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Multilayer, hybrid PVD coatings on Ti6Al4V titanium alloy

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ABSTRACT

Purpose: The main purpose of this paper was to develop hybrid PVD technology of deposition wear resistant, multilayer coatings onto diffusion-hardened Ti6Al4V titanium alloy. Titanium and its alloys are desirable materials in modern constructions and vehicles. They have a high specific strength and very good corrosion resistance and biocompatibility. On the other hand, they have a low load-bearing capacity and poor tribological properties, as, for example, high friction coefficient, low resistance to adhesive and abrasive wear and tendency to galling. Development of multiplex coatings depositions techniques is vital for expanding of areas of titanium alloys usage.
Design/methodology/approach: In the present work a new approach to coatings deposition onto diffusion hardened in glow discharge plasma (in Ar+O_2 atmosphere) Ti6Al4V titanium alloy was proposed by means of a hybrid PVD method including three coatings deposition methods: Reactive Magnetron Sputtering (RMS), Filtered Cathodic Arc Evaporation (FCAE) and Pulsed Cathodic Arc Deposition (PCAD). The main aim of the work was to develop multilayer coatings combined of sublayers of titanium or chromium carbonitrides or of pure, hard carbon ones.
Findings: It was concluded from the results of investigations that not every proposed multilayer structure ensure good frictional properties of Ti6Al4V alloy even when the coating posses very high hardness. The lowest value of wear and friction coefficient was determined for multilayer coating with $(TiC/C)_{x3}$ structure.
Research limitations/implications: Further research is necessary for a better understanding of the mechanisms of friction and wear as well as the origin of superhardness of particular multilayers.
Practical implications: Multilayer coatings deposited by means of the hybrid PVD technique can be used for low friction and wear protection of titanium alloys.
Originality/value: Originality value of this paper consists in use in one process of three different PVD techniques for coatings deposition: FCAE, RMS and PCAD. Moreover, the coatings were deposited onto diffusion hardened by interstitial oxygen atoms Ti6Al4V alloy.
Keywords: Surface treatment; Hybrid PVD coatings; Titanium alloys; Friction and wear

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1. Introduction

A quote from an article written by Donnet and Erdemir [1]: "... development of structured coating (e.g. nanocomposite, superlattice, gradient, etc.) did not prevent the emergence of new 'single' structures or original concepts in solid lubrication..." is a good explanation of permanent interest in new coatings deposition technologies. Present work describes an original concept of multilayer coatings deposition by means of a hybrid PVD technique including three different coatings deposition methods: Reactive Magnetron Sputtering (RMS), Filtered Cathodic Arc Deposition (FCAE) and Pulsed Cathodic Arc Deposition (PCAD). The main aim of the work was to develop multilayer coatings combined of sublayers of titanium or chromium carbonitrides and of pure, hard carbon ones on diffusion hardened in glow discharge plasma (in Ar+O_2 atmosphere) Ti6Al4V titanium alloy.

Titanium and its alloys are desirable materials in modern constructions and vehicles owing to high value of their strength-to-weight ratio, corrosion resistance and good biocompatibility. On the other hand, they have low load-bearing capacity and poor tribological properties, for example high friction coefficient, low resistance to adhesive and abrasive wear and proneness to galling.

One can find only a few examples of multiplex technologies for wear protection of titanium alloys. It is crucial in this aspect to select a convenient coating material and suitable technology of its deposition. One of that is a duplex treatment of titanium alloys consisting nitriding in a glow discharge with subsequent deposition of TiN coating [2], but it does not provide a low friction coefficient. In another one, after plasma carburizing of Ti6Al4V alloy and CrN coating deposition, the wear volume was reduced, but not the friction coefficient [3, 4]. On the other hand, different carbon coatings exhibit very good frictional properties. Bell et al. [5] have proposed another duplex technology combined of boost diffusion of oxygen treated Ti6Al4V alloy and, as a next step, deposition of a gradient TiN-TiCN-TiC-DLC coating. As a result, for investigated alloy the static load-bearing capacity increased four times. In Poland, a number of multiplex techniques were elaborated among others by Wendler and Pawlak [6], Major et al. [7], Mróz et al. [8] or Cłapa and Batory [9, 10]. It is possible to find in a literature also a computational approach to the problem of coatings deposition onto titanium alloys [11].

2. Experimental procedure

2.1. Substrate preparation

Discs from Ti6Al4V alloy (25.4 mm in diameter and 6 mm thick) were used as the substrates. After grinding and mirror polishing of one of the discs' end faces with the use of colloidal silica (0.04 µm mesh) the substrates were diffusion hardened in glow discharge plasma (in Ar+O_2 atmosphere) during 10.8 ks according to a procedure described elsewhere [6, 12].

In order to adopt a uniform surface finish all the specimens after diffusion hardening were polished with the use of 3 µm diamond paste. After polishing, the surface hardness was approximately 850 HV0.1.

For some studies (for example for EDS analysis, nanoindentation or Raman shifts spectroscopy) monocrystalline pure Si (100) substrates (0.56 mm thick) were used as well. For tribological investigations of monolayer DLC coatings hard ASP 2023 HSS disks were used instead of the Ti6Al4V ones. The samples were cleaned firstly in detergent and secondly in ultrasonic acetone bath and dried in high purity nitrogen flow.

2.2. Hybrid PVD coatings deposition

The coatings were deposited in an industrial, multipurpose unit URM 079. It was equipped with two independent continuous, filtered arc sources for metallic plasma (arc current up to 180 A), two pulsed arc sources for carbon plasma (mean power of the carbon arc discharge 1 kW) and one high-power (max. 10 kW) magnetron sputtering source. For easy movement of substrates against different sources of plasma, the two-axis, digitally controlled, robotic arm with samples holder was designed and well-made. A schematic view of the vacuum chamber architecture is presented in Fig. 1.

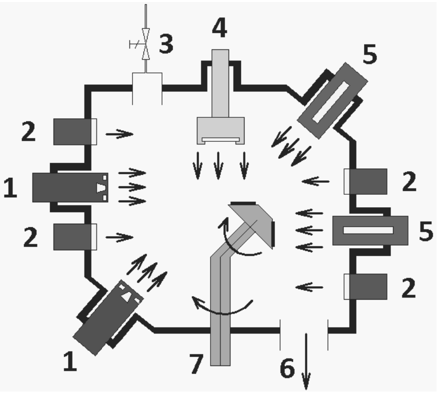

Fig. 1. Scheme of the vacuum chamber equipment of a multipurpose installation for hybrid PVD coatings deposition: 1-two independent arc sources of metallic plasma working in continuous mode; 2-four independent 4 kV Ar ions guns; 3 - gas flow control system; 4-magnetron sputtering source; 5-two independent pulsed arc sources of carbon plasma; 6-connection to vacuum pumps; 7-two-axis, rotary table for specimens with digital, position control system

After attachment of the substrates to the sample holder and evacuating the air to residual pressure of approx. 10^{-4} Pa, high-energy (approx. 1, 2 keV) argon ions cleaning was switched on. During 20 minutes of sputtering of the samples surface, a negative bias of the samples was increased from 0 V to 1500 V. In case of coatings deposited by means of FCAE an additional step of substrates heating with Ti^+ or Cr^+ ions (from arc sources with pure Ti or Cr targets) of the energy approx. 1keV during 90-300s have been performed. Thereafter, a thin (~100nm) metallic titanium or chromium layer was deposited for better coatings adhesion. In a case of magnetron sputtering deposition also pure Ti or Cr targets were used. Parameters of deposition of carbon, TiC, TiN and CrN monolayer coatings are given in Table 1. The layer sequences in multilayer coatings are presented in Table 2. Due to very high level of residual stresses generated in multilayer coatings deposited only by two methods: $(FCAE+PCAD)_{xn}$ or $(RMS+PCAD)_{xn}$ all that coatings suffer from delamination. The solution was an original concept to use as first sublayer in multilayer coatings the one deposited by means of FCAE and next, after carbon deposition as second sublayer, consecutively magnetron sputtered sublayers of TiN or TiC or CrN and PCAD carbon ones. In every multilayer the carbon layer was also deposited as the last one, in order to achieve a low value of friction coefficient.

Table 1.
Deposition parameters for carbon, TiN, TiC and CrN monolayer coatings

Designation	Type of coating	Deposition method	Reactive gas flow [sccm]		Pressure during deposition	Source parameters		Max. time of deposition
			N_2	C_2H_2	[Pa]	Current [A]	Power [kW]	[s]
A-TiN	TiN	FCAE	14	-	3.7×10^{-3}	55	1.65	5400
A-TiC	TiC		-	8	1.5×10^{-3}			
A-CrN	CrN		7.5	-	4.9×10^{-3}	47	1.50	1800
B-TiN	TiN	RMS	16	-	2.7×10^{-1}	4	3	5400
B-TiC	TiC		-	8		3.9	3	4800
B-CrN	CrN		20.5	-	6.5×10^{-1}	4.2	1.5	1800
C	DLC	PCAD	-	-	1.0×10^{-3}	Cathode potential	Impulses frequency	Count of pulses
						[V]	[Hz]	-
						275	7	up to 12 000

Table 2.
Implemented layer sequences during multilayer coatings depositions

Designation	Type of coating	Layer sequence in multilayer coatings 1	2	3	4	5	6	7	8	9	10
M-1	$(TiN/C)_{x5}$	A-TiN/240*	C/4500	B-TiN/300	C/4500	B-TiN/300	C/5000	B-TiN/300	C/5200	B-TiN/300	C/6000
M-2	$(TiN/C)_{x3}$	A-TiN/240	C/4500	B-TiN/120	C/4500	B-TiN/120	C/4500				
M-3	$(TiC/C)_{x3}$	A-TiC/240	C/4500	B-TiC/120	C/4500	B-TiC/120	C/4500				
M-4	$(CrN/C)_{x2}$	A-CrN/120	C/6000	A-CrN/180	C/6000						
M-5	$(CrN/C)_{x5}$	A-CrN/90	C/2100	B-CrN/60	C/2100	B-CrN/60	C/2100	B-CrN/60	C/2100	B-CrN/60	C/2500

* - type of coating/deposition time in seconds for A-and B- type coatings or count of pulses for C-type ones

2.3. Characterisation of deposited coatings

Fundamental investigations of deposited coatings include thickness measurement (by means of Calo-test or of SEM observations of brittle coatings' fractures as well as of ellipsometry and of AFM measurements), micro- and nanohardness measurements (with the use of CLEMEX microhardness tester and MTS G200 nanoindenter, in Continuous Stiffness Mode with maximum load of 500mN respectively), measurements by means of a scratch tester, measurements of the chemical and phase composition (with EDS Thermo Noran attachment or Siemens D500 with $Co_{K\alpha}$ radiation respectively), morphology investigations with the use of optical microscopy and SEM - Hitachi S3000N electron microscope, surface roughness measurement with the use of a Hommel Tester T1000 profilometer as well as friction and wear investigations with the use of a 'ball-on-disc' tester T11. In the case of the last ones, a dry friction coefficient of the coatings was measured against a hard 100Cr6 steel bearing ball of the diameter of 5 mm under different loads up to 10 N, at a constant linear velocity of 0.1 m/s, at a temperature (296±3) K in static air of relative humidity (48±4) %. Track radii of 4, 7, and 10 mm have been used for different friction tests on the same sample.

The results of investigations of tribological properties were compared with those for the samples of the Ti6Al4V alloy as delivered and after diffusion hardening by interstitial oxygen atoms. For carbon layers the Raman shifts spectroscopy with the use of Yobin Yvon microspectrometer T 64000 was also used with 514.5 nm laser wavelength and 60s exposition time. For some of multilayer coatings XPS in-depth-distributions have been performed with the use of Physical Electronics spectrometer PHI 5700/660. Analyses of monochromatic Al excitation radiation of 250 W power and at 45 deg incident angle were conducted every 20 minutes after 5 keV Ar-ions sputtering of 2x2 mm area.

3. Description of achieved results

In the course of research a series of monolayer as well as multilayer coatings were deposited by means of a hybrid PVD technique. Monolayer coatings consisting titanium carbide or nitrides of titanium or chromium were deposited by means of FCAE or RMS. In order to verify their chemical and phase composition by means of EDS and XRD investigations (The results of the latter not presented in this paper) thicker coatings were deposited as presented in Tables 2 and 3. The results of calculations of the coefficient of wear and nanohardness estimations for Ti6Al4V alloy substrate as delivered and after diffusion hardening in glow discharge plasma are given in Table 3 as well. Monolayer DLC coatings were deposited by means of the PCAD technique. An example of a Raman spectrum for these coatings is presented in Fig. 2, an AFM image of a scratched surface of the DLC coating together with the profilogram of the scratched allowing to measure the coatings' thickness are given in Fig. 3 and the results of friction tests are presented in Fig. 4. The results of the ellipsometric investigations of the coatings' thickness as well as of the refractive index are presented in Table 4.

Table 3.
Results of investigations of Ti6Al4V substrate after different treatments as well as of monolayer coatings deposited by PVD methods

Designation	Thickness	Chemical composition [%at.]					Wear rate	Nanohardness
	[μm]	Cr	Ti	C	N	Other	$[m^3 \cdot N^{-1} \cdot m^{-1}]$	[GPa]
As delivered Ti6Al4V	-	-	-	-	-	-	$(5.5 \pm 0.8) \times 10^{-13}$	n. a.
Diffusion hardened Ti6Al4V	≥50	-	-	-	-	-	$(8.7 \pm 0.4) \times 10^{-14}$	9.0
A-TiN	2.8	-	49	-	51	-	$(4.5 \pm 1.4) \times 10^{-14}$	34.5
A-TiC	1.8	-	20	80	-	-	$(5.7 \pm 2.8) \times 10^{-15}$	n. a.
A-CrN	1.1	74	-	-	26	-	$(6.3 \pm 3.7) \times 10^{-14}$	26.0
B-TiN	1.3	-	71	-	29		$(1.2 \pm 1.1) \times 10^{-14}$	13.9
B-TiC	4.0	-	69	31	-	-	$(2.1 \pm 0.9) \times 10^{-15}$	27.3
B-CrN	3.1	88	-	-	12	-	$(1.9 \pm 0.1) \times 10^{-14}$	20.6

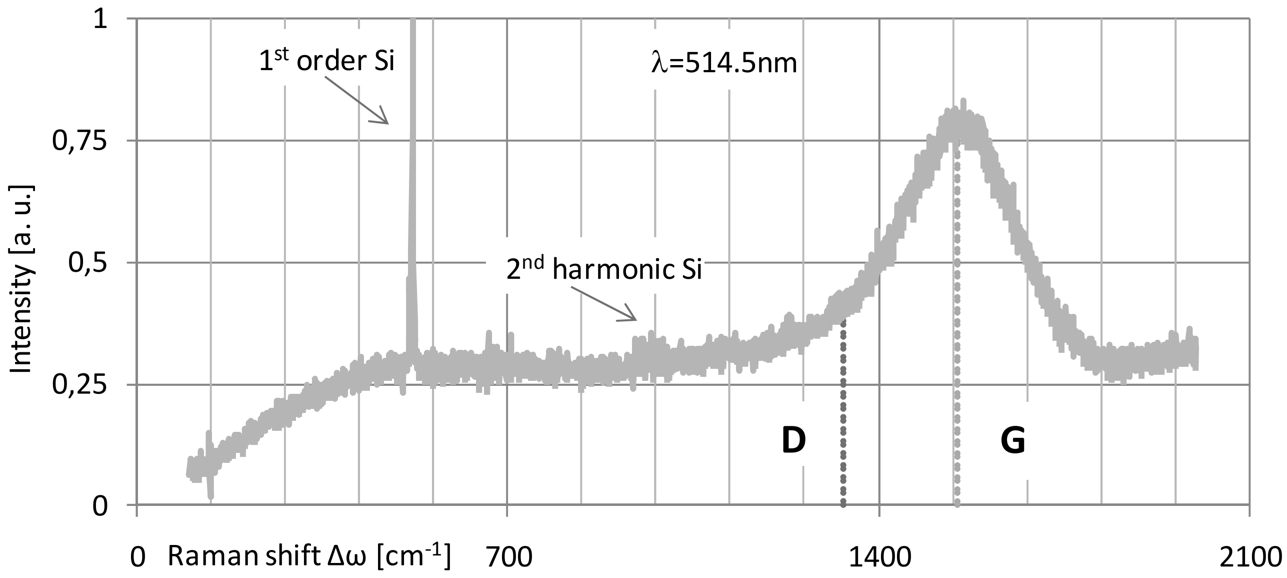

Fig. 2. Raman spectrum of the DLC layer on pure Si substrate

In a similar way as the data presented in Table 3, the ones concerning the results of investigations for multilayer coatings including their thicknesses, chemical compositions, wear rates and nanohardness are presented in Table 5.

SEM image of a fracture of one of the multilayer coating (M5), composed of 10 sublayers, is given in Fig. 5. XPS 'in-depth' profiles of the for C1s and Ti2p electron energy spectra for the M3 multilayer coating is presented in Fig. 6. Comparison of friction coefficient values measured during dry sliding both for as delivered and after diffusion hardening of the Ti6Al4V alloy as well as for multilayer coatings is given in Fig. 7. Finally, a comparison of the results of hardness measurement as well as of the values of the nanohardness-to-nanomodulus of elasticity ratio (H/E) is presented in Fig. 8.

It was found that the monolayer TiN, TiC or CrN coatings deposited onto diffusion hardened Ti6Al4V substrates by means of FCAE or RMS do not protect satisfactorily against friction and wear. Coefficients of wear were decreased from ~ 10^{-13} $m^3 \cdot N^{-1} \cdot m^{-1}$ to ~10^{-15} $m^3 \cdot N^{-1} \cdot m^{-1}$ only for TiC coatings, regardless of deposition technique. For diffusion hardened substrates and coated with TiN or CrN monolayer coatings, the wear rate was in the range of 10^{-14} $m^3 \cdot N^{-1} \cdot m^{-1}$. The friction coefficients for these coatings were greater than that for Ti6Al4V alloy as delivered (>0.6). The thickness 168nm from ellipsometry measurements of the DLC coatings was confirmed by AFM investigations of scratches in the coatings made with the use of a sharp diamond stylus (see Fig. 3). It allows to use an 'a-C model' implemented into the ellipsometer software for further measurements of carbon coatings deposited by means of PCAD. Moreover, the dependence of friction coefficient on the load during dry sliding is shown in Fig. 4. It is worth mentioning that the coatings were deposited onto the Vanadis 23HSS steel and the loads were low (≤ 5 N) in comparison with the 10 N load used during friction tests of multilayer coatings.

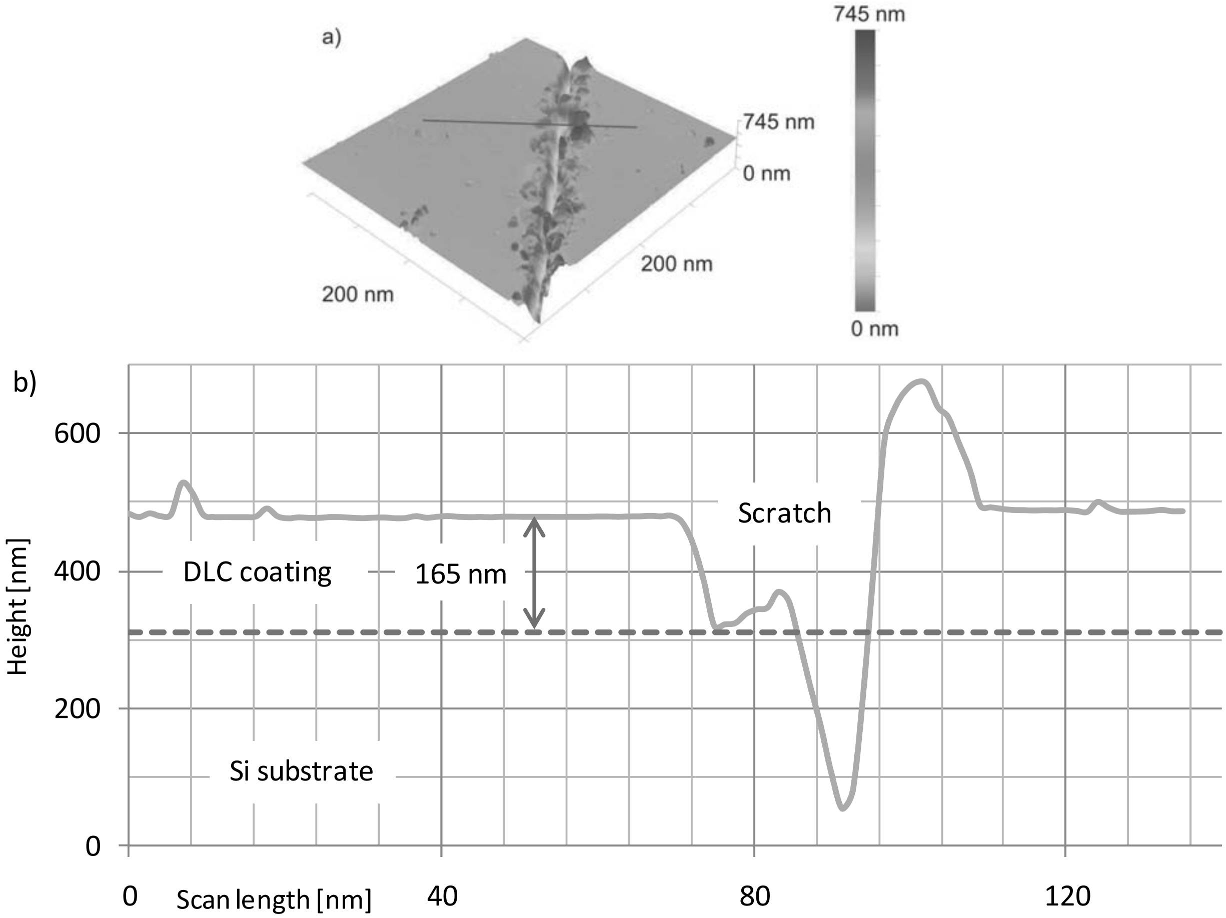

Fig. 3. a) AFM topography of the surface of the DLC coating deposited onto pure Si substrate with a scratch track made with use of a sharp diamond stylus during an adhesion test. b) Surface profile made along a red line shown in Fig 3a

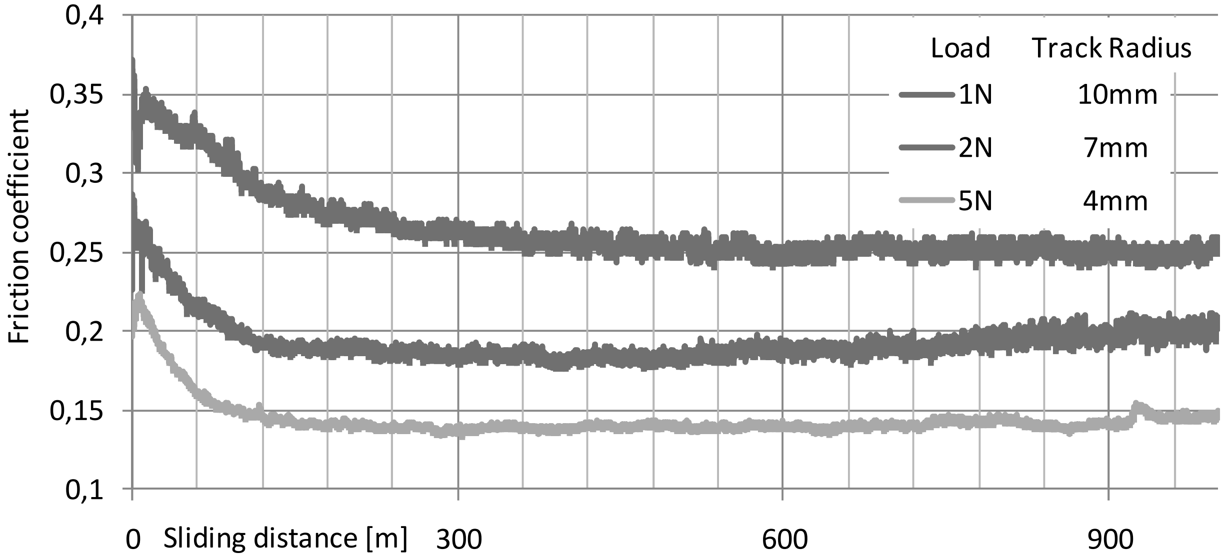

Fig. 4. Friction coefficient of the same DLC coating (designed as C in Table 1) under different loads and at constant linear velocity of $0.1 m \cdot s^{-1}$

Table 4.
Results of investigations of DLC coating deposited by means of PCAD method

Designation	Thickness	Index of refraction	Dry friction coefficient		
	[nm]		1N	2N	5N
C	168±3	2.405	0.25	0.18	0.14

Table 5.
Results of investigations of multilayer coatings deposited by means of a hybrid PVD method

Designation	Thickness	Chemical composition [%at.]					Wear rate	Nanohardness
	[μm]	Cr	Ti	C	N	Other	[$m^3 \cdot N^{-1} \cdot m^{-1}$]	[GPa]
M-1	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	$(5.5\pm0.4)x10^{-15}$	47.7
M-2	0.9	-	32.0	65.4	2.1	Al: 0.2; V:0.2	$(3.8\pm4.8)x10^{-16}$	44.6
M-3	0.9	-	28.4	71.4	0.0	Al: 0.1; V:0.1	$(2.2\pm1.0)x10^{-16}$	52.7
M-4	0.9	n.a.	n.a.	n.a.	n.a.	n.a.	$(3.1\pm0.5)x10^{-15}$	58.1
M-5	0.85	22.2	14.0	57.9	4.2	Al:1.1; V:0.6	n.a.	29.1

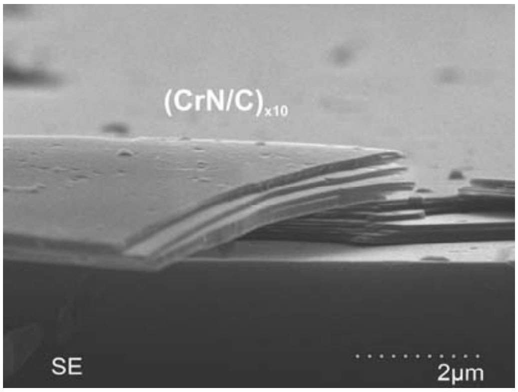

Fig. 5. SEM image of a fracture of M5 multilayer coating composed of 10 sublayers deposited onto a pure Si substrate

The Raman spectrum of the DLC coating is very similar to that described by Lifshitz in [13] or Stanishevsky in [14] for a ta-C coating. In case of Raman spectra excited in such coatings with use of a green laser light radiation (of the wavelength 514.5 nm a symmetric, very broad maximum appears at 1550 cm^{-1} and the so-called 'D-line' at 1330 cm^{-1} is not easily distinguished. It allows to estimate the value of the fraction of the sp^3 hybridization in the DLC coating investigated in the present paper is not lower than 75%.

It follows Table 5 that the thickness of all the multilayer coatings did not exceed 1 μm. This fact did not interfere with a very high hardness and good protection of the Ti6Al4V alloy against wear. The values of wear coefficients of the multilayer coatings were ~ 10^{-15} $m^3 \cdot N^{-1} \cdot m^{-1}$ for M1 and M4 coatings and ~ 10^{-16} $m^3 \cdot N^{-1} \cdot m^{-1}$ for M2 and M3 ones. The last two coatings have the lowest values of dry friction coefficients: 0.13 and 0.15, respectively. M4 multilayer coating was the hardest (58.1 GPa) and was composed of only four sublayers (two CrN and two of ta-C type). M5 coating with the microstructure shown in Fig. 6, had the lowest value of hardness (29.1 GPa) and delaminated from the titanium substrate during friction tests.

In order to confirm the sequence of chemical composition within the multilayer coatings a sequence of the XPS spectra 'in-depth' from the coatings' surface has been performed as well. One can see from Fig. 6 that in case of the C1s electron energy spectrum of carbon atoms registered three different values of maximum energy. At the surface of the multilayer coating the carbon atoms are bound in hydrocarbons, lower down in depth from the coatings' surface they are bound together in a ta-C sublayer and next they are bound with Ti atoms in a TiC compound sublayer. This last statement is confirmed by electron energy profiles for the Ti2p electrons in the same M3 multilayer coating: starting from the spectrum no.8 in Fig. 6 (b) the both Ti2p electron energy maxima are emerging and simultaneously the intensity of the maximum energy of the C1s electrons decreases to a great extent. This simultaneity confirms a sequence of C/TiC/C/… sublayers in the M3 multilayer.

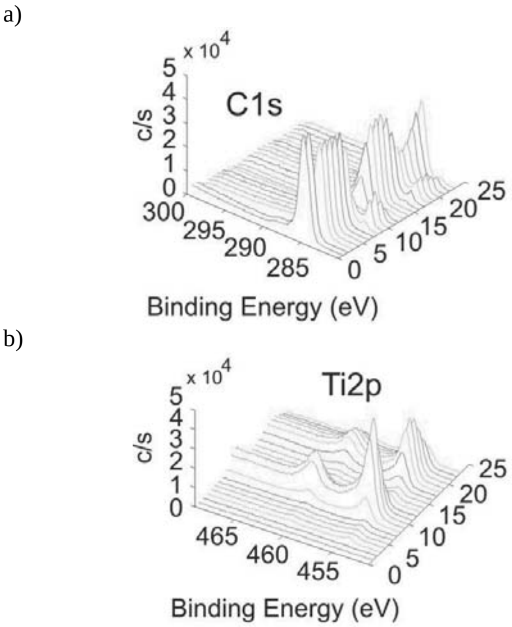

Fig. 6. XPS in-depth electron energy profiles for (a) C1s and (b) Ti2p electrons made for M3 multilayer coating

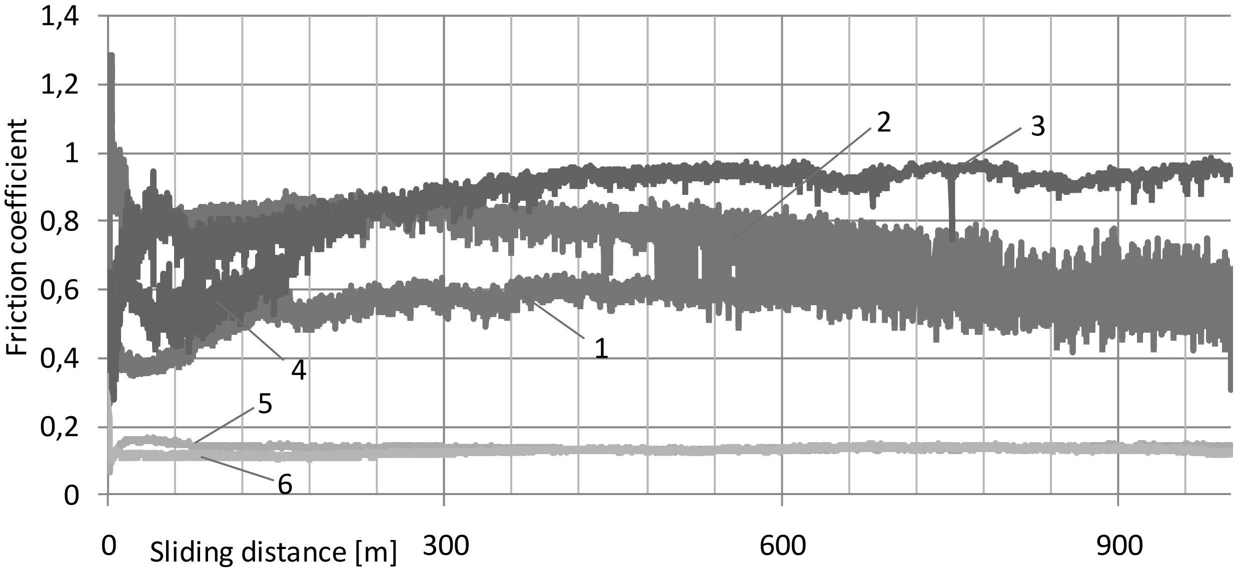

Fig. 7. Dry friction coefficient for as delivered Ti6Al4V alloy (1); the same alloy after diffusion hardening (2) and for different coatings: M1(3); M4(4); M2(5) and M3(6) as a function of the length of the friction path. See also Table 3

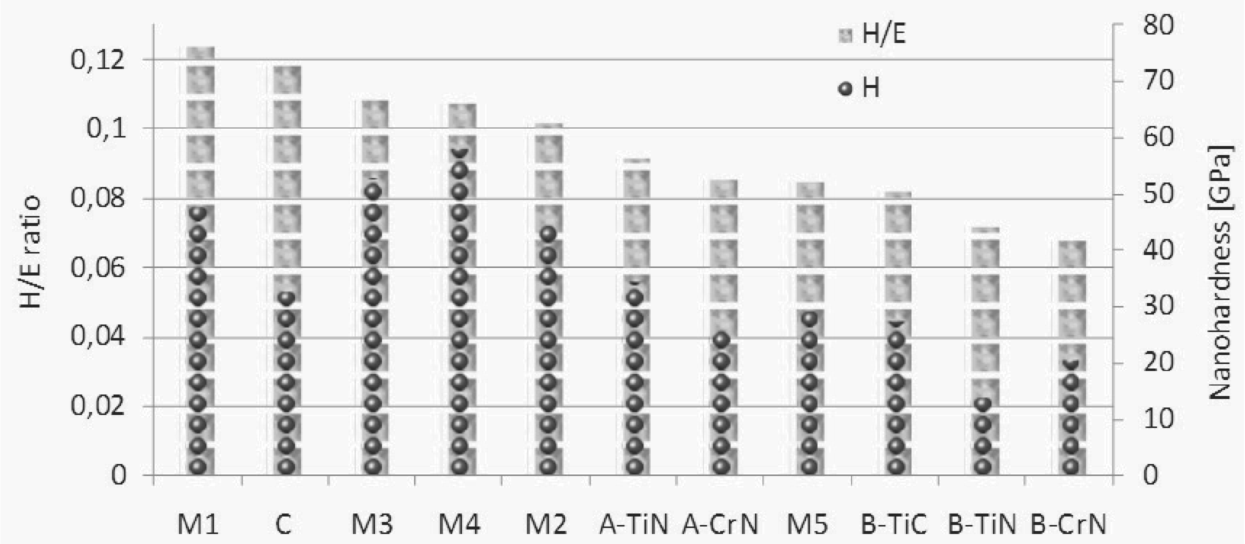

Fig. 8. Nanohardness and (H/E) ratio for all of the investigated coatings

According to [15] the (H/E) ratio is one of the main features determining usefulness of superhard coatings for tribological applications. During present investigations it was found that the coatings M2 and M3 had very good frictional properties (with the lowest values of friction and wear coefficients) and very similar values of the (H/E) ratio, for example, the M4 coating. Simultaneously, the hardness of the M4 coating was the highest from all the investigated coatings. It seems therefore, that there should be another parameter crucial for good frictional properties of the proposed type of multilayer coatings. It is true that titanium carbide based multilayer coatings like the M3 has the best tribological characteristics of all the investigated coatings. Unfortunately, explanation of this feature needs further investigations. It is believed, that titanium based sublayers (especially titanium carbides) have a good synergistic effect onto the carbon sublayers, owing to a small amount of hydrogen incorporated into carbon coating during deposition, just after a preceding titanium carbide sublayer which was synthesized in an atmosphere of a mixture of Ar+C_2H_2. Another reason for which the titanium carbide sublayers turned out to be better than the others when alternating in the multilayer with the carbon sublayers could be that titanium carbide consists of carbon atoms, which facilitate the growth of a subsequent carbon sublayers.

4. Conclusions

1. The proposed hybrid PVD technique suits well for deposition of hard single CrN, TiN, TiC and DLC coatings as well as for multilayers composed of the single sublayers.
2. Wear coefficients of monolayer TiN, TiC or CrN coatings were friction coefficients greater than that of bare substrate, however the wear coefficients for those coatings were decreased by one or two orders of magnitude.
3. It turned out that the adhesion between the DLC coatings and Ti6Al4V titanium alloy after treatment in oxygen plasma has the lowest value of all the investigated coatings.
4. Some of the deposited multilayer coatings had a very high hardness, but it did not prevent the substrates from high wear during dry sliding.
5. Multilayer $(TiN/C)_{x3}$ and $(TiC/C)_{x3}$ coatings have low friction coefficient during dry sliding and they can be used for wear protection of diffusion hardened Ti6Al4V alloy due to a very low wear coefficient ~ 10^{-16} $m^3 \cdot N^{-1} \cdot m^{-1}$.

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