(20):5898–5904.