Journal of Achievements in Materials and Manufacturing Engineering
VOLUME 37 ISSUE 2 December 2009

Low friction and wear resistant nanocomposite nc-MeC/a-C and nc-MeC/a-C:H coatings

K. Włodarczyk, M. Makówka*, P. Nolbrzak, B. Wendler
Institute of Materials Science and Engineering, Technical University of Lodz, ul. Stefanowskiego 1/15, 90-924 Łódź, Poland
* Corresponding author: E-mail address: m.makowka@gmail.com

Received 17.09.2009; published in revised form 01.12.2009

Materials

ABSTRACT

Purpose: Elaboration of nanocomposite, low friction and wear resistant coatings in order to increase the life-time and reliability of friction couples especially in aviation industry, car industry and of cutting tools. These coatings consist of nanocrystallites of chromium or titanium carbides built into amorphous carbon matrix.
Design/methodology/approach: Coatings type nc-MeC/a-C and nc-MeC/a-C:H (where Me means Cr or Ti transition metal) are deposited by a PVD method based on magnetron sputtering of pure Ti or Cr and pure graphite targets in the atmosphere of Ar or Ar+H_2, respectively. The coatings are deposited onto the surface of quenched and tempered HSS steel Vanadis23 and diffusion hardened titanium alloy Ti6Al4V.
Findings: Depending on deposition parameters, like the power ratio of transition metal to carbon targets or the substrate bias, it is possible to obtain different morphological and tribological properties of coatings. These latter are very important for designing friction couples in mechanical applications.
Originality/value: The coatings are characterized of very low friction coefficient (0.06 for nc-TiC/a-C and 0.08 for nc-TiC/a-C:H and nc-CrC/a-C:H coatings).
Keywords: Nanocomposite; Low friction; Wear resistant; (Ti, Cr)C/a-C(:H); Magnetron sputtering

Reference to this paper should be given in the following way:
K. Włodarczyk, M. Makówka, P. Nolbrzak, B. Wendler, Low friction and wear resistant nanocomposite nc-MeC/a-C and nc-MeC/a-C:H coatings, Journal of Achievements in Materials and Manufacturing Engineering 37/2 (2009) 354-360.

1. Introduction

PVD and CVD methods are best choice for improving of tribological properties of machine parts and tools. Using those methods allows to obtain variety of coating's structures (like mono and multilayer [1-3], gradient [2, 4, 5] or composite and nanocomposite [2, 7-9]) and in consequences various properties. The improvement of tribological properties of tools covered with coatings was investigated by many researchers [1, 2, 5] and affirm elongation of life-time and increasing of reliability.

Nanocomposite nc-MeC/a-C, nc-MeC/a-C:H coatings (where Me means transition metals Cr or Ti) are widely used in friction couples, as coatings for cutting tools or as decorative ones because of a number of important properties as, for example, low friction coefficient, high resistance against wear and good adhesion to metallic substrates [10-14].

There are different methods of deposition of nc-MeC/a-C or nc-MeC/a-C:H coatings: plasma assisted chemical vapor deposition process (PACVD) [12], nonreactive closed-field unbalanced magnetron sputtering process [15-17], or a reactive ones [11, 13 ,14, 18], plasma- assisted CVD method using a reactive gas mixture $TiCl_4+CH_4$ [19, 20], filtered cathodic vacuum arc (FCVA) [10, 21], or by hybride methods based on magnetron sputtering and cathodic arc evaporation [22]. Different metal and gas sources are used in these methods as, for example, magnetron targets made from pure Cr, Ti, graphite (C) or chemical compound as TiC [23] in atmospheres of pure Ar or $Ar+H_2$. When using magnetron sputtering for deposition it is possible to change chemical composition of the coatings to a great extent and, as a result, to influence the tribological properties of the coatings. Simultaneously, it is possible to built nanocrystals of chromium or titanium carbides into the amorphous carbon matrix [14, 21].

Many researchers tried to improve the adhesion of the coatings to the substrate surface which is crucial for the most of potential applications. To solve this problem different interlayers were deposited between the nanocomposite nc-C/a-C(:H) or nc-CrC/a-C(:H) coating and the substrate as, for example, Cr [12, 15, 16, 22, 24] or CrN [25], Mo or Ti [26]. The content of a transition metal in the interlayer evanesces to zero and the one of the proper, a-C or a-C:H component increases up to 100%.

The coatings which are characteristic of columnar structure have poor tribological properties. With use of a proper substrate bias and a suitable acetylene gas flow it is possible to restrain the columnar growth of the coatings and constitute a much smoother structure which is almost column-free [16, 27]. Furthermore nanocrystalline particles built into amorphous carbon matrix free of columnar structure prevent the nucleation and crack growth in the coatings. In addition the increase of the carbon content influences friction coefficient and hardness of the nc-MeC/a-C and nc-MeC/a-C:H coatings. With increasing acetylene flow during deposition process the hardness of coatings increases and the friction coefficient decreases to a great extent: in case of hydrogenated nanocomposite nc-TiC/a-C:H coatings the hardness changes in a range of 30-65GPa, whereas for the nonhydrogenated ones it is only 5-25GPa [21, 27]. As it concerns the coefficient of wear resistance, it changes from $1\cdot10^{-16}$ $m^3\cdot N^{-1}\cdot m^{-1}$ for hydrogenated coatings [27] to $1\cdot10^{-15}$ $m^3\cdot N^{-1}\cdot m^{-1}$ for the nonhydrogenated ones [24]. In case of nc-CrC/a-C coatings, stress concentration can bring about delamination and cracking of the coating. To prevent this phenomenon the amorphous carbon matrix can be hydrogenized [11-13, 18]. For the same coatings the friction coefficient as low as 0.1 can be achieved for rather low amount of chromium carbides and at relatively low hardness (~10 GPa). In this case low hardness does not preclude a high resistance to wear. The friction coefficient increases with chromium content. It can achieve a value of 0.35 and the hardness value of 40 GPa for essentially a pure CrC compound without amorphous a-C(:H) phase [11, 14].

By controlling the ratio of the hard phase to the soft one, it is possible to adjust properties suitable for a broad range of applications. Decrease of the friction coefficient and simultaneous increase of wear resistance of coated elements increase the life-time and reliability of machine parts and reduces operating costs. In addition, the self-lubricious nc-MeC/a-C or nc-MeC/a-C:H coatings allow to abridge the use of costly lubricants, eliminate harmful oil wastes and has a significant effect on the protecting of the environment.

2. Experimental

2.1. Materials and processing

The coatings consisting of nanocrystallites of titanium or chromium carbides embedded into amorphous carbon matrix have been deposited by magnetron sputtering of three pure graphite targets and one of pure Ti or Cr target in atmosphere of pure Ar or of a mixture of $Ar+H_2$.

The coatings were deposited onto the surface of diffusion hardened with interstitial oxygen atoms [28] Ti6Al4V alloy (~33 HRC), of a bulk-hardened high-speed steel Vanadis 23 or ASP 2023 (~64HRC) and of pure Si wafers. The dimensions of the metal samples were Ø25x6mm and those from the Si ones were 10x10x0.56 mm. Before deposition the specimens from the high-speed steel and titanium alloy were ground with use of abrasive papers up to 2000 grit and next polished with use of a mixture of diamond powder (1 μm) with lubricant. After polishing the samples were washed in warm water with detergent admixture, rinsed in pure water and next in acetone in ultrasonic bath. Rectangular specimens from Si wafers were only cleaned in acetone in an ultrasonic bath.

Samples prepared that way were suspended under the rotary table in the center of the vacuum chamber of a multipurpose magnetron sputtering unit B90 with four circular magnetrons situated symmetrically around the vertical axis of symmetry of the vacuum chamber each 90 deg at the distance of 200 mm.

After pumping down of the vacuum chamber to residual pressure of $1\cdot10^{-3}$ Pa all the samples were cleaned by sputtering in a glow discharge in the atmosphere of Ar at a pressure of 4 Pa and at Ar flow 44 sccm. This step was prosecuted until the current of discharge stabilized at a current level (~1 A) at a discharge voltage of 1 kW. During deposition of the nc-CrC/a-C or TiC/a-C coatings the Ar pressure in the vacuum chamber was adjusted to 0.4 Pa for deposition of nc-CrC/a-C or nc-TiC/a-C coatings or a mixture of Ar and H_2 gases was let into the chamber for nc-TiC/a-C:H or CrC/a-C:H coating deposition.

For improving coatings' adhesion to the substrate, a thin intermediate layer of pure Ti or Cr was deposited as a first step. The deposition time was 300s with gradually increasing power of the magnetron with Ti or Cr targets (respectively) until a value of 1 kW. In the next step all the four targets were sputtered (i.e., three graphite targets and one from Ti or Cr, respectively) at permanent rotation of the table with the specimens. The power of the magnetron with Ti (or Cr) target was different in different processes (from 0.1 kW to 1.1 kW) and that for magnetrons with graphite targets was changing from 0.5 kW to 1.4 kW in order to find optimal parameters which are presented in Tab. 1. The substrate bias in all the processes was - 50 V, with impulses of a base frequency 160kHz and at a frequency of modulation of 2 kHz at a value of the bias current 100-130 mA.

2.2. Methodology

Tribological properties of coatings were measured using a ball-on-disk T-11 tribometer. During each test the friction force, temperature and vertical displacement were recorded. The value of the relative humidity during each test was between 50% and 55%, the diameter of the ball made from 100Cr6 bearing steel was 1/4", the friction distance was 1000 m, the linear speed 0.1 $m \cdot s^{-1}$, the load 10 N and the radius of a circular friction trajectory was 0.01 m (therefore the number of friction cycles was approximately 16000).

For examining adhesion quality of the coatings to the substrates the Daimler-Benz test has been carried using Rockwell diamond indenter with the radius of curvature at the apex 0.2 mm [29].

Coatings thickness was measured by means of optical interferometry or with use of scanning electron microscopy or with use of a calotest technique.

The chemical composition of the coatings was measured by means of the EDS method with use of a special attachment (by NORAN Instruments) to the scanning electron microscope Hitachi S-3000N. Coatings for the examination of chemical composition were deposited onto the surface of pure silicon substrates. Hydrogen content in hydrogenated a-C phase was investigated using LECO TCH600 hydrogen tester.

Coatings nanohardness and Young's modulus were measured with use of a G-200 nanoindenter in a CSM dynamic mode (i.e., of a Continuous Stiffness Measurement). The coatings for these measurements were deposited on the surface of pure silicon substrate too.

3. Results

3.1. Tribological tests

Tribological tests carried-out for nc-CrC/a-C(:H) and nc-TiC/a-C(:H) coatings confirmed a low friction and resistance to wear of the coatings. The values of the friction coefficient change in the range 0.06-0.28 (Tab. 2) and the lowest value was obtained for the nc-TiC/a-C coating: the friction coefficient for this coating was 0.06 (Fig. 1) and 0.08 for nc-TiC/a-C:H. That latter value (0.08) was also obtained for an nc-CrC/a-C:H coating (Fig. 2). A characteristic effect of self lubrication was observed for all the measured nc-TiC/a-C coatings (like it is presented in Fig. 1): at the beginning the friction coefficient is increasing for first 100m of friction path and during next 300m it is decreasing and stabilizing at a lowest value. It is possible that a part of the coating material is transferred from samples surface onto the ball surface at the beginning of the friction test. Such an effect was not observed for nc-CrC/a-C:H coating.

Table 1.
Parameters of deposition of different nanocomposite coatings

Coating	Deposition of interlayer		Process of deposition				
	Ti or Cr magnetron power [kW]	Time [s]	Ti or Cr magnetron power [kW]	C total magnetrons power [kW]	Pressure [Pa]	Ar flow [sccm]/ /H2 flow [sccm]	Time [min]
nc-TiC/a-C	0.5	120	0.3	3.36	0.4	18.9 / 0	65
	1	180					
nc-TiC/a-C:H	0.5	120	0.3	3.36	0.43	19 / 15	65
	1	180					
nc-CrC/a-C	0.5	120	0.21	3.64	0.4	31.4 / 0	65
	1	180					
nc-CrC/a-C:H	0.5	120	0.21	3.66	0.4	17.7 / 5	125

Table 2.
Friction coefficients and atomic concentration ratios Ti/C and Cr/C of nc-TiC/a-C, nc-TiC/a-C:H, nc-CrC/a-C and nc-CrC/a-C:H ctgs

Process	Coatings	Ratio of atomic concentration Ti/C or Cr/C	Friction coefficient *f*
TiC-C-1	TiC/a-C	0.08	0.28
TiC-C-2	TiC/a-C	0.14	0.2
TiC-C-3	TiC/a-C	0.32	0.3
TiC-C-8	TiC/a-C	0.08	0.06
TiC-C-10	TiC/a-C	0.13	0.24
TiC-C-H-1	TiC/a-C:H	0.05	0.2
TiC-C-H-2	TiC/a-C:H	0.05	0.1
TiC-C-H-3	TiC/a-C:H	0.05	0.08
TiC-C-H-4	TiC/a-C:H	0.06	0.15
CrC-C-1	CrC/a-C	0.08	0.16
CrC-C-5	CrC/a-C	0.14	0.13
CrC-C-6	CrC/a-C	0.11	0.14
CrC-C-7	CrC/a-C:H	0.24	0.09
CrC-C-8	CrC/a-C:H	0.18	0.11
CrC-C-9	CrC/a-C:H	0.18	0.11
CrC-C-10	CrC/a-C	0.22	0.15
CrC-C-11	CrC/a-C:H	0.23	0.08

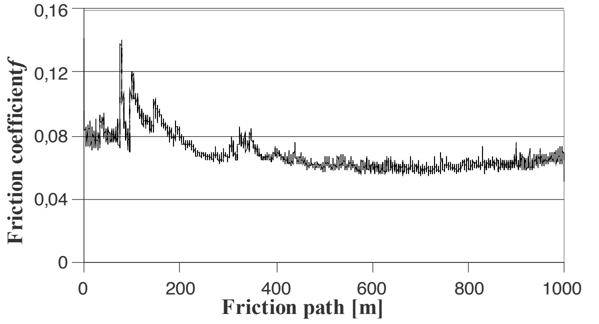

Fig. 1. Friction coefficient of the nc-TiC/a-C coating no. 8 as a function of the friction path

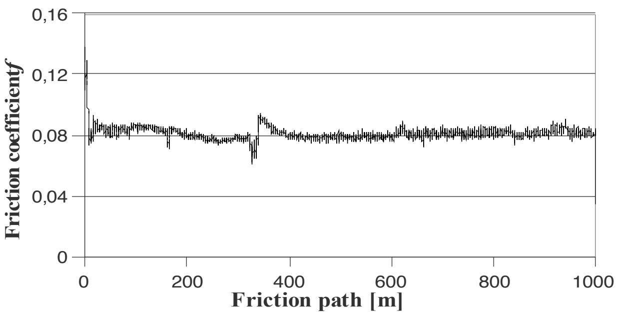

Fig. 2. Friction coefficient of the nc-CrC/a-C:H coating no. 11 as a function of friction path

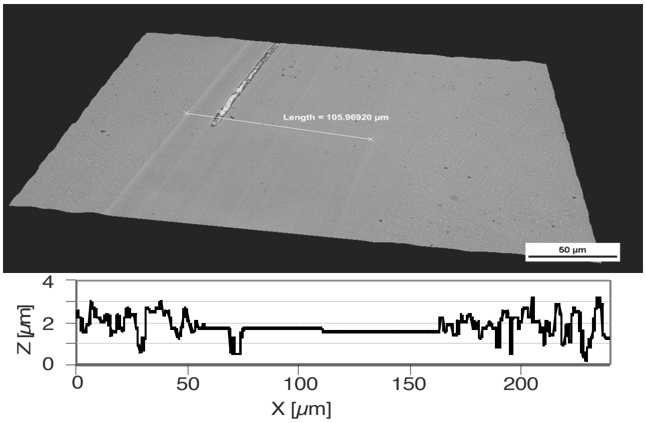

Fig. 3. Wear track on the surface of the nc-CrC/a-C coating no. 6 after a ball-on-disk test along 1000m friction path (photo at the top) and its profilogram (lower down)

In case of the nanocomposite carbon-based coatings with Cr atoms the effect of the admixture of H atoms was significant in that the friction coefficient decreased to 0.08 whereas for the non-hydrogenated ones the lowest value was only 0.13. The effect of hydrogenation was not so important for nc-TiC/a-C coatings for which the lowest value of the friction coefficient was 0.08 for hydrogenated and 0.06 for nonhydrogenated.

After the friction test the observations of the wear tracks were carried-out with use of an optical microscope. There was no significant wear of the both kinds of coatings deposited onto substrate surface. Profilograms and optical observation of the surface of the nc-CrC/a-C coating, after the ball-on-disk friction test, prove very smooth wear track with no damage of the substrate surface (Fig. 3).

3.2. Chemical composition

Titanium content in the nc-TiC/a-C and nc-TiC/a-C:H coatings changes from 0.4 to 24 at. % (with the rest of C atoms) (Tab. 3.). In case of the nc-CrC/a-C and nc-CrC/a-C:H coatings the lowest chromium content was 7 and the highest one 20 at. % while rest was carbon. Chemical composition has an important effect on coating's properties. The lowest friction coefficient was obtained for titanium-to-carbon ratio 0.5-0.8 in case of nc-TiC/a-C and nc-TiC/a-C:H and for chromium-to-carbon ratio 0.22 for nc-CrC/a-C and nc-CrC/a-C:H coatings (Tab. 3.). Hydrogenated coatings contained up to 30 at. % of hydrogen.

3.3. Adhesion

Adhesion quality for all the investigated nc-TiC/a-C, nc-TiC/a-C:H, nc-CrC/a-C or nc-CrC/a-C:H coatings was HF1 in Daimler-Benz test i.e., the best of the six-stage scale for the coatings` thickness up to 0.5 µm (Tab. 4.). No cracks or delamination of coatings on the circumference of the D-B test pits were encountered on Vanadis 23 HSS steel (Fig. 4 b and Fig. 5 b). In contrast to that the investigations of the coatings surface on the diffusion-hardened Ti6Al4V titanium alloy after the Daimler-Benz test shows radial cracks but no delamination as well (Fig. 4 a and Fig. 5 a). This different behavior of the same coatings in the vicinity of the circumference of the pits is due to different mechanical properties of the both substrates. In case of the HSS steel with higher hardness and Young`s modulus value than the pertinent ones for the titanium Ti6Al4V alloy the plastic deformation of the former of the both substrates is smaller and so are the stresses in the coatings on the Vanadis 23 HSS steel.

Introducing of hydrogen to the Ar atmosphere brings an increased adhesion in case of thicker (up to 0.7 µm) nc-CrC/a-C:H coatings from HF5 to HF1 on the Vanadis 23 HSS steel (Fig. 5 b). Nevertheless, the adhesion to titanium alloy substrate was still HF1 for either hydrogenated or nonhydrogenated nc-CrC/a-C coatings with thickness up to 0.7 µm (Fig. 5 a). The effect of the hydrogenation onto the adhesion of the nc-TiC/a-C coatings on the Vanadis 23 HSS steel substrates was unnoticeable.

Table 3.
Chemical composition of nc-TiC/a-C, nc-TiC/a-C:H, nc-CrC/a-C and nc-CrC/a-C:H coatings together with a value of the relative metal-to-carbon concentration

Process	Coating	Concentration of atomic %		Ratio
		Ti	C	Ti/C
TiC-C-1	TiC/a-C	7.79	92.21	0.08
TiC-C-2	TiC/a-C	12.5	87.5	0.14
TiC-C-3	TiC/a-C	24.12	75.88	0.32
TiC-C-8	TiC/a-C	7.51	92.49	0.08
TiC-C-10	TiC/a-C	11.37	88.63	0.13
TiC-C-H-1	TiC/a-C:H	4.41	95.5	0.05
TiC-C-H-2	TiC/a-C:H	4.76	95.2	0.05
TiC-C-H-3	TiC/a-C:H	4.58	95.4	0.05
TiC-C-H-4	TiC/a-C:H	5.51	94.4	0.06
		Cr	C	Cr/C
CrC-C-1	CrC/a-C	7.14	92.86	0.08
CrC-C-5	CrC/a-C	12.65	87.3	0.14
CrC-C-6	CrC/a-C	9.99	90.1	0.11
CrC-C-7	CrC/a-C:H	19.5	80.5	0.24
CrC-C-8	CrC/a-C:H	15.17	84.83	0.18
CrC-C-10	CrC/a-C	18.02	81.98	0.22
CrC-C-11	CrC/a-C:H	18.37	81.63	0.23

Table 4.
Quality of adhesion to a quenched and tempered Vanadis 23 HSS steel and to diffusion-hardened titanium alloy measured with use of a Daimler-Benz six-stage HF test

Prosess	Coating	Adhesion quality in HF scale base		Thickness of coating [μm]
		Vanadis 23	Ti6Al4V(O2)	
TiC-C-1	TiC/a-C	1	1	0.4
TiC-C-2	TiC/a-C	1	1	0.28
TiC-C-3	TiC/a-C	1	1	0.34
TiC-C-8	TiC/a-C	1	1	0.37
TiC-C-10	TiC/a-C	5	1	0.8
TiC-C-H-1	TiC/a-C:H	1	1	0.44
TiC-C-H-2	TiC/a-C:H	1	1	0.49
TiC-C-H-3	TiC/a-C:H	1	1	0.46
TiC-C-H-4	TiC/a-C:H	1	1	0.45
TiC-C-H-5	TiC/a-C:H	5	1	0.8
CrC-C-1	CrC/a-C	1	1	0.23
CrC-C-5	CrC/a-C	1	1	0.28
CrC-C-6	CrC/a-C	1	1	0.31
CrC-C-7	CrC/a-C:H	1	1	0.29
CrC-C-8	CrC/a-C:H	1	1	0.35
CrC-C-9	CrC/a-C:H	1	1	0.32
CrC-C-10	CrC/a-C	5	1	0.7
CrC-C-11	CrC/a-C:H	1	1	0.65

Table 5.
Mechanical properties and thickness of the nc-TiC/a-C, nc-TiC/a-C:H, nc-CrC/a-C or nc-CrC/a-C:H coatings

Process	Coating	Hardness [GPa]	Young modulus [GPa]	Thickness [μm]
TiC-C-8	TiC/a-C	17-20	200	0.37
TiC-C-10	TiC/a-C	17-20	200	0.8
TiC-C-H-3	TiC/a-C:H	15	170	0.46
TiC-C-H-5	TiC/a-C:H	15	170	0.8
CrC-C-5	CrC/a-C	17	213	0.28
CrC-C-6	CrC/a-C	15.5	202	0.31
CrC-C-10	CrC/a-C	16.2	190	0.67
CrC-C-11	CrC/a-C:H	17.6	190	0.65

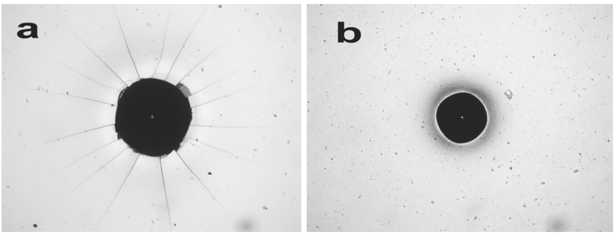

Fig. 4. Photo-micrographs of the pits in the coatings surface after a Daimler-Benz test: a) – nc-TiC/a-C coating deposited in the process TiC-C-8 on the hardened Ti6Al4V alloy; b) – nc-TiC/a-C coating deposited in the process TiC-C-8 onto the surface of quenched-and-tempered Vanadis 23 HSS steel

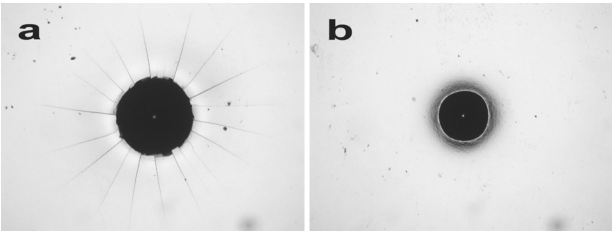

Fig. 5. Photo-micrographs of the pits in the coatings surface after a Daimler-Benz test: a) – nc-CrC/a-C:H coating deposited in the process CrC-C-11 on the hardened Ti6Al4V alloy; b) – nc-CrC/a-C coating deposited in the process CrC-C-11 onto the surface of quenched-and-tempered Vanadis 23 HSS steel

3.4. Hardness and Young modulus

Hardness of the nc-TiC/a-C and nc-TiC/a-C:H coatings as well as of the nc-CrC/a-C and nc-CrC/a-C:H coatings was rather low: 15 GPa to 20 GPa for the former and 15 GPa to 17 GPa for the latter (Tab. 5).

Higher values are characteristic for coatings with higher ratio of a transition metal (Ti or Cr) to carbon. Young`s modulus for the nc-TiC/a-C coatings was 200 GPa and for the nc-TiC/a-C:H ones it was 170 GPa. In case of the nc-CrC/a-C coatings a pertinent value was 213 GPa and for the hydrogenated ones it was 190 GPa (Tab. 5).

Despite those mechanical properties not very impressive the coatings preserve good resistance against wear and fatigue (the latter statement is based on observations of the unnoticeable effect of a rather high number 16000 of stress cycles of the value of ~1.5 GPa during the friction ball-on-disk test).

4. Conclusions

The nanocomposite nc-TiC/a-C, nc-TiC/a-C:H, nc-CrC/a-C and nc-CrC/a-C:H coatings deposited by magnetron sputtering exhibit excellent tribological properties like low friction coefficient, high resistance against adhesive wear and fatigue together with very good adhesion to quenched-and-tempered Vanadis 23 HSS steel and to diffusion-hardened Ti6Al4V titanium alloy. Owing to these properties the nanocomposite carbon-based coatings with Cr or Ti admixture can find application in machine, automobile and aviation industry.

Acknowledgements

This work was made in the frame of the project “Composites & Nanocomposites for Aviation and Car Industry“ financed from the funds of the European pool "National Cohesion Strategy" in the frame of the "Operational Programme: Innovative Economy".

K. Włodarczyk and M. Makówka are exhibitioners of the project „Scholarship supporting innovative scientific research of post-graduate students“ financed by Social European Fund and Budget of Poland in the frame of the Integration Programme 2.6 of the Operational Programme: Regional Development.

References

[1] J. Kusinski, M. Rozmus, J. Bujak, Investigation of the life-time of drills covered with the anti-wear Cr(C,N) complex coatings, deposited by means of Arc-PVD technique, Journal of Achievements in Materials and Manufacturing Engineering 33/1 (2009) 86-93.
[2] L.A. Dobrzański, K. Gołombek, J. Mikuła, D. Pakuła, Multilayer and gradient PVD coatings on the sintered tool materials, Journal of Achievements in Materials and Manufacturing Engineering 31/2 (2008) 170-190.
[3] L.A. Dobrzański, K. Lukaszkowicz, K. Labisz, Structure of monolayer coatings deposited by PVD techniques, Journal of Achievements in Materials and Manufacturing Engineering 18 (2008) 271-274.
[4] W. Kaczorowski, D. Batory, Carbon and titanium based layers for wood-based materials, Journal of Achievements in Materials and Manufacturing Engineering 27/2 (2008) 187-190.
[5] M. Cłapa, D. Batory, Improving adhesion and wear resistance of carbon coatings using Ti:C gradient layers, Journal of Achievements in Materials and Manufacturing Engineering 20 (2007) 415-418.
[6] L.A. Dobrzański, K. Gołombek, J. Mikuła, D. Pakuła, Cutting ability improvement of coated tool materials, Journal of Achievements in Materials and Manufacturing Engineering 17 (2006) 41-44.
[7] S. Mitura, K. Mitura, P. Niedzielski, P. Louda, V. Danilenko, Nanocrystalline diamond, its synthesis, properties and applications, Journal of Achievements in Material and Manufacturing Engineering 16 (2006) 9-16.
[8] L.A. Dobrzański, L. Wosińska, K. Gołombek, J. Mikuła, Structure of multicomponent and gradient PVD coatings deposited on sintered tool materials, Journal of Achievements in Materials and Manufacturing Engineering 20 (2007) 99-102.
[9] K. Gołombek, J. Mikuła, D. Pakuła, L.W. Żukowska, L.A. Dobrzański, Sintered tool materials with multi-

component PVD gradient coatings, Journal of Achievements in Materials and Manufacturing Engineering 31/1 (2008) 15-22.
[10] Y. Wang, X. Zhang, X. Wu, H. Zhang, X. Zhang; Compositional, structural and mechanical characteristics of nc-TiC/a-C:H nanocomposite films, Appiled Surface Science 255 (2008) 1801-1905.
[11] G. Gassner, J. Patscheider, P.H. Mayrhofer, S. Sturm, C. Scheu, Ch. Mitterer, Tribological Properties of Nanocomposite CrC_X/a-C:H, Thin Films, Tribology Letters 27 (2007) 97-104.
[12] M. Andritschky, M. Atfeh, K. Pischow, Multilayered decorative a-C:H/CrC coatings on stainless steel, Surface and Coatings Technology 203/8 (2008) 952-956.
[13] G. Gassner, P.H. Mayrhofer, C. Mitterer, J. Kiefer, Structure-property relations in Cr-C/a-C:H coatings deposited by reactive magnetron sputtering, Surface and Coatings Technology 200 (2005) 1147-1150.
[14] S. Yang, D.G. Teer, Investigation of sputtered carbon and carbon/chromium multi-layered coatings, Surface and Coatings Technology 131 (2000) 412-416.
[15] Y.T. Pei, C.Q. Chen, K.P. Shaha, J.Th.M. De Hosson, J.W. Bradley, S.A. Voronin, M. Cada, Microstructural control of TiC/a-C nanocomposite coatings with pulsed magnetron sputtering, Acta Materialia 56 (2008) 696-709.
[16] D. Galvan, Y.T. Pei, J.Th.M. De Hosson, TEM characterization of Cr/Ti/TiC graded interlayer for magnetron-sputtered TiC/a-C:H nanocomposite coatings, Acta Materiala 53 (2005) 3925-3934.
[17] W. Gulbinski, S. Mathur, H. Shen, T. Suszko, A. Gilewicz, B. Warcholinski, Evaluation of phase, composition, microstructure and properties in TiC/a-C:H thin films deposited by magnetron sputtering, Applied Surface Science 239 (2005) 302-310.
[18] G. Gassner, P.H. Mayrhofer, J. Patscheider, C. Mitterer, Thermal stability of nanocomposite CrC/a-C:H thin films, Thin Solid Films 515 (2007) 5411-5417.
[19] H. Liepack, K. Bartsch, W. Brukner, A. Leonhardt, Mechanical behavior of PACVD TiC-amorphous carbon composite layers, Surface and Coatings Technology 183 (2004) 69-73.
[20] H. Liepack, K. Bartsch, W. Bauer, X. Liu, M. Knupfer, A. Leonhardt, Characteristic of excess carbon in PACVD TiC-amorphous carbon layers, Diamond and Related Materials 13 (2004) 106-110.
[21] Y. Wang, X. Zhang, X. Wu, H. Zhang, X. Zhang, Superhard nanocomposite nc-TiC/a-C:H film fabricated by filtered cathodic vacuum arc technique, Applied Surface Science 254 (2008) 5085-5088.
[22] P.Eh. Hovsepian, D.B. Lewis, C. Constable, Q. Lou, Y.N. Kok, W.D. Munz, Combined steered cathodic arc/unbalanced magnetron grown C/Cr nanoscale multilayer coatings for tribological applications, Surface and Coatings Technology 174-175 (2003) 762-769.
[23] T. Pei, D. Galvan, J.Th.M. De Hosson, A. Cavaleiro, Nanostructured TiC/a-C coatings for low friction and wear resistant applications, Surface and Coatings Technology 198 (2005) 44-50.
[24] Y.T. Pei, D. Galvan, J.Th.M. De Hosson, Nanostructure and properties of TiC/a-C:H composite coatings, Acta Materialia 53 (2005) 4505-4521.
[25] Y.N. Kok, P.Eh. Hovsepian, Resistance of nanoscale multilayer C/Cr coatings against environmental attack, Surface and Coatings Technology 201 (2006) 3596-3605.
[26] J. Tang, L. Feng, J.S. Zabinski, The effects of metal interlayer insertion on the friction, wear and adhesion of TiC coatings, Surface and Coatings Technology 99 (1998) 242-247.
[27] D. Martinez-Martinez, C. Lopez-Cartes, A. Fernandez, J.C. Sanchez-Lopez, Influence of the microstructural on the mechnical and tribological behavior of TiC/a-C nanocomposite coatings, Thin Solid Films 517 (2009) 1662-1671.
[28] B. Januszewicz, B. Wendler, T. Liśkiewicz, Ł. Kaczmarek, Structure and hardness of Ti6Al4V alloy after hardening treatment by oxidation, Materials Engineering 5 (2005) 654-656.
[29] German standards, VDI guidelines 3128, 1991.