DOI: 10.1515/amm-2015-0379

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THE WEAR MECHANISMS DESCRIPTION OF MULTILAYER COATINGS, PERFORMED BY TRANSMISSION ELECTRON MICROSCOPY – AN OVERVIEW OF THE OWN RESEARCH WORK

OPIS MECHANIZMU ZUŻYCIA WIELOWARSTWOWYCH POWŁOK W OPARCIU O TRANSMISYJNĄ MIKROSKOPIĘ ELEKTRONOWĄ – PRZEGLĄD WŁASNYCH BADAŃ DOŚWIADCZALNYCH

The aim of the presented paper was to describe the wear mechanisms operating at the small length scale in multilayer coatings subjected to a mechanical testing. A hybrid PLD system (Pulsed Laser Deposition connected with magnetron sputtering) was used for the multi-layer coating deposition. Coatings were subjected to indentation, ball-on disc wear and scratch adhesion tests. Microstructure of the as-deposited coating and after mechanical tests was studied using the Scanning (SEM) and the Transmission (TEM) Electron Microscopes. The research work revealed that application of innovative multilayer coatings may allow to predict their life time and to steer their properties.

Keywords: multilayer coatings, TEM characterization, wear mechanisms

Celem pracy było określenie mechanizmów zużycia wielowarstwowych powłok tribologicznych, poddanych testom mechanicznym na zużycie. Powłoki wytwarzane przy zastosowaniu hybrydowego układu PLD (technika laserowej ablacji połączona z rozpylaniem magnetronowym) poddane zostały mechanicznym testom na zużycie (indentacja oraz test kula-tarcza), a także testowi przylegania powłoki do podłoża (test zarysowania). Charakterystykę mikrostruktury powłok przed i po testach mechanicznych przeprowadzono za pomocą skaningowej (SEM) oraz transmisyjnej (TEM) mikroskopii elektronowej. Badania wykazały, że poprzez stosowanie innowacyjnych powłok wielowarstwowych można przewidzieć czas ich eksploatacji oraz dają możliwość sterowania właściwościami.

1. Introduction

Surface engineering has become an indispensable technology for improving many properties of solid surfaces. Almost all types of materials, including metals, ceramics, polymers and composites can be coated with thin films fabricating surface structures of similar or dissimilar materials. Functional surface engineering has provided advancements, such as extending the life of tools, engine parts and medical implants.

The surface engineering requires that thin films and low dimensional structures can be deposited on solid surfaces. The electrical, optical, mechanical, and tribological properties as well as the structure and microstructure of thin films can vary over wide range, which is highly dependent on the deposition process used. Transition metal nitrides films deposited by physical vapor deposition (PVD) process have now been used in a wide range of engineered applications because of their desirable properties including a high hardness and chemical inertness, thus they are often used as protective coatings. Nowadays, it is a tendency to connect properties of different type of materials, like for example combination of hard and soft phases in composite or multilayer system. A hard phase is responsible for wear resistant properties, while a soft one may stop propagation of possible cracks during plastic deformation [1,2]. Introduction of a number of interfaces parallel to the substrate surface can act to deflect cracks propagation and thus increasing the toughness and hardness of the coating. The wear of hard coatings can be changed dramatically with adjustment of parameters like load, sliding speed, contact geometry and humidity. Cracks initiation and propagation are often responsible for wear. Multilayers can lead to benefit in performance over comparable single-layer coatings as they combine the attractive properties of different materials in a single protective layer [3,4].

Despite much research has been done on the development of multilayer coatings with superior mechanical and tribologi-

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cal properties, a question still remains about the mechanisms, operating at the smallest length scale, underlying the mechanical response [5]. The aim of the presented paper was to describe the wear mechanisms operating at the small length scale in multilayer coatings subjected to mechanical testing, basing on the own already published work and on the latest, not- published research findings.

2. Materials and Methods

2.1. Deposition technique

A hybrid PLD system (Pulsed Laser Deposition connected with magnetron sputtering) equipped with a high purity targets (99.9%) was used for the multi-layer coating deposition. By application of magnetron sputtering in PLD coating plants, higher deposition rates can be reached and a very good adhesion is achieved even at room temperature. Details of the deposition process have been described elsewhere [6]. Several types of multilayer coatings were fabricated like:

- Titanium / titanium nitride (Ti / TiN)
- Titanium nitride / amorphous, hydrogenated carbon (TiN / a-C:H)
- Chromium / chromium nitride (Cr / CrN) + amorphous, hydrogenated carbon implanted by chromium nano-particles (a-C:H+Cr nano)

2.2. Mechanical tests

Mechanical properties of coatings were investigated by means of the scratch adhesion test using the Rockwell C indenter with the curvature radius of 200 μm. The length of a scratch path was 5mm. Uploading for each coating was gradually increased from 0 to 30N. The indentation tests were carried out using the Berkovich indenter with 2 and 5 mN of the applied load. The mechanical ball-on-disc wear test was done using 1 N and 5 N of the applied loadsfor 20000 cycles. All mechanical tests were performed in natural atmosphere (in air). An Al_2O_3 alumina ball with 6 mm diameter was used for the test. The linear speed of the ball, which was applied in the test was of 0.06 m/s.

2.3. Microstructure characterization

The microstructure of the as-deposited coatings and after the mechanical tests, was studied using the Scanning (SEM) (QUANTA 200 3D) and the Transmission (TEM) (TECNAI G^2 F20 FEG (200 kV)) Electron Microscopes, which allow microstructure observation in the smallest scale (HRTEM- High Resolution TEM). The TEM characterization was performed in bright field mode (TEM BF), in scanning TEM mode (STEM) as well as in high resolution TEM mode (HRTEM). Chemical composition was analyzed by Energy Dispersive X-ray Spectroscopy technique (EDS). Thin foils for the TEM analysis were prepared using Focused Ion Beam technique (FIB-Gallium Ions) (QUANTA 200 3D Dual Beam), together with the OmniProbe in-situ lift out system. The procedure allowed to prepare foils directly from places of interest, namely, from mechanically deformed areas.

3. Results and Discussion

Deformation of the Ti / TiN multilayer with modulation ratio TiN:Ti = 1:1 coating, was done by indentation mechanical test. It caused the intergranular shear sliding and plastic flow of soft titanium layers, while ceramic layers (TiN) revealed the brittle cracking [7]. So called deformation lines were propagating across the total coating at an angle of 45° to the surface, which is a typical angle for plastic deformation of poly-crystalline metallic materials (Fig. 1) [7]. It informed, that plastic deformation dominated over the whole coating.

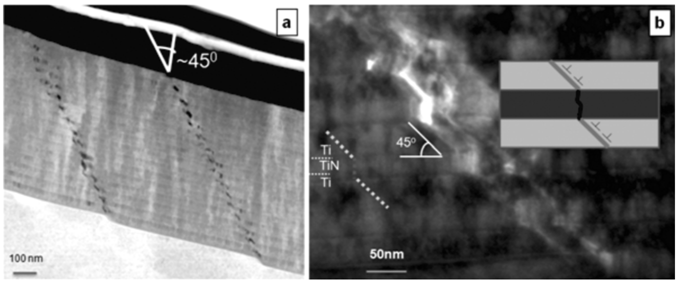

Fig. 1. Cross section TEM image of a 16 bilayer multilayer coating with modulation ratio TiN:T = 1:1; a). overview (STEM image) and b). detail of deformation mechanisms (schematics of deformation and cracking) (TEM BF image) [7]

Energy of brittle cracking in ceramic layers was converted into plastic deformation in metallic ones. Similar behavior was found for Cr / Cr_2N multilayer coating (Fig. 2) [8,9].

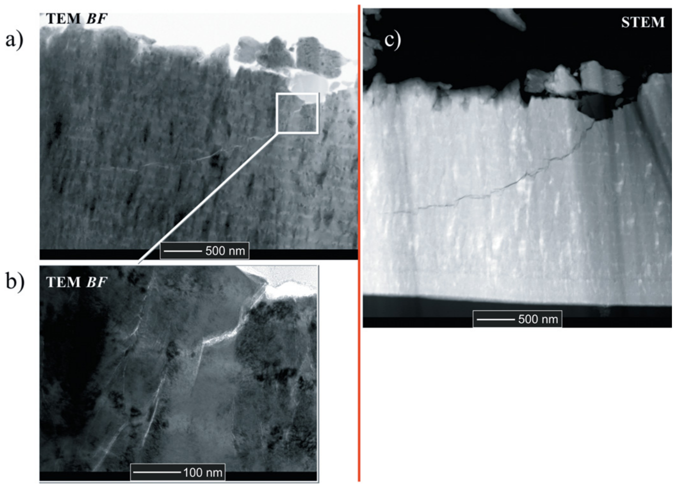

Fig. 2. Microstructure characterization of the Cr / Cr_2N part of the coating (first part from the substrate) after the 5 N and 20000 cycles wear test; a). TEM BF image; b). TEM BF image-higher magnification; c). STEM image [8]

Coatings were subjected to mechanical ball-on-disc wear test with 5N of the applied load. This is an another type of deformation process, however, the operating mechanism in microstructure was very similar. Conversion of brittle cracking to plastic deformation at the ceramic / metallic interface was confirmed by HRTEM image (Fig. 3).

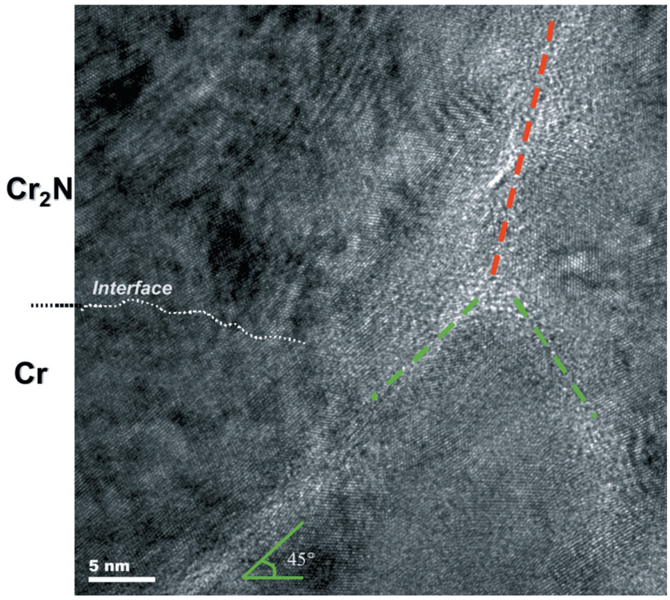

Fig. 3. HRTEM image of the Cr / Cr_2N interface [8]

Cr_2N ceramic layers brittle cracked, while metallic Cr deformed plastically, reducing the cracking energy. Plastic deformation in metallic Cr layers was realized at 45°, which is a typical angle for plastic deformation of polycrystalline, metallic materials.

Requirements for modern coatings are constantly increasing. They should combine various properties. One of the innovative solution in coatings designing is additional deposition of the other material at the top of the typical multilayer structure. Although, this type of coating contains an inner (first from the substrate) and the outer part. Our latest research activity was connected with such type of coatings development. Cr / Cr_2N multilayers were deposited as an inner part. Its role was to compensate residual stresses in the coating. The outer part formed the amorphous carbon layer. The outer part of the coating plays the important role as a diffusion barrier during the wear process in aggressive, corrosive atmosphere or at elevated temperature. This type of coatings was deposited at the carbon-fiber-composite substrates [8] (Fig. 4).

Details of the coating architecture were better visible by the application of the higher magnification in TEM bright field mode as well as in STEM (Fig. 5) [8].

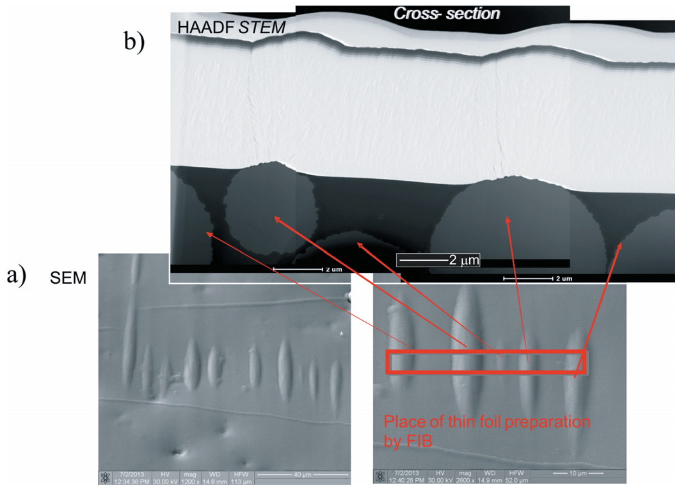

Fig. 4. Microstructure characterization of an as deposited coating; a). image obtained using SEM technique; b). image obtained by TEM technique in STEM mode [8]

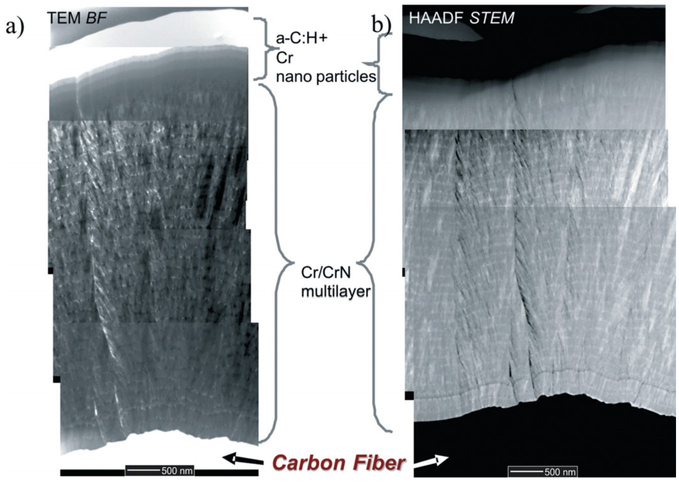

Fig. 5. Microstructure characterization of the coating at the cross- section, performed by TEM technique; a). TEM BF image; b). STEM image [8]

It is well-known that *a*-C:H coatings have low friction coefficients and low wear rates [10, 11]. Thus, the amorphous carbon coatings are very promising tribo-materials. However, the poor adhesion strength to substrate, high residual stress and weak thermal stability would limit their application. Currently, many metallic elements (Ti, W, Ag, Cr etc.) have been utilized to modify their structure, and it has been proved that the metal doping is an effective method to reduce the residual stress and enhance the adhesion strength of the film. In case of coatings developed by our group, *a*-C:H was gradually implanted by Cr [8] (Fig. 6).

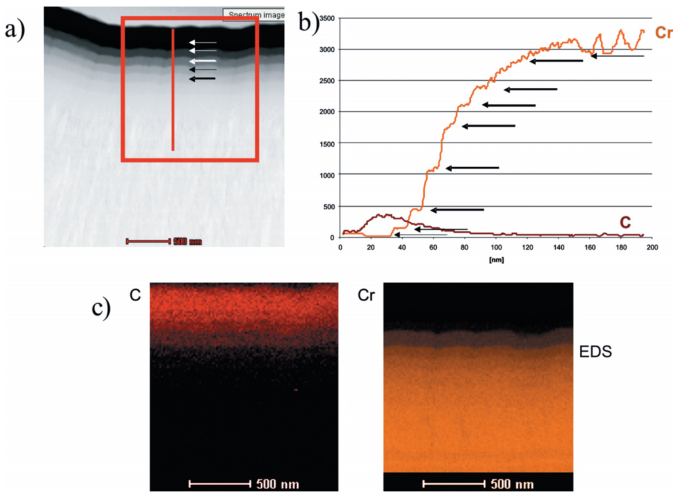

Fig. 6. Qualitative EDS chemical analysis; a). STEM image; b). diagram of selected elements distribution along the line marked at the STEM image; c). maps of selected elements [8]

The higher the distance from the interface with the inner part of the coating (Cr / Cr_2N), the lower amount of Cr nano-crystals. Almost at the top part of the coating, the stage of implantation was practically negligible. Looking at the diagram which presents the chromium distribution in the a-C:H part of the coating, along the line perpendicular to the substrate, one may indicate formation of steps (Fig. 6b). Each step corresponded to the individual a-C:H layer with different amount of Cr nano-crystals concentration. The gradient concentration of chromium nano-particle in a-C:H structure was confirmed by selected area electron diffraction pattern (Fig. 7).

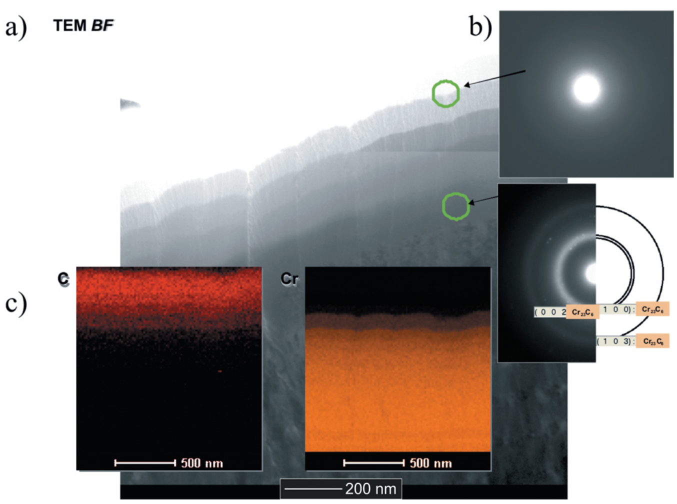

Fig. 7. Microstructure characterization of the amorphous carbon part of the coating (outer part) using TEM technique; a). TEM BF image; b). selected electron diffraction patterns (phase analysis); c). maps of selected elements obtained by EDS technique [8]

The character of the diffraction pattern changed with the distance from the interface with the inner part of the coating to the coating surface. Close to the interface, it had a nano-crystalline character (fine ring pattern). Close to the coating surface it had almost amorphous character (two blurred rings round the main spot). The diffraction pattern not only confirm the gradient concentration of nano-particles implantation, but also indicated, that chromium which was inserted into a-C:H structure reacted with carbon during deposition (in plasma), forming chromium carbides ($Cr_{23}C_6$).

A role of chromium carbide nano-particles in wear resistant properties of coating was significant. Some cracks propagating through a-C:H layers with relatively low amount of $Cr_{23}C_6$ nano-particles, were stopped at interfaces with a-C:H layers with higher amount of $Cr_{23}C_6$ nano-crystals (Fig. 8) [8].

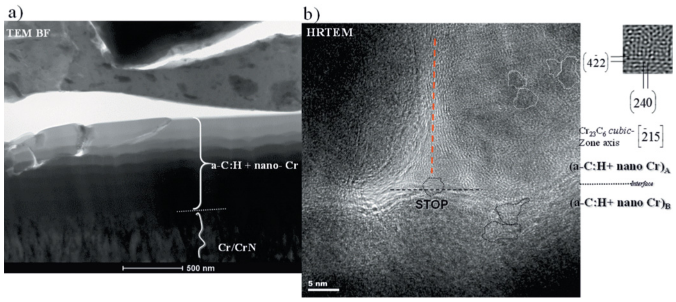

Fig. 8. Microstructure characterization of the amorphous carbon part of the coating after ball-on-disc wear test; a). TEM BF image; b). HRTEM image [8]

Focusing on the surface topography, it has been noticed that at the top of the coating graphite was formed during the wear process (Fig. 9).

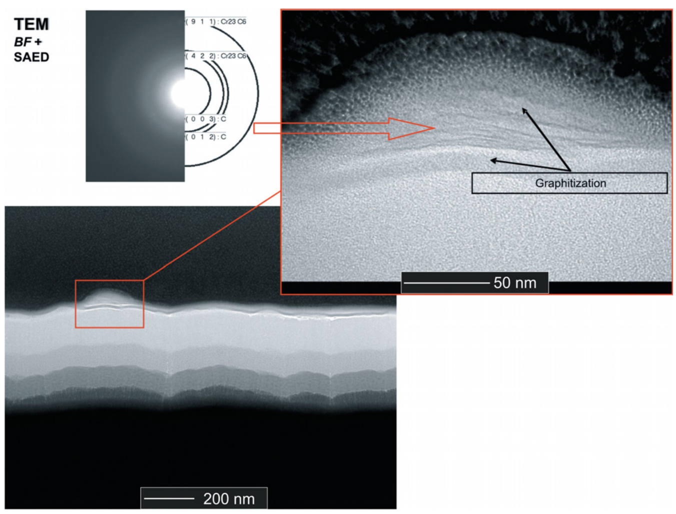

Fig. 9. Microstructure characterization of the tribo-film formed after ball-on-disc wear test, performed by TEM technique [8,12]

The phase analysis performed by the diffraction pattern, showed the presence of graphite and chromium carbides in the tribo-film [8,12]. Tribo-film is a material which is usually formed during wear process from the removed fragments of material. A well designed outer part of the coating is a very important factor in its wear resistant properties.

Another subject was studied, because of some unpredictable aspects. The application of the outer part may even speed up the wear process of total coating. The coating was deposited on metallic substrate (tool steel-316L) consisting of two parts. The inner part (the first from the substrate) was formed by conventional Cr / Cr_2N multilayer system, while the outer part by a-C:H / Cr multilayer (Fig. 10).

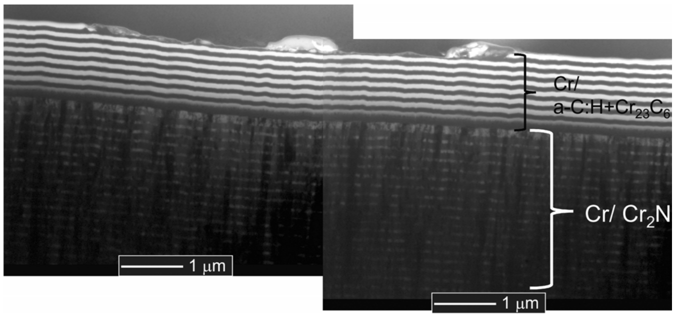

Fig. 10. Microstructure characterization of the Cr / Cr_2N+a-C:H / Cr multilayer coating, performed at the cross- section, by transmission electron microscopy technique (bright field)

Additionally a-C:H was implanted by $Cr_{23}C_6$ nano-multilayers (Fig. 11).

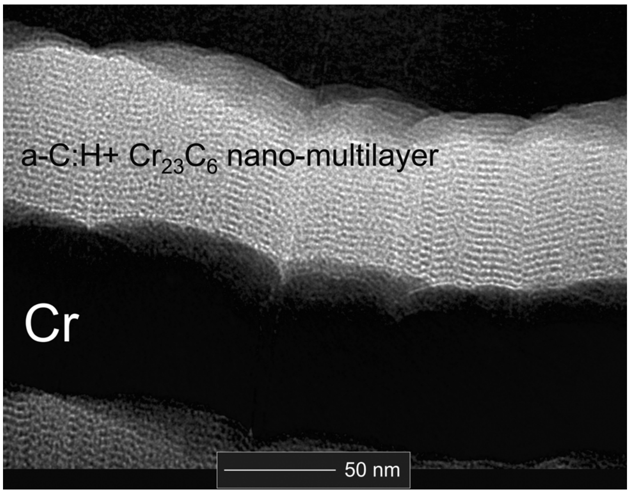

Fig. 11. Microstructure characterization of the outer part of the coating (a-C:H / Cr), particularly a-C:H implanted by $Cr_{23}C_6$ nano-particles, performed at the cross- section, by transmission electron microscopy technique (bright field)

As it was presented before, on one of the previous images (Fig. 9), formation of the tribo-film during a wear process may have a positive aspect. It may contain high amount of graphite, which is a good lubricant. In the presented case agglomerated $Cr_{23}C_6$ nano-particles in the wear process, which were initially as nano-multilayers in a-C:H layers, accelerated layers removal (Fig. 12).

The phase composition was confirmed by HRTEM analysis (Fig. 13).

It is impossible to predict all negative properties of coatings at the designing stage. Some of them are eliminated by a numerical modelling, some of them reveal at the experimental testing stage, like it was in case of the above presented subject.

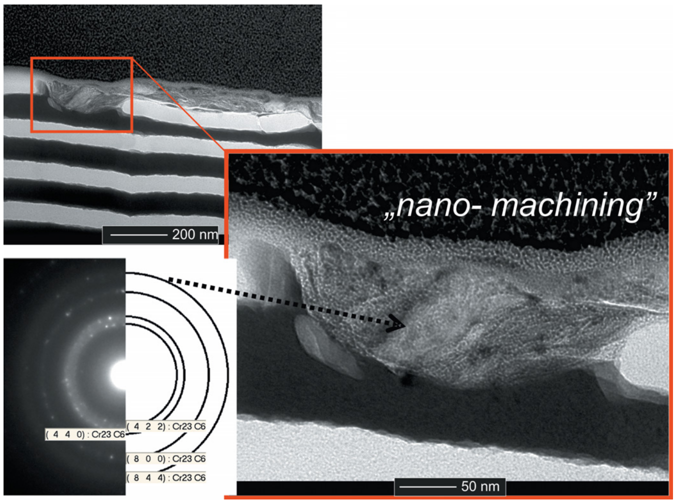

Fig.12. Microstructure characterization of the outer part of the coating (a-C:H / Cr), after mechanical wear test, performed by transmission electron microscopy technique (bright field)

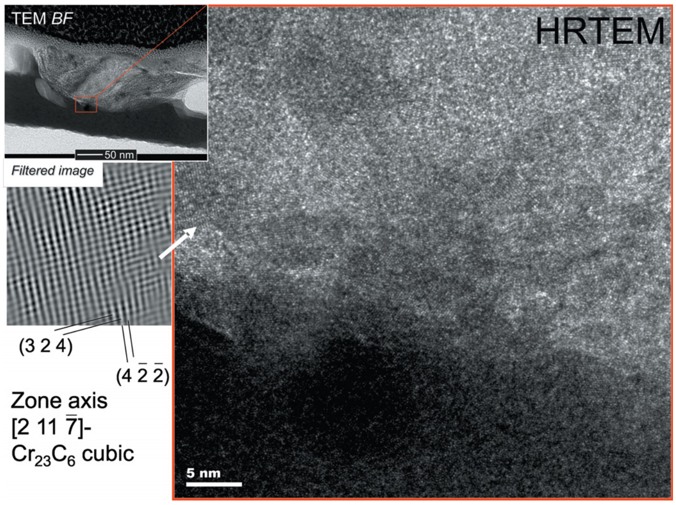

Fig. 13. HRTEM characterization of the tribofilm

Another innovative solution in coating designing was application of very thin metallic interlayers at the ceramic / ceramic multialayer structure TiN / Ti / a-C:H (Fig. 14) [13].

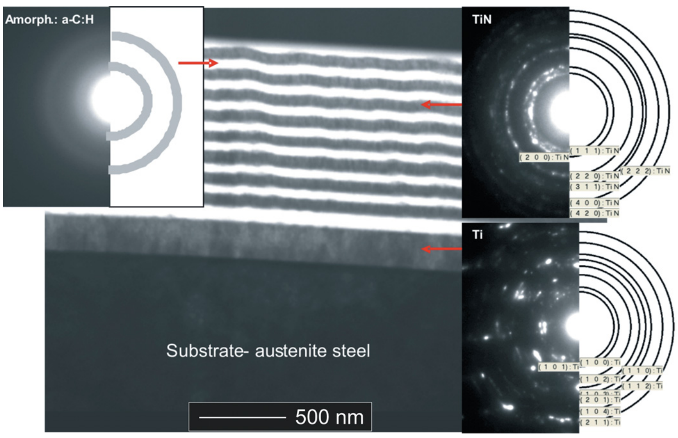

Fig. 14. TEM bright field image of an as-deposited 8 TiN / Ti/a-C:H multilayer coating, together with selected area electron diffraction patterns from selected parts of the coating [13]

The first layer from the substrate, it was a pure, metallic titanium buffer layer. Its role was to increase adhesion of the coating to the metallic substrate. Then, the multilayer structure was deposited. The titanium nitride layers were sequentially placed with amorphous carbon layers. Additionally at each TiN / a-C:H interface, very thin (~7 nm) metallic, titanium layers were produced. Their presence was visible at higher magnification in the bright field mode (Fig. 15) [13].

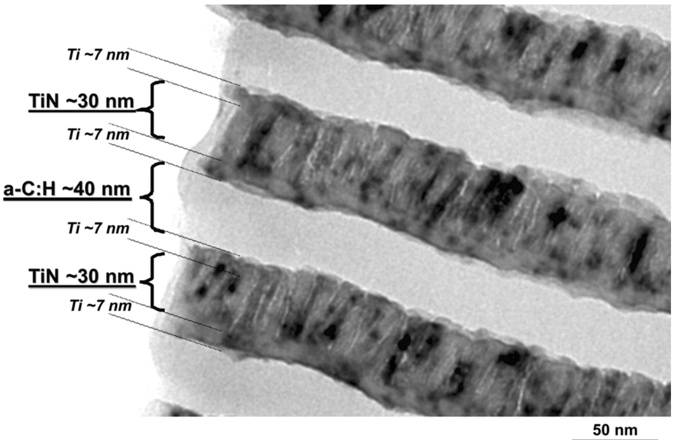

Fig. 15. TEM bright field image of an as-deposited 8TiN / Ti / a-C : H multilayer coating (higher magnification than (Fig. 12), revealing thin Ti layers presented at each interface) [13]

One of the main advantages of the described coatings was that cracking had not been performed suddenly. It occurred layer-by-layer. The highest, localized stress concentration was moved during the coating deformation from the bottom to the top part of the coating, which was modelled by the finite elements method [13] (Fig. 16).

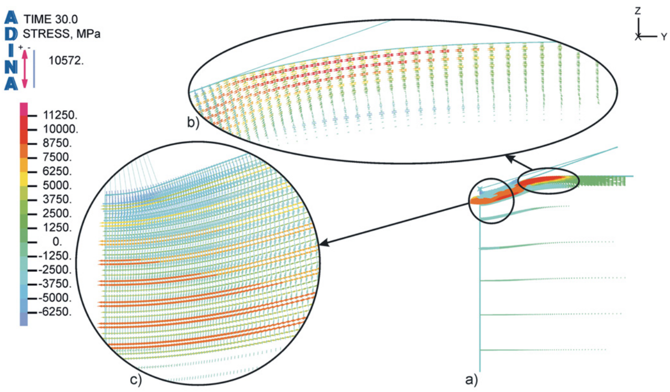

Fig. 16. Finite elements modelling of residual stress distribution during the mechanical test; a). residual stress distribution in the total coating; b). magnification of the top part of the coating; c). magnification of the bottom part of the coating [13]

The numerical modelling was confirmed by TEM characterization of the wear mechanism in the real material (Fig. 17).

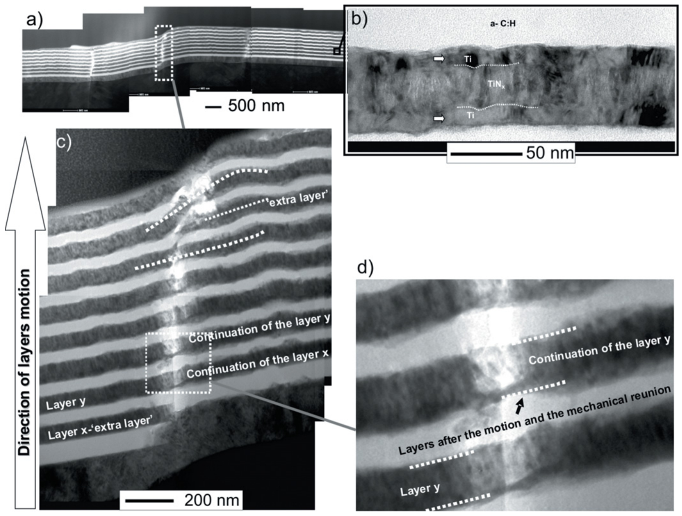

Fig. 17. TEM bright field image of the cracking place in an 8TiN / Ti / *a*-C : H coating (cross section): a). TEM bright field image of the cracked place; b). image revealing presence of thin Ti metallic layers at each TiN / *a*-C : H interface; c). the magnified area of one crack presenting the 'layers motion mechanism'; d). place of layers reunion after 'layers motion' [13]

The highest, localized stress concentration was moved during the coating deformation from the bottom to the top part of the coating. The layers reunion after movement of individual layers to the closest layer of the same phase was possible by the presence of metallic thin layers at each interface.

These type of coating exhibited also a good mechanical adhesion which was confirmed by the scratch test analysis. Detailed TEM microstructure analysis allowed to present stages of coating delamination during mechanical uploading (in the scratch test). During the scratch adhesion test, first cracks which are usually formed on the scratch track are called cohesive cracks. They are formed in the opposite way to the penetrator movement. Final cracking is called adhesive which is connected with coating delamination from the substrate. The TEM microstructure investigation allowed to describe, from the microstructure point of view, these two types of cracks (Fig. 18) [14].

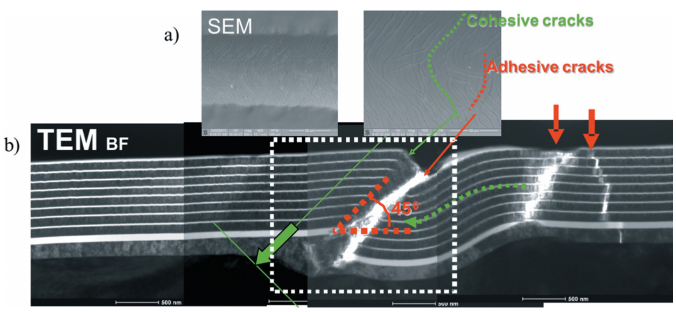

Fig. 18. Microstructure analysis of 8×TiN / Ti / a-C:H multilayer coating with 4:1 (TiN:a-C:H) phases ratio, after scratch adhesion test; a). topography analysis by SEM technique, b). microstructure analysis on the cross- section by TEM technique (bright field mode) [14]

The another thin foil prepared for TEM observation allowed to study the earlier deformation stage in the cohesive cracking (Fig. 19) [14].

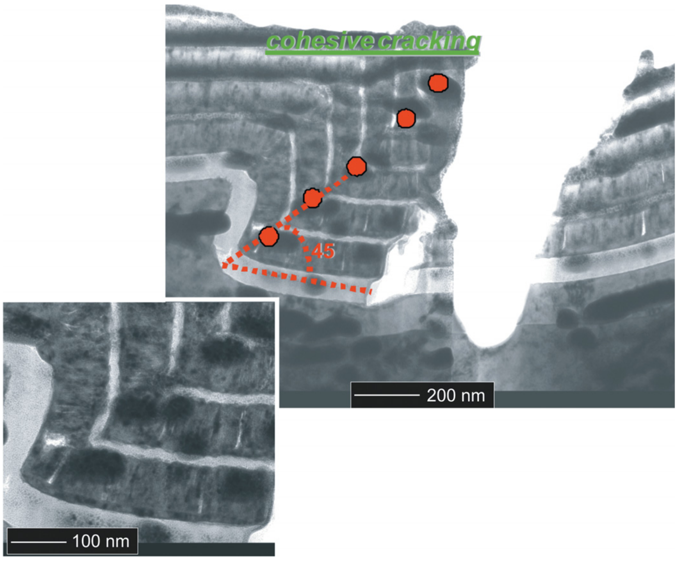

Fig. 19. Microstructure analysis of 8xTiN / Ti / a-C:H multilayer coating with 4:1 (TiN:a-C:H) phases ratio, after scratch adhesion test-earlier stage of cohesive cracking than presented in Fig. 18 [14]

In cohesive cracking, ceramic TiN and a-C:H layers brittle cracked, while the crack propagation was fixed by very thin Ti layers at each TiN / a-C:H interfaces. The dots were placed on points where individual layers were bended.

In the subsequent stage, with higher uploading (when adhesive cracking started to dominate), the crack was formed along line at 45°, however, the coating adhesion to the substrate was so strong that the plastic deformation of the metallic substrate pulled down the coating fragment (Fig. 20) [14].

Such behavior is a proof of a very good coating adhesion to the substrate.

Summing up, several types of coatings were taken under investigation and different mechanical tests were applied to study their mechanical properties. The wear mechanisms were investigated by means of transmission electron microscopy techniques. Different types of coatings subjected to different types of wear test may have very similar wear mechanism. It is an example with Ti / TiN and Cr / Cr_2N multilayer coatings. The first multilayer system was subjected to indentation test, while the second system to ball-on-disc wear test. In both cases the very similar wear mechanism was presented.

Our research work also showed that application of innovative multilayer coatings may allow to predict their life time and to steer their properties. It was an example with the TiN / a-C:H multilayer coating with very thin metallic interlayers (Ti) at each ceramic / ceramic interface. The cracking process performed in such a way that coating cracked layer-by-layer and a movement to the closest neighbor of the same phase. This phenomena was very similar to the dislocation movement, where atomic bonds are locally broken.

a) b) c)

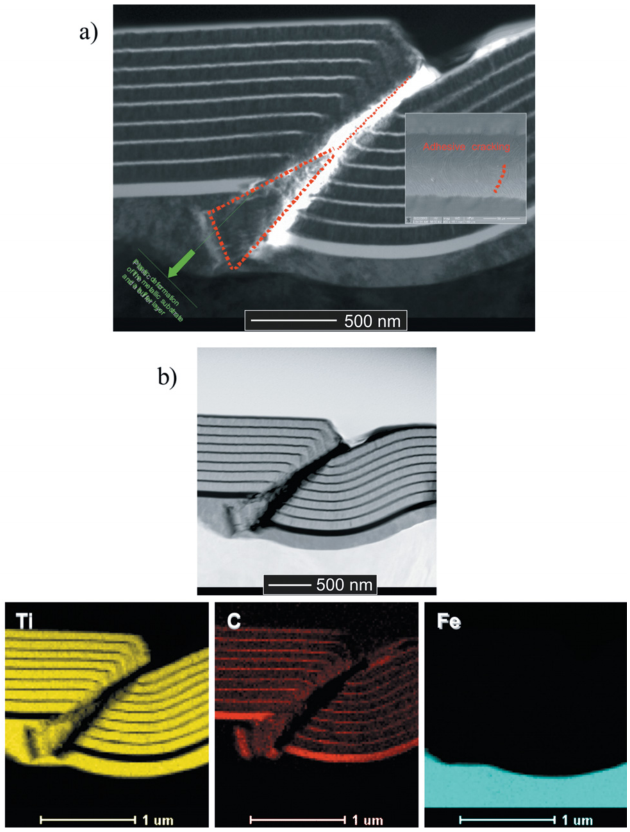

Fig. 20. Microstructure analysis of 8×TiN / Ti / *a*-C:H multilayer coating with 4:1 (TiN:a-C:H) phases ratio, after scratch adhesion test-adhesive cracking; a). TEM bright field image, b). image in the Z-contrast (contrast dependent on atomic number Z), c). maps of selected elements obtained in qualitative chemical analysis EDS [14]

Finally, the investigation also showed that it was impossible to predict all negative aspects which may appear during wear process. It may happen that application of modern type of coating may even speed up the wear process.

4. Conclusions

The performed examinations lad to the following conclusions:

– In case of conventional Ti / TiN or Cr / Cr_2N The Cr / Cr_2N ceramic layers brittle cracked, while metallic Cr deformed plastically, reducing the cracking energy in coating
– Wear of multilayer coatings is usually performed by two types of mechanisms: by cracking; and by layer-by-layer remove and tribo-film formation
– Application of the outer part of the coating (deposition of the additional part at the conventional metal/ceramic multilayer system), may additionally increase wear resistance properties of total coating; the HRTEM image presented that a crack propagating through a a-C:H layer with lower $Cr_{23}C_6$ nanoparticles content had been stopped at the interface with another layer of a-C:H with higher amount of $Cr_{23}C_6$.

– A positive influence on wear process was found for *a*-C:H which was gradiently implanted by $Cr_{23}C_6$ nano-particles, while other example of the outer part of the coating (Cr / a-C:H+ $Cr_{23}C_6$ nano-multilayers) speeded up the wear process. The carbides agglomerated during wear causing so- called "nano-machining" process of the coating.
– Multilayer structure and metallic interlayers in the TiN / Ti / a-C:H coatings played major roles in controlling the deformation process.
– Propagation of the deformation was realized layer-by-layer in TiN/Ti/a-C:H system.
– Cracking lines, due to the presence of very thin Ti layers at each interface, could move through the multilayer coating in the direction of the applied stress by breaking only one layer at a time in TiN / Ti / a-C:H system.

Acknowledgment

The author expresses his acknowledgment to Dr Juergen M. Lackner and the Institute for Surface Technologies and Photonics Joanneum Research Materials Leoben, Austria for elaboration of multilayer coatings.
It is highly acknowledged to the following research projects:
– Research Project (National Science Centre): Develop and diagnostics of multifunctional ceramic / hydrogenated amorphous carbon coatings for elements of pumps for artificial heart chambers. Number: **3066/B/T02/2011/40**
– Research Project (National Science Centre): Multilayered, wear resistant, self-healing, protective coatings elaboration for carbon fiber composite materials. Number: **2012/06/M/ST8/00408**.
– Research Project (National Science Centre): Bio-mechanical and micro-structure analysis of multilayer nano-composite, protective coatings for metallic substrates for tissue interaction. Number: **2012/07/B/ST8/03396**

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Received: 20 April 2015