

Nanocrystalline Cr/CrN and Ti/TiN multilayer coatings produced by pulsed laser deposition at room temperature

J.M. LACKNER¹, W. WALDHAUSER¹, L. MAJOR², J. MORGIEL², M. KOT³, and B. MAJOR^{3*}

¹Joanneum Research Forschungsgesellschaft mbH, Laser Center Leoben, Leoben, Austria

²Institute of Metallurgy and Materials Science, Polish Academy of Sciences, 25 Reymonta St., 30-059 Cracow, Poland

³AGH University of Science and Technology, 30 Mickiewicza Ave, 30-059 Cracow, Poland

Abstract. Mechanical components and tools in modern industry are facing increasing performance requirements leading to the growing need for advanced materials and thus, for modern frictional systems. In the last decades, the Pulsed Laser Deposition (PLD) has emerged as an unique tool to grow high quality mono- as well as multilayers surfaces in metallic/ceramic systems. Building up a knowledge base of tribological properties of industrially-scaled, room temperature deposited PLD hard coatings are the most important step for the application of these coatings in engineering design. Although single-layer coatings find a range of applications, there are an increasing number of applications where the properties of a single material are not sufficient. One way to surmount this problem is to use a multilayer coating. Application of metallic interlayers improves adhesion of nitride hard layer in multilayer systems, which has been used in PVD processes for many years, however, the PLD technique gives new possibilities to produce system comprising many bilayers at room temperature. Tribological coatings consisted of 2, 4 and 16 bilayers of Cr/CrN and Ti/TiN type were fabricated with the Pulsed Laser Deposition (PLD) technique in the presented work. It is found in transmission electron examinations on thin foils prepared from cross-section that both nitride-based multilayer structures studied are characterized by small columnar crystallite sizes and high defect density, what might rise their hardness but compromise coating adhesion. The intermediate metallic layers contained larger sized and less defective columnar structure compared to the nitride layers, which should improve the coatings toughness. Switching from single layer to multi-layer metal/nitride composition improved resistance to delamination.

Key words: coatings, multilayers, laser ablation, deposition, microstructure TEM, tribology.

1. Introduction

Extending the efficiency of machinery, optimizing energy consumption, and conserving scarce material resources are the main needs of modern tool industry. Reaching of these demands and reducing the use of hazardous lubricants are just some examples. High hardness and temperature strength, chemical stability and high toughness are demanded by coatings. In order to reduce friction and wear, the tool surface has to form stable compounds at the contact interface. As generally recognized, it is impossible to combine all these properties together in a single conventional tool material. Leading to tailor-made composite and surface-engineered materials, a large variety of functional properties can be optimized separately for bulk material and surface by applying appropriate coatings.

Since the last 30 years, titanium nitride coatings, have been widely accepted in a range of industrial applications with high demands on wear resistance and adhesion to the substrate. They could be deposited using different techniques and are still one of the most popular hard coatings in industry [1,2]. However, requirements to withstand aggressive environments at elevated temperatures have resulted in switching interest to chromium nitride coatings, which form a surface passive oxide layer stopping their further degradation [3–7].

The majority of commercial TiN tool coatings consist of a single layer which could be sensitive for crack propagation. Placing softer layers in between hard ones may allow arrest

crack propagation and increase toughness of coating. The rise in coating hardness matched with control of their stress level should result in markedly improved wear resistance of tools [8,9]. Most of established deposition techniques, require or result in substrate heating. However, temperature sensitive materials have to be protected against such an exposure and therefore, techniques like pulsed laser deposition (PLD), which allows producing coatings with good adhesion also at room temperature, should be applied [10–16].

The presented research work was focused on fabrication of tribological nanocrystalline multilayers of Ti/TiN and Cr/CrN type in form of 2 to 16 bilayers with total thickness 1 μm using the PLD technique at room temperature and their complex TEM microstructure studies on cross-sections and tests of tribological properties.

2. Experimental procedures

2.1. Coating deposition conditions. Multilayer coatings based on Cr/CrN and Ti/TiN were deposited on austenite substrate (AISI 301, DIN CrNi 18 8). High purity targets (99.9%Ti and 99.9%Cr) were used in ablation experiments with a pulsed Nd:YAG laser system operating at 1064 nm wavelength with 0.6 J pulse energy and 10 ns pulse duration at a repetition rate of 50 Hz. Targets were rotated during the laser irradiation in order to avoid the formation of deep craters. The emitted species were deposited at room temperature (approx. 25°C)

*e-mail: nmmajor@imim-pan.krakow.pl

onto austenitic steel substrates mounted parallel to the target surface at total pressure from vacuum (10^{-5} mbar) to 4 Pa and continuous flow of N_2 of order of 30 sccm. To provide homogenous film thickness over the whole coated surface, the substrates were moved through the plasma plumes during deposition. No bias was used. The Cr as well as Ti interface layers were deposited in Ar atmosphere (99.99), while for deposition of nitrides N_2 (99.99) was used.

2.2. Coating design. The fabricated coatings consisted of 2, 4 and 16 Cr/CrN or Ti/TiN bilayers, respectively. They were deposited using the same approach, i.e. the titanium or chromium ablation was started under low argon pressure atmosphere and subsequently at intervals corresponding to planned nitride layers, nitrogen mixed with argon was introduced. Multilayers setup is specified in Table 1.

Table 1
Cr/CrN and Ti/TiN multilayer coatings setup

No. of bilayer	Target	Coating properties
2	Cr	$2 \times (0.25 \mu\text{m Cr} + 0.25 \mu\text{m CrN})$
4	Cr	$4 \times (0.125 \mu\text{m Cr} + 0.125 \mu\text{m CrN})$
16	Cr	$16 \times (0.03 \mu\text{m Cr} + 0.03 \mu\text{m CrN})$
2	Ti	$2 \times (0.25 \mu\text{m Ti} + 0.25 \mu\text{m TiN})$
4	Ti	$4 \times (0.125 \mu\text{m Ti} + 0.125 \mu\text{m TiN})$
16	Ti	$16 \times (0.03 \mu\text{m Ti} + 0.03 \mu\text{m TiN})$

2.3. Thin foils preparation and observation conditions.

Transmission electron microscopy (TEM) was performed on a Philips CM20 (200 kV) as well as on a JEOL EX4000 (400 kV) which were used for microstructure investigations of the cross-section of coatings. An Energy Dispersive Spectroscopy (EDS) Phoenix EDAX analyzer was used for local chemical analysis. Focus Ion Beam (FIB) or "tripod" polishing followed by an Ar^+ ion milling has been applied for thin foils preparation.

2.4. Coatings mechanical testing. Adhesion was examined by a scratch test (Rockwell HRC penetrator). The applied scratch length was 2 mm on which load increased linearly from 0.03 N up to 30 N.

3. Results

3.1. Microstructure. The Cr/CrN – 2 bilayered coatings deposited using Cr target in varying of Ar and N_2 gas pressure exhibit a clearly defined layered structure (Fig. 1).

All investigated layers of the sample were characterized by highly defective columnar microstructure. The Cr buffer layer between the nitride layers as well as the Cr initially thin layer, working as a precursor during deposition at the onset of process, was built of slightly coarser columnar crystallites corresponding to those observed in the CrN layer. The selected area diffraction patterns acquired predominantly from the Cr buffer and the first CrN layer contained rings of diameters giving a good agreement with the Cr and CrN lattice spacing, respectively. Thus electron diffraction patterns confirm the phase identification, in the case of such thin layers for which the size of aperture was comparable with the layer thickness; some signal mixing have to be accepted. The EDS mapping (Fig. 2) not only stated that layers depleted in chromium contained nitrogen, but also indicated a raised level of oxygen in the first Cr buffer layer from the substrate. The line scan taken across the deposited layer and perpendicular to the surface was acquired at longer acquisition time than pixels in the map which resulted in increased measurement sensitivity showing the presence of chromium content gradient in the buffer layer. Coatings consisting of higher number of Cr and CrN bilayers, like 4 and 16 stacks (Fig. 3), presented generally similar microstructure characteristics as the one built of 2 bilayers. Their common most characteristic feature was manifested in much smaller width of columnar crystallites in the buffer layer. Decreasing

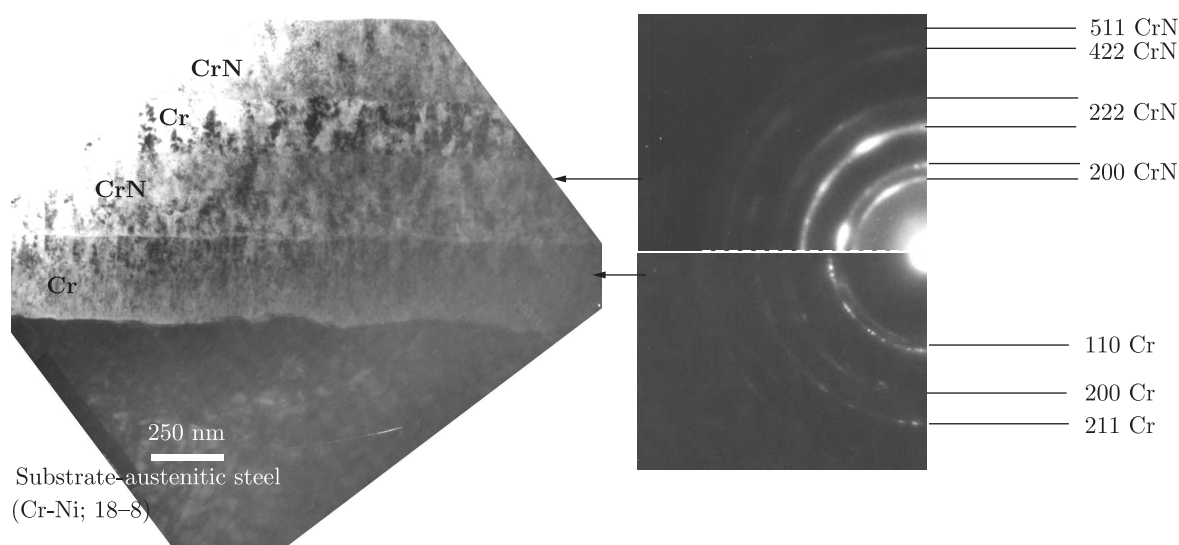


Fig. 1. TEM micrograph of the cross-section of 2 Cr/CrN bilayer coating

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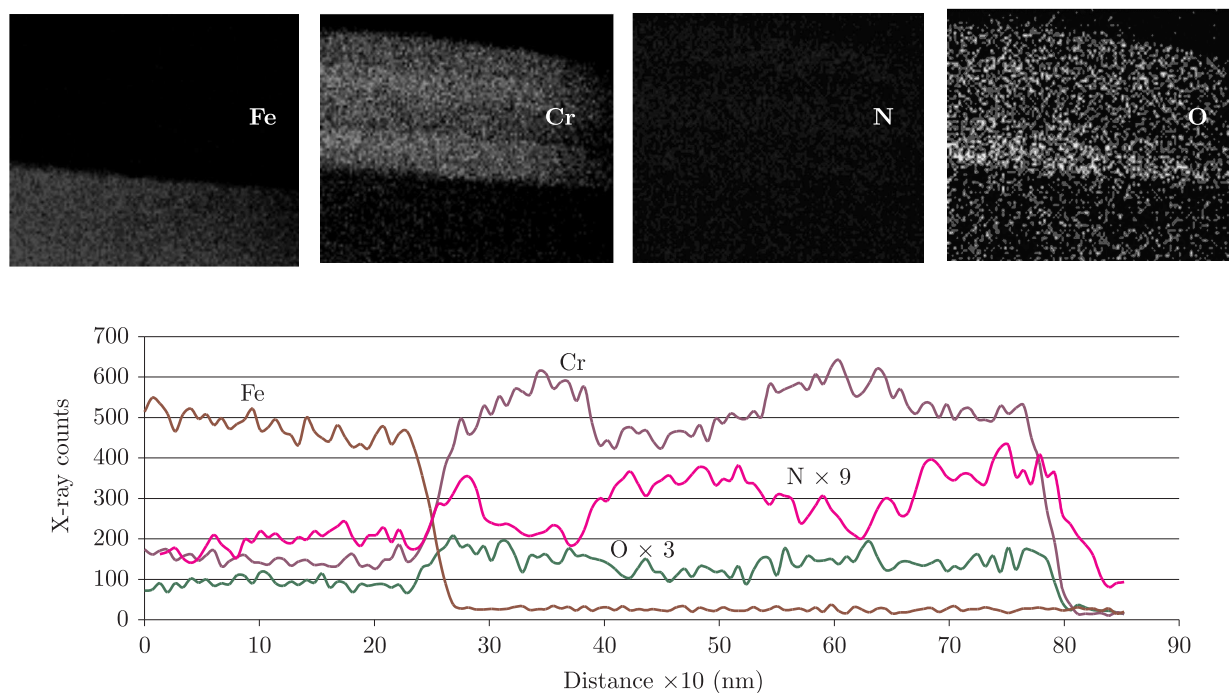


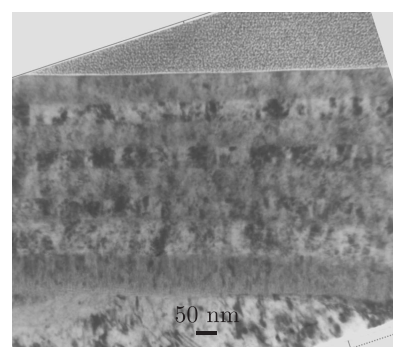
Fig. 2. EDS maps of distribution of Cr, N, O and Fe (upper pictures) and the line scan through the 2 Cr/CrN bilayer coating thickness (nitrogen and oxygen signal was multiplied 9 and 3 times, respectively)

thickness of layers in multilayer coatings resulted in a coarser microstructure than observed in the coatings having a lower number of layers. Observations performed at relatively thin areas showed stronger and sharper diffraction contrast in all Cr layers, what might indicate that these layers were less defective than CrN layers characterized by fluctuating diffuse grayish changes. Observed higher contrast level in the Cr layers resulted probably from less defective structure. This might be beneficial due to the possibility of arresting the crack propagation and toughening the final coating.

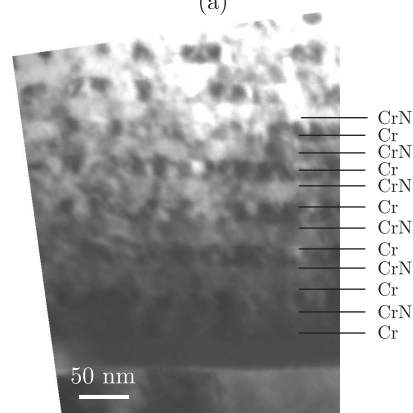
Switching from ablation of the chromium to the titanium target at alternating argon and nitrogen gas flows allowed the production of coatings of varying number of titanium and titanium nitride layers, as confirmed by selected area diffraction (Fig. 4). Both 2 and 16 layered Ti/TiN coatings have been taken under investigations. These observations were performed on thicker areas of thin foil and therefore they showed alternating lighter and darker diffuse contrast proper for more and less dense Ti and TiN layers, respectively. The finer nature of crystallites in the first Ti layer, i.e. in a buffer, compared to the subsequently following Ti layers, could be clearly visible in their diffraction patterns, showing fine nearly continuous rings while the others present much more spotty and coarser rings.

The maps of local chemical composition obtained by the Energy Dispersive X-ray Spectroscopy (EDS) confirmed a slight depletion of titanium in every second layer accompanied by increased of nitrogen level (Fig. 5). The presence of a weak nitrogen signal from nominally titanium layers might result from the residual gas atmosphere in the reactive chamber after switching from argon to nitrogen flow resulting in the surface layer formed during the final stage of the sample prepara-

tion. Additionally, an increased concentration of oxygen was noted at the substrate i.e. at the interface of the Ti buffer layer.



(a)



(b)

Fig. 3. TEM micrograph of the cross-section of 4 (a) and 16 (b) Cr/CrN bilayer coatings

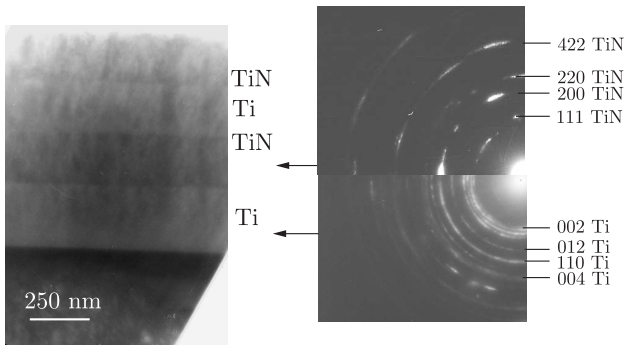


Fig. 4. TEM micrograph of the cross-section of 2 Ti/TiN bilayer coating

The Ti/TiN coatings consisting of higher number of layers showed similar microstructure as those of the Cr/CrN coatings, i.e. very fine columnar crystallites in nitride layers and less defective structure in the metallic inter-layers (Fig. 6).

3.2. Mechanical tests. Scratch test was used to assess mechanical properties of multilayered Cr/CrN and Ti/TiN type coatings. Additionally, single layer coatings of these materials were analyzed as a reference. The contact of the scratch indenter with the single Cr layer under small, i.e. ~ 5 N load resulted in formation of very small buckling cracks of an unconformal type within a scratch track (Fig. 7a).

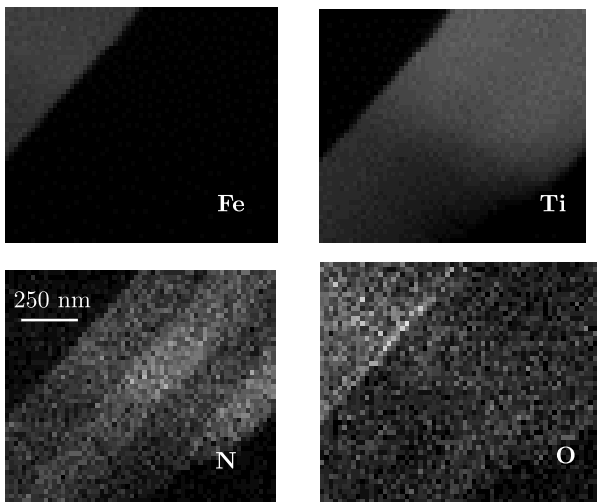


Fig. 5. EDS maps of Ti, N, O and Fe distribution of 2 Ti/TiN bilayer coating

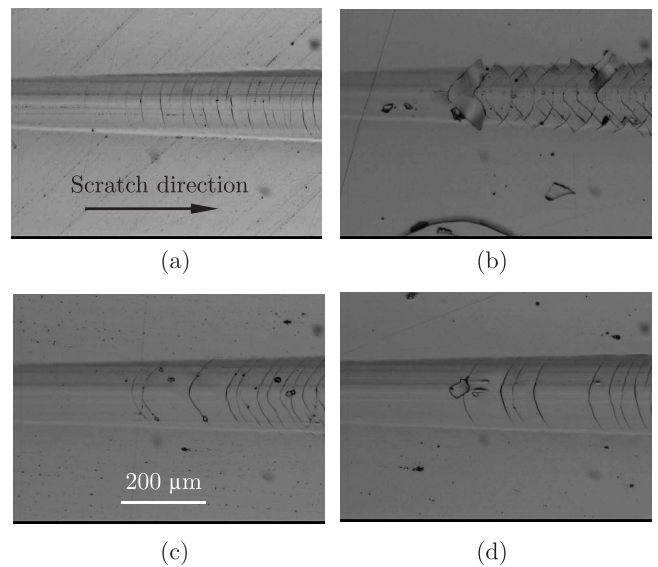


Fig. 7. Images of the scratch path up to the critical load L_c for: (a) Cr single layer, (b) CrN single layer, (c) 2 Cr/CrN bilayers, (d) 16 Cr/CrN bilayers

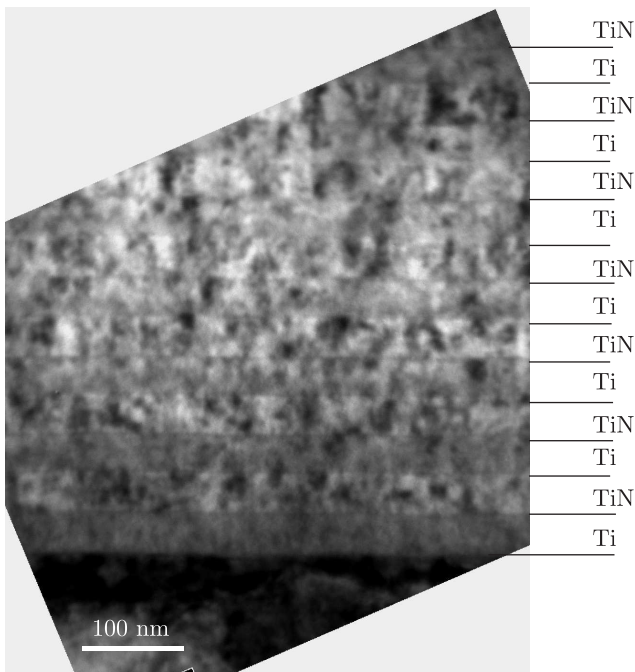


Fig. 6. TEM micrograph of the cross-section of 16 Ti/TiN bilayer coating

Only an application of much higher loads, i.e. above 20 N causes cracks at the edges of the scratch track, which however remain limited to near track areas even at a load up to 30 N. The load under which side cracks started to develop was defined as the critical load L_c . Generally, that type of wear traces indicates a good adhesion of the fabricated coatings to the substrate. Scratch tests performed on the single CrN layer caused the formation of a net of extensive chevron cracks already at 4N (Fig. 2b). Thus this load was taken as L_c . The rise of load to 10N caused total destruction of the coating. Cr/CrN multilayers subjected to the same test showed intermediate resistance to cracking under the indenter as compared to the Cr and CrN coatings. The first unconformal type of buckling cracks on the wear track appeared under the load of 6 N, which was taken as L_c . Under the higher loading applied i.e. from 9 to 13 N, conformal type buckling cracks were developed. The behaviour of the Cr/CrN bilayers was different, thus two kinds of cracks (unconformal and conformal) appeared at the same load. Results of critical value of load for the Cr/CrN system are presented in Table 2.

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Table 2

Scratch test results of the multilayer materials based on Cr/CrN

Sample	Max. load (N)	L_c (N)
Cr		5
CrN		4.4
Cr/CrN		5.6
2 × Cr/CrN	30	7.1
4 × Cr/CrN		7.7
16 × Cr/CrN		6.6

Results of the scratch test of the multilayer materials based on the Ti/TiN composition are presented in Table 3 and Fig. 8. The titanium coating was softer and showed a crack formation much earlier than the chromium films (see Fig. 8c). On the other hand, the TiN coating turned out more cracking resistance than the CrN also in case of the multilayer coatings. In all cases the Ti/TiN type coatings presented conformal type buckling cracks (Fig. 8).

Table 3

Scratch test results of the multilayer materials based on Ti/TiN

Sample	Max. Applied load (N)	L_c (N)
Ti		8.5
TiN		16.4
TiTiN		23.3
2 × TiTiN	30	16.1
4 × TiTiN		13.6
8 × TiTiN		21.8
16 × TiTiN		22.9

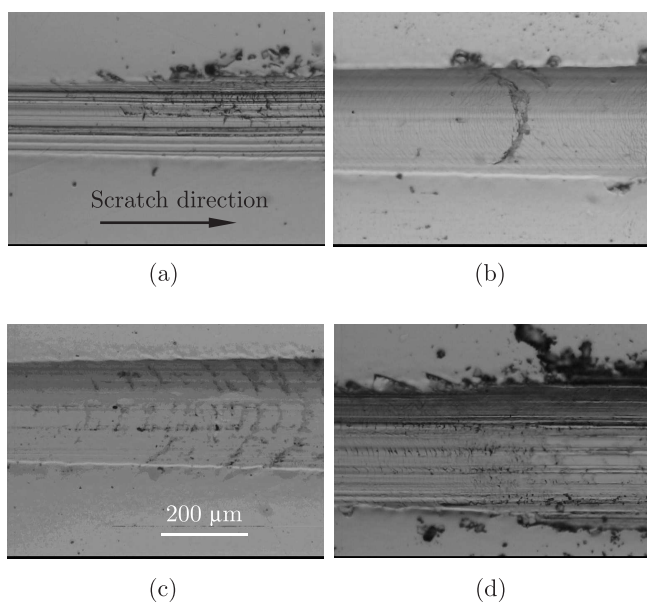


Fig. 8. Images of the scratch path up to the critical load L_c for: (a) Ti single layer, (b) TiN single layer, (c) 2 Ti/TiN bilayer, (d) 16 Ti/TiN bilayers

4. Discussion

Microstructure observations of Cr/CrN and Ti/TiN multilayer coatings showed that the PLD method gives a good control

over individual metallic or nitride layer thickness down at least to 30 nm. Referring to the introduced in the literature spacing parameters of the repeat in the structure, the multilayer period varied in the range 30 to 250. The first metallic layer, serving as a buffer for the whole coating, was characterized by a very fine microstructure. The next metallic layers located between the nitride layers showed coarser less defective structures compared to the nitride layers. It could indicate that they might be quite effective in crack arresting. The reason of different microstructure of the buffer layer might result from deposition serves as a final pumping stage of the vacuum and therefore it either contains oxides or higher level of oxygen as confirmed by the EDS microanalysis. The presence of the oxides usually increase material brittleness and compromise the coating adherence, so the target ablation should start with the substrate covered with shutter or protected using other ways.

The scratch test experiments confirmed good resistance to cracking of the chromium layer and rather poor of the CrN. The single Ti layer of titanium showed a medium resistance to cracking, while the TiN exhibits an increase of about two times. The Ti/TiN multilayers, similarly like the Cr/CrN, presented varying resistance to cracking with an increasing number of layers, which is in line with the reported results [5], but in this case the average resistance to cracking for the majority of coatings was significantly higher than for the starting TiN.

It is impossible to compare directly the presented results in this work for the coatings produced using the PLD method to other PVD ones, especially in a case of different total thickness. In our experiments, the total thickness was 1 μm , thus increasing number of bilayers, the individual layer thickness diminishes dramatically to about 30 nm in 16 bilayer system which corresponds to multilayer period in the range 30 to 250. Presented results of our experiments are in good agreement with the TiN multilayer coatings deposited onto austenitic stainless steel substrates by sputter ion plating (SIP) [9], however the authors reported results for 3 μm total thickness. The critical load measured for their multilayers was in the range of 15 to 20 N for low multilayer period and dramatically decreased to about 10 N for larger periods (over 25 multilayer period and for single layer). Thus the obtained values for the fabricated multilayers in the current work, which are in the range of 8.5 to 23 N are optimistic. The reported in the literature [5] quality of Cr/CrN multilayers deposited by both RF magnetron sputtering and cathodic arc deposition with the total thickness close to 1.4 μm was good, however, the microstructure of the cross-section was examined by SEM images. The deposition was performed at the substrate heating to 350°C.

Thin foil preparation for TEM in case of multilayer coatings is usually difficult thus the presented in this paper TEM images of the total thickness, which allow to distinguish individual layers, seems to be unique. HRTEM examinations of the materials presented in this work are in progress for study of interface between the hard (nitride) and buffer (metallic) layers and this problem is of great importance due to determination of sensitivity to delamination and crack arresting.

5. Conclusions

1. The PLD technique allows to produce coatings consisting of a well distinguishable layer of thickness down to at least 30 nm.
2. The hard nitride layers are characterized by small columnar crystallite structure with a high defect density, what might rise their hardness but compromise coating adhesion.
3. The buffer metallic layers showed larger and less defected columnar structure as compared with the nitride layers, what should improve coatings toughness.
4. The switching from single layer to multi-layered metal/nitride coatings of the same thickness improved resistance to scratching.

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