

Silicon carbonitride layers deposited on titanium and polyurethane by PACVD method

JADWIGA KONEFAŁ-GÓRAL^{1*}, ANNA MAŁEK¹, STANISŁAWA KLUSKA¹, WITOLD JASTRZĘBSKI¹, SŁAWOMIR ZIMOWSKI², STANISŁAWA JONAS¹, JERZY LIS¹

¹AGH University of Science and Technology, Faculty of Material Science and Ceramics,
30 Mickiewicza Av., 30-059 Krakow, Poland

²AGH University of Science and Technology, Faculty of Mechanical Engineering and Robotics,
30 Mickiewicza Av., 30-059 Krakow, Poland

This work reports the results concerning formation and tribological properties of $\text{SiC}_x\text{N}_y(\text{H})$ layers deposited on Ti Grade 2 and polyurethane foil. Depending on the substrate, two variants of PACVD were used. The $\text{SiC}_x\text{N}_y(\text{H})$ layers on titanium were deposited with application of MWCVD (2.45 GHz, 2 kW). The layers on polyurethane were deposited using RFCVD (13.56 MHz, 400 W). Good adhesion between the $\text{SiC}_x\text{N}_y(\text{H})$ layers and polymeric foil was achieved by formation of a transitional C:N:H layer and incorporating Si gradient into the structure of the $\text{SiC}_x\text{N}_y(\text{H})$ layer. The chemical composition of the layers was tailored by precise control of the gaseous precursors ratios: $[\text{SiH}_4]/[\text{NH}_3]$, $[\text{SiH}_4]/[\text{NH}_3]/[\text{CH}_4]$, $[\text{SiH}_4]/[\text{CH}_4]$ or $[\text{SiH}_4]/[\text{N}_2]/[\text{CH}_4]$. The structure and chemical composition of the obtained layers were subjected to further studies (FTIR, SEM/EDS). The roughness, friction coefficient and wear resistance were also measured. The results show that $\text{SiC}_x\text{N}_y(\text{H})$ layers offer attractive tribological properties which make them good candidates for various applications, including biomedical devices.

Keywords: PACVD; silicon carbonitride layers; tribology

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1. Introduction

Silicon carbonitride layers deposited on different substrates are very promising for various applications. Due to their chemical resistance, including outstanding oxidation resistance and thermal stability, they can be used as anti-corrosion layers [1–5]. Good mechanical (high hardness, mechanical strength) and tribological (low friction coefficient, high wear resistance) properties make them suitable for protective layers against abrasion [1–3, 5]. Moreover, thanks to the wide band gap (3.8 eV), they are considered as attractive materials for optoelectronic devices [1–3, 5].

A reliable method of fabricating $\text{SiC}_x\text{N}_y(\text{H})$ layers is Plasma Assisted Chemical Vapor Deposition (PACVD) [3–5]. When the processing parameters are well chosen, the layers exhibit high homogene-

ity, purity and have a tailored chemical composition. The purpose of this work is to show that PACVD may be applied to fabricate well adhesive $\text{SiC}_x\text{N}_y(\text{H})$ layer on Ti and polyurethane – the two substrates which are used in medical devices and that the obtained layers improve tribological parameters of these substrates.

Titanium is used as a material for orthopedic, surgical implants, in veterinary medicine, dentistry or as a material for operational equipment [6, 7]. Polyurethane (PUR) is mainly used as material for contact with blood in valves and elements of artificial heart [8]. Both titanium and PUR have, however, some limitations. In the case of titanium, the biggest problems concern a danger of an allergy at the implant – bone interface and metallosis phenomenon in the vicinity of metal implants, due to corrosion or hypersensitivity reaction [9]. Polyurethane can be operated safely and reliably in contact with the blood only for a short time pe-

*E-mail: konefal@agh.edu.pl

riod. During long-term working, a risk of degradation of the polymer chain increases and fatigue strength becomes insufficient. It causes large danger of blood clotting [8].

This is why it is so important to find a suitable method for modifying the surfaces of both materials. The authors of this work anticipate that the modification of Ti and PUR surface by silicon carbonitride layers make them proper for use as materials for long-term contact with human body. In the case of PUR, it is expected that $\text{SiC}_x\text{N}_y(\text{H})$ layers will reduce thrombogenicity whereas, in the case of titanium, they will increase the time of application and eliminate the problem of allergy [10].

In the following sections of this work we describe the details concerning PACVD technology providing well adhesive $\text{SiC}_x\text{N}_y(\text{H})$ layers (both on metallic and polymeric substrates) of a given chemical composition and with tribological parameters improved compared to $\text{Si}_x\text{N}_y(\text{H})$, $\text{Si}_x\text{C}_y(\text{H})$ and DLC. The presented idea together with the experimental data show a new direction of the search for new layer materials for the applications as functional coatings.

2. Materials and methods

The series of silicon carbonitride layers on Ti Grade 2 and polyurethane foil were deposited by chemical vapor deposition in the AGH laboratory equipped with multi-EDS-RFCVD designed by Elettrovava. The same layers were obtained on monocrystalline silicon (001)Si for structural studies. The $\text{SiC}_x\text{N}_y(\text{H})$ layers were deposited on titanium with application of MicroWave CVD (MWCVD at the frequency 2.45 GHz, 2 kW). For comparison, the Ti samples with $\text{Si}_x\text{N}_y(\text{H})$ and $\text{Si}_x\text{C}_y(\text{H})$ layers were fabricated. To avoid microwave heating of the substrate during the deposition, the layers on the polyurethane foil (sensitive to high temperature) were deposited using Radio Frequency plasma (RFCVD at a frequency of 13.56 MHz, 400 W). Good adhesion between the $\text{SiC}_x\text{N}_y(\text{H})$ layer and polymeric foil was achieved by formation a graded interlayer with a composition gradient of Si atoms perpendicular to the coating surface.

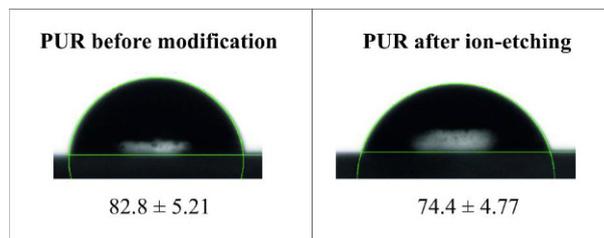


Fig. 1. Microscopic image of a deionized water drop for unmodified PUR and after ion-etching measured using a sessile drop method.

Before deposition, the substrates were pre-cleaned: Ti with acetone and PUR with isopropyl alcohol. The formation of the layers was preceded by glow discharge cleaning in argon plasma during 10 minutes. In the case of titanium substrate this stage caused surface cleaning and elimination of the TiO_x surface layer. After 10 minutes of ion treatment, titanium oxide had not been detected on the surface of Ti substrate neither with XRD nor FTIR technique. In the case of polyurethane substrate, the glow discharge cleaning made possible to create an interface, which was essential for achieving a good adhesion of the subsequent layer to this substrate. It allowed formation of unsaturated dangling bonds at the surface, which were “ready” to create new bonds with the particles (atoms, ions and radicals) from the gas phase. This treatment led to the formation of an interlayer with increased surface energy as evidenced by a contact angle decrease (Fig. 1). During formation of $\text{SiC}_x\text{N}_y(\text{H})$ layers on metallic surfaces, SiH_4 , NH_3 and CH_4 at various ratios (Table 1) were used as reactive gases. Dilute silane and argon flows (due to health and safety requirements) were kept at unchanged level but the flow rates of NH_3 and CH_4 were changed as given in Table 1. The flows of ammonia gas – NH_3 and methane – CH_4 were changed in a manner that the sum of the flows of these gases was kept at a constant level. In this way three types of coatings were obtained: $\text{Si}_x\text{N}_y(\text{H})$, $\text{SiC}_x\text{N}_y(\text{H})$ and $\text{Si}_x\text{C}_y(\text{H})$. In each case the deposition time was 30 minutes. The other parameters were as follows: pressure in reaction chamber – 40 Pa, the substrate temperature – 600 °C and the power of the microwave plasma generator – 400 W.

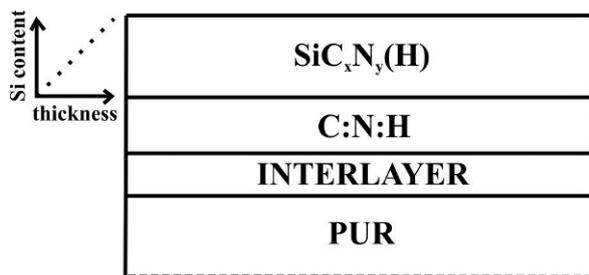


Fig. 2. Scheme of a layer on PUR substrate system.

Obtaining layers with good adhesion to PUR substrate made a lot of difficulties. The best result was achieved by the deposition of a transition C:N:H layers between the substrate and the proper $\text{SiC}_x\text{N}_y(\text{H})$ layer. The external silicon carbonitride layer was manufactured with gradient of Si perpendicular to the coating external surface. A scheme of the obtained composite C:N:H/ $\text{SiC}_x\text{N}_y(\text{H})$ layer is presented in Fig. 2. The optimized composition of the gas mixture is given in Table 1. The layers were deposited during 45 minutes at a room temperature, under the pressure in the reactor chamber equal to 53 Pa and at the power of RF plasma discharge 80 W. The thickness of the C:N:H/ $\text{SiC}_x\text{N}_y(\text{H})$ layers was measured with the use of an atomic force microscope (AFM). For this purpose a step on the polymeric surface was created. The interatomic bonds in the layers were identified with the use of FTIR transmission spectra registered in the range of 500 cm^{-1} to 4000 cm^{-1} . The spectra were obtained with the use of Bio-Rad FTS 60 V spectrophotometer of resolution 4 cm^{-1} and number of scans 256. Chemical compositions of the layers were examined using high resolution scanning electron microscope FEI Nova Nano SEM 200 with a field electron emission gun (FEG) equipped with EDAX EDS system and Genesis software. The composition was also confirmed by the application of XPS (to a depth of about 5 nm) using X-ray tube with an aluminum anode of the characteristic radiation energy $\text{Al K}\alpha$ equal to 1486.6 eV.

The effect of surface modification onto the surface roughness was examined with the use of a T 500 Hommelwerke profilometer.

The dry friction and wear coefficients of coatings deposited onto Ti substrate at sliding during rotation were studied using a “sphere-plane”

type tribotester (ball-on-disc), in accordance with ASTM G 99-05 or ISO 20808:2004 standards. A 6 mm diameter ball made of bearing steel was used as the counter-specimen during the tests.

The studies of tribological properties of the C:N:H/ $\text{SiC}_x\text{N}_y(\text{H})$ coating system on PUR substrate, including measurements of scratch resistance and friction coefficient, were performed with a Micro-Combi-Tester from CSEM. The scratch test was made using Rockwell C diamond indenter with the radius of curvature at the apex equal to $200\text{ }\mu\text{m}$, under the load linearly increasing from 0.03 N to 1 N. Scratch length was 5 mm and the speed of the indenter displacement was 5 mm/min.

3. Chemical composition and atomic structure

Fig. 3 shows an AFM image of C:N:H/ $\text{SiC}_x\text{N}_y(\text{H})$ layer on PUR which was used in evaluation of the layer thickness. It follows from the Fig. 3 that the layer is about 850 nm thick. As it is known, CVD process allows obtaining layers with different chemical composition, structure, morphology and thickness, depending on the parameters of deposition process. The layers were designed individually for each type of substrate. In the case of the polymer-ceramic layer and metal-ceramic layer system our experience indicates that the process parameters shown in Table 1 allow obtaining layers with good adhesion to substrates and with optimal tribological parameters. The spectrum of the layer, deposited on (001)Si substrate in MWCVD system (Fig. 4) is dominated by a broad band within the range of $500 - 1100\text{ cm}^{-1}$. The band relates to overlapping wagging vibrations of Si-H (about 640 cm^{-1}), C-Si-N stretching (about 820 cm^{-1}) and Si-N stretching in Si-N-Si group (about 990 cm^{-1}) [3, 11]. Moreover, there are two additional weak but clear bands within $2100 - 2130\text{ cm}^{-1}$ and $2800 - 3550\text{ cm}^{-1}$. The first is assigned to Si-H bonds and the second one to overlapping CH_n , N-H and O-H bonds. [3, 11–14]. The FTIR transmission spectrum of C:N:H/ $\text{SiC}_x\text{N}_y(\text{H})$ layer deposited in RFCVD system at room temperature

Table 1. The composition of gas mixtures applied in plasma assisted CVD of $\text{SiC}_x\text{N}_y(\text{H})$ layers.

System	Substrate	Layer	Gas flow [cm^3/min]					
			Ar	N_2	NH_3	CH_4	SiH_4	
MWCVD	Ti, (001)Si	$\text{Si}_x\text{N}_y(\text{H})$	225	–	150	–	3	
	Ti, (001)Si	$\text{SiC}_x\text{N}_y(\text{H})$	225	–	130	20	3	
	Ti, (001)Si	$\text{Si}_x\text{C}_y(\text{H})$	225	–	–	25	3	
RFCVD	PUR,(001)Si	C:N:H/ $\text{SiC}_x\text{N}_y(\text{H})$	75	104	–	25	0→20min	20→45min
							0	2→5

(Fig. 5) is different and is composed of overlapping bands from particular layers. It shows relatively weak absorption bands at 760 cm^{-1} and 960 cm^{-1} corresponding to stretching vibrations of SiC and Si–N bonds [3, 14, 15]. The absorption at about 625 cm^{-1} and 2185 cm^{-1} is associated with deformation and stretching vibrations of terminal Si–H bonds [3, 14–16]. Some contribution to the absorption at 2200 cm^{-1} may come from the vibration of triple $\text{C}\equiv\text{C}$ bonds. Relatively broad band within $1550 - 1700\text{ cm}^{-1}$ may be assigned to double $\text{C}=\text{C}$, $\text{C}=\text{N}$ bonds in chains and rings [16]. The absorption band within $2800 - 3000\text{ cm}^{-1}$ is characteristic of hydrogenated carbon. It may be considered as an effect of overlapping of three bands assigned to C–H vibrations in the following groups: $\equiv\text{CH}$ (2880 cm^{-1}), $=\text{CH}_2$ (2935 cm^{-1}), $-\text{CH}_3$ (2965 cm^{-1}) [3, 15, 16]. The broad band located between 3200 and 3550 cm^{-1} confirms an activity of stretching vibrations of O–H and –N–H bonds (in $-\text{NH}_2$, $-\text{C}-\text{NH}_2$ and $-\text{C}=\text{NH}$) [14]. It also demonstrates a presence of hydrogen bridges between nitrogen atoms ($-\text{N}-\text{H}\cdots\text{N}-$). Strong band at about 1100 cm^{-1} is attributed to the vibrations of Si–O and Si–C (in $\text{Si}-\text{CH}_2-\text{Si}$ grouping) [3, 14–16]. It cannot be resolved into singular bands due to their significant overlapping. XPS analysis of $\text{SiC}_x\text{N}_y(\text{H})/\text{Ti}$ and $\text{C:N:H}/\text{SiC}_x\text{N}_y(\text{H})/\text{PUR}$ samples was also performed. The results confirmed the presence of silicon, carbon and nitrogen as well as oxygen absorbed from the atmosphere at the surface of both samples.

Additional information about chemical composition of $\text{SiC}_x\text{N}_y(\text{H})$ layer on Ti surface was obtained by SEM technique. The cross-section of this

system and the analysis of chemical composition along the marked line is presented in Fig. 6. As it is shown, the layer thickness is about 196 nm. Based on this result the presence of nitrogen along the whole cross-section was confirmed. It may be explained by nitrogen diffusion into the titanium substrate. Moreover, the larger quantities of silicon and carbon in the area near the surface evidence the presence of silicon carbonitride layer on metallic surface.

4. Properties

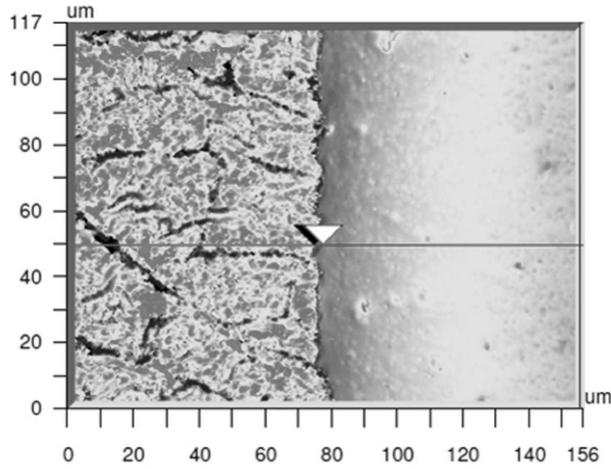
Surface roughness is an important tribological parameter which has an impact on friction coefficient and wear resistance of a material; the more rough surface, the higher friction coefficient and lower wear resistance. In the case of biomaterials it is desirable to reduce friction and to increase their wear resistance. It would be possible if surface modification did not increase its roughness.

In the present studies of surface roughness the following parameters were measured: arithmetic average of the roughness profile (R_a), maximal difference between the highest peak and lowest valley (R_t) and average height of the roughness profile (R_z) determined from five highest peaks and five lowest valleys. The measurements were performed for unmodified Ti and PUR substrates (raw sample) and compared with the results for the substrates subjected to glow discharge cleaning and the substrates coated with the layers.

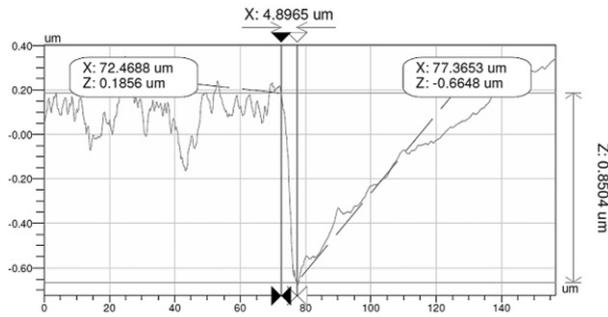
The obtained results are presented in Fig. 7 which shows the values of roughness profile average (R_a) for various surfaces. The results con-

Table 2. Roughness parameters for Ti and PUR before modification (raw substrate), after ion etching and after modification with a layer.

	Ti _{raw}	Ti _{ie}	Ti _{mod}	PUR _{raw}	PUR _{ie}	PUR _{mod}
R _a [μm]	0.11 ± 0.01	0.18 ± 0.01	0.11 ± 0.01	0.24 ± 0.01	0.32 ± 0.07	0.26 ± 0.02
R _z [μm]	3.58 ± 1.74	6.52 ± 1.94	3.78 ± 0.68	3.40 ± 0.29	3.41 ± 0.90	3.12 ± 0.38
R _t [μm]	1.40 ± 0.93	2.00 ± 0.43	1.11 ± 0.19	11.93 ± 3.41	6.53 ± 2.37	6.59 ± 0.99



(a)



(b)

Fig. 3. (a) 2D AFM image of C:N:H/SiC_xN_y(H) layer on PUR, (b) the section profile. The layer obtained in RFCVD system under following parameters: 75 cm³/min Ar, 104 cm³/min N₂, 25 cm³/min CH₄, 2 – 5 cm³/min SiH₄, p = 53 Pa, P = 80 W, t = 45 min.

firm that glow discharge cleaning of a substrate increases its surface roughness. In contrast to that, deposition of a layer smoothens the surface again. The changes of the other roughness parameters,

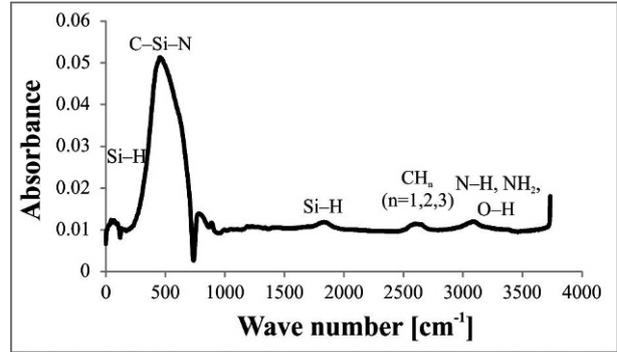


Fig. 4. FTIR spectrum of SiC_xN_y(H) layer deposited on (001)Si in MWCVD system.

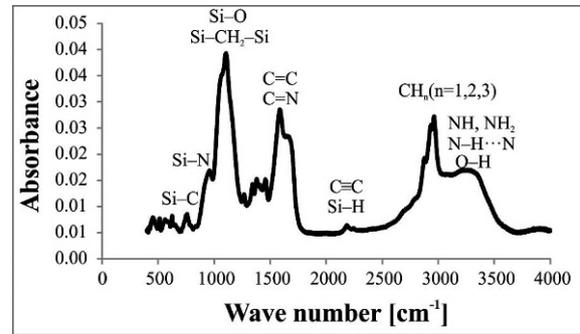
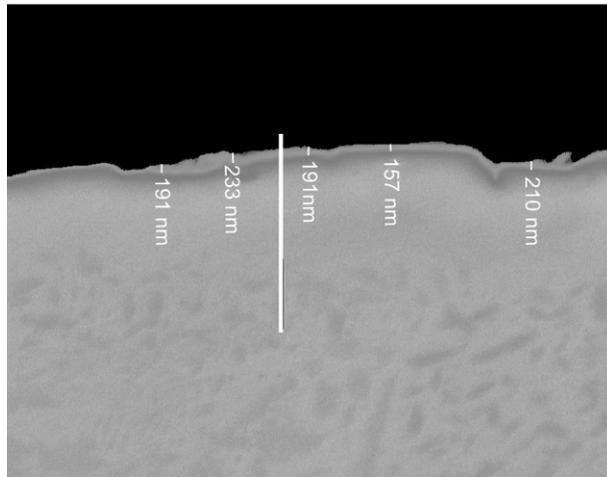
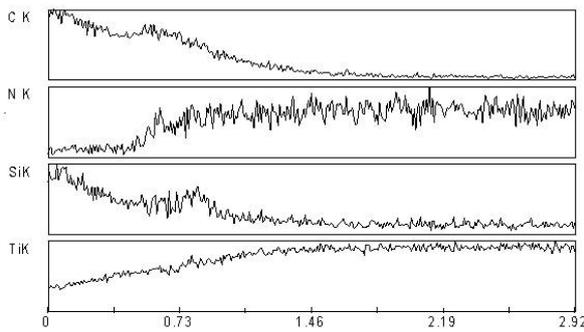


Fig. 5. FTIR spectrum of C:N:H/SiC_xN_y(H) layer deposited on (001)Si in RFCVD system.

i.e. R_z and R_t, correlate with R_a (Table 2). The exception is R_t measured for PUR and PUR with the C:N:H/SiC_xN_y(H) layer. Studies of tribological properties of the layers deposited on Ti substrate included measurements of the friction coefficient at sliding during rotation and measurements of resistance to wear during sliding friction. Fig. 8 shows a comparison of the average values of the friction coefficients measured for unmodified Ti and for Si_xN_y(H)/Ti, SiC_xN_y(H)/Ti, Si_xC_y(H)/Ti systems.



(a)



(b)

Fig. 6. The SEM image of (a) a cross section of $\text{SiC}_x\text{N}_y(\text{H})/\text{Ti}$ system, (b) the analysis of chemical composition along the line. The layer was obtained in MWCVD system under following parameters: $225 \text{ cm}^3/\text{min}$ Ar, $130 \text{ cm}^3/\text{min}$ NH_3 , $20 \text{ cm}^3/\text{min}$ CH_4 , $3 \text{ cm}^3/\text{min}$ SiH_4 , $p = 40 \text{ Pa}$, $T = 600 \text{ }^\circ\text{C}$, $P = 400 \text{ W}$, $t = 30 \text{ min}$.

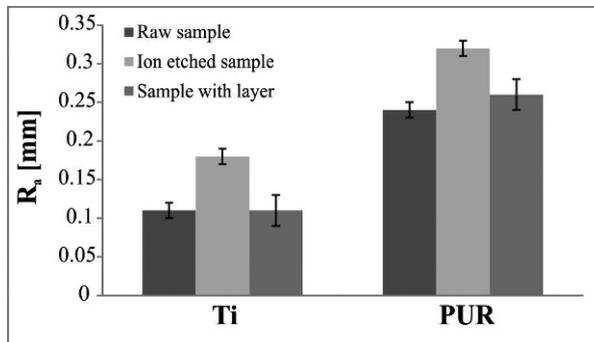


Fig. 7. R_a parameter measured for Ti and PUR: before modification, after ion etching and for the samples with $\text{SiC}_x\text{N}_y(\text{H})$ layers.

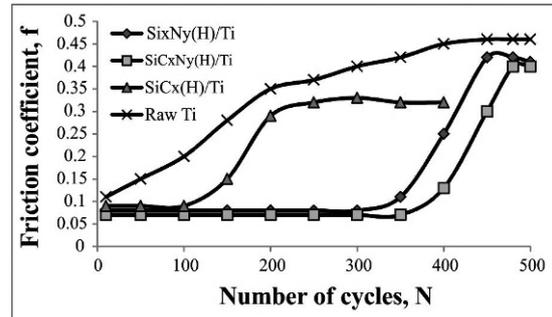


Fig. 8. Friction coefficient measured for unmodified Ti and for the substrate with the deposited layers. The load for unmodified Ti was equal to 0.5 N and for the samples with the layers it was 0.25 N .

The highest friction coefficient (within 500 cycles) had Ti substrate without any layer. The samples with $\text{Si}_x\text{N}_y(\text{H})$ and $\text{SiC}_x\text{N}_y(\text{H})$ layers exhibited very good sliding properties up to 350 cycles ($f < 0.1$). Then the friction coefficient increased as a result of the layer wear. Nevertheless, it remained at the level lower than the values for unmodified Ti. The smallest friction coefficients were measured for titanium with $\text{SiC}_x\text{N}_y(\text{H})$ layer. The observed wear of the samples had mainly abrasive character. The adhesive wear could take place only on the substrate surface. The results of the measurements of wear resistance are presented in Fig. 9. The highest wear resistance exhibited the sample with $\text{SiC}_x\text{N}_y(\text{H})$ layer but the smallest one was measured for the sample with $\text{Si}_x\text{C}_y(\text{H})$ layer. Thus, the addition of nitrogen improves resistance of the layer to abrasive wear. It can be assumed that the admixture of nitrogen atoms should not be too high so as to preserve the elasticity of the $\text{SiC}_x\text{N}_y(\text{H})$, in contrast to brittle silicon carbide. Obtaining a layer with a good adhesion to the polymer, which is susceptible to a considerable thermal deformation is an essential technological problem. The scratch resistance and friction coefficient against the diamond indenter were measured for unmodified polyurethane and polyurethane with $\text{C:N:H/SiC}_x\text{N}_y(\text{H})$ layer. Optical microscope images taken during the measurement are presented in Fig. 10. First cracks of $\text{C:N:H/SiC}_x\text{N}_y(\text{H})$ layer were observed under the load of 0.15 N , which corresponded to the indenter penetration depth about

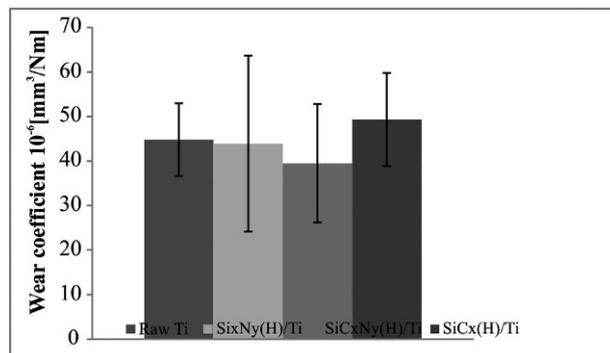


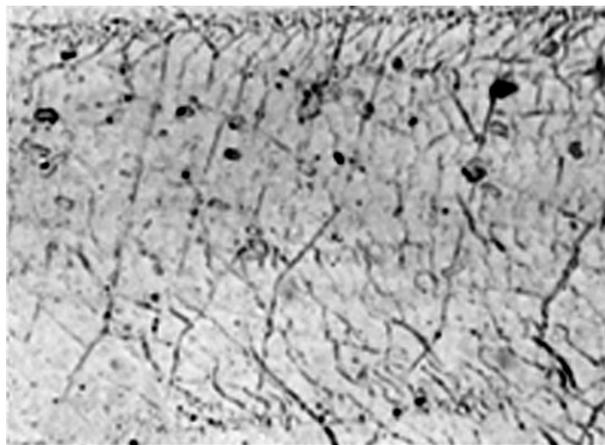
Fig. 9. Wear coefficient measured for unmodified Ti and for the substrate with the deposited layers.

35 μm (Fig. 10a). The increase of the load caused a significant strengthening of the cracking process. Crushing of the layer was observed under the load of 0.7 – 0.8 N (with the penetration depth about 100 μm). It was accompanied by delamination of narrow layer areas from the substrate (Fig. 10c). These small delaminating areas were observed in the vicinity of cohesive cracks (Fig. 10b). There was no large delamination up to maximal applied load of 1 N (i.e. for the penetration depth in the range of 110 – 120 μm). These results give a proof of a good adhesion of the C:N:H/SiC_xN_y(H) layer to PUR substrate.

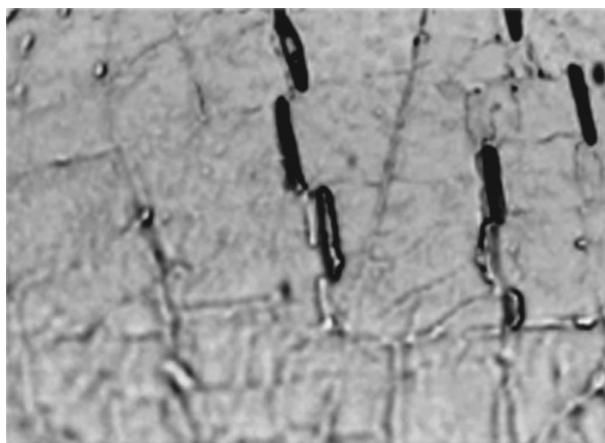
The results of friction coefficient measurements confirmed that application of C:N:H/SiC_xN_y(H) coating system on to the PUR substrate reduces the resistance to motion. The friction coefficient decreased from 1.0 – 1.3 for unmodified PUR to 0.2 – 0.3 for a synergic PUR-layer system (Fig. 11).

5. Conclusions

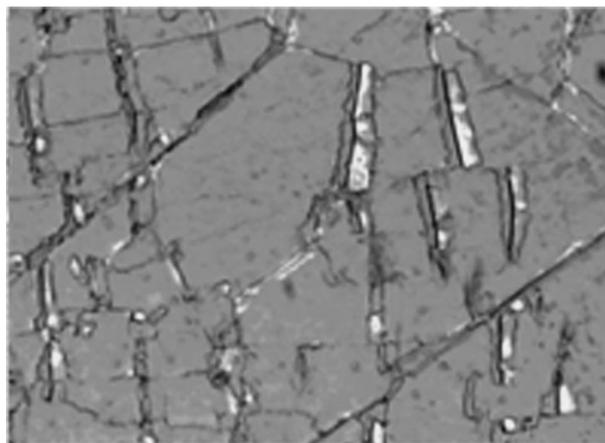
The processing conditions for surface modification of titanium Grade 2 and polyurethane with silicon carbonitride layers deposited in PACVD system were elaborated using MW and RF CVD methods. The C:N:H/SiC_xN_y(H) layer thickness measured with AFM was equal to 850 nm. The chemical composition of the deposited layers was examined with SEM, FTIR and XPS techniques. In the case of the SiC_xN_y(H) layers on Ti (deposited in MWCVD system) FTIR spectra were dominated by the band in



(a)



(b)



(c)

Fig. 10. Scratch track of C:N:H/SiC_xN_y(H) layer deposited on PUR substrate: (a) cracks under the load of 0.15 N (zoom 200 \times), (b) cohesive cracks (zoom 500 \times), (c) layer crushing under the load of 0.7 N (zoom 500 \times).

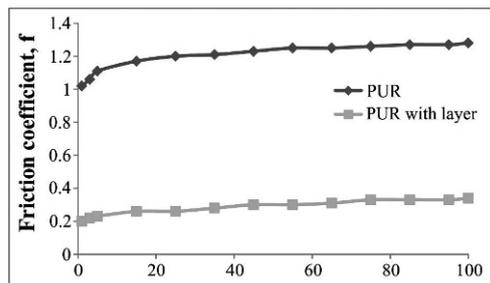


Fig. 11. Friction coefficient measured for unmodified PUR and for substrate with deposited layer. The load was equal to 0.25 N.

the range of $500 - 1100 \text{ cm}^{-1}$ assigned to Si–H, Si–C, Si–N vibrations. Next to this band there were weak bands assigned to Si–H, CH_n , N–H, NH_2 , O–H bonds. The layers on the polyurethane surface (deposited in RFCVD) had a complex structure. FTIR spectra showed the bands with clearly visible peaks, assigned to vibration modes of Si, C and N atoms in various surroundings. SEM analysis of metallic sample confirmed the presence $\text{SiC}_x\text{N}_y(\text{H})$ layer on Ti surface and indicated nitrogen diffusion into the titanium structure.

It was shown that the glow discharge cleaning increased the roughness of the modified surfaces, whereas deposition of the coatings decreased it. The roughness of the substrate with the layer was at the same level as the roughness of the unmodified substrate before ion etching. The most important results of the reported studies include confirmation that the $\text{SiC}_x\text{N}_y(\text{H})$ layers deposited on Ti Grade 2 and PUR have good tribological properties: they increase the wear resistance and decrease the friction coefficient in comparison with raw substrates.

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