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TEM Investigations of Wear Mechanisms of Single and Multilayer Coatings

Łukasz Major[1], Jürgen M. Lackner[2] and Jerzy Morgiel[1]
[1]*Institute of Metallurgy and Materials Science Polish Academy of Sciences,*
[2]*Joanneum Research Forschungsges. m. b. H.,*
Institute for Surface Technologies and Photonics,
[1]*Poland*
[2]*Austria*

1. Introduction

Wear resistant ceramic coatings deposited by physical vapour deposition (PVD) techniques, like magnetron sputtering, ion beam assisted deposition, arc evaporation and pulsed laser deposition (PLD), are successfully used to protect surfaces of mechanical components working under high wear loads for nearly half century.

The titanium nitride (TiN) is of special interest due to its corrosion resistance and high hardness (R. F. Bunshah, 2001, D. S. Rickerby & A. Matthews, 1991). The other promising material for wear resistant applications is amorphous, hydrogenated carbon (a-C:H). The a-C:H coatings are characterised by very low friction and biological inertness (V. Kumar et al., 2011). The tribology- related engineering applications for highly- stressed components require the development of new multifunctional thin films materials providing superior mechanical, tribological, chemical and high- temperature performance. It could be achieved by connecting the properties of different type of materials in multilayer coatings (Li Chen et al., 2008, M. Stueber et al., 2009, E. Martinez et al., 2003, J. Smolik et al., 1999, Y. L. Su et al., 1998, N. Dück et al., 2001, M. Nordin et al., 1999).

The multilayer properties could be controlled by appropriate chemical composition, microstructure and thickness of individual layers. In many tribological applications, coatings with a stack of soft and hard layers can offer much improved mechanical properties compared to single- layered hard coatings (Ł. Major et al., 2010, Ł. Major & J. Morgiel, 2009, M. Bromark et al., 1997, A. Leyland & A. Matthews, 1994, A. Matthews & S. S. Eskilden, 1994, K. Holmberg et al., 1998). The multilayered titanium/titanium nitride (Ti/TiN) coatings display much improved fracture resistance as compared to single- layered TiN. The presence of plastically deformable metallic layers play an important role in cancelling cracks propagation mechanisms.

The coatings for medical application and especially those remaining in contact with human body fluid should both pre- sent high mechanical properties and contain as limited metallic material as possible. Otherwise such coatings may start the metalosis (the metal ions adverse interaction with human organism). The carbon, being part of most tissue of plants and animals is definitely the best material for such coatings. Carbon provides the framework for all tissues of plants and animals. These tissues are built of elements grouped around in chains and rings made of carbon atoms (J. Grabczyk et al., 2007). This is why in bio- application a development of multilayered coatings with carbon spacers are also of great importance.

The aim of the present paper was to describe the microstructure changes of single (ceramic) layered coating, multilayer ceramic/metallic (with different ratio) coating, and multilayer ceramic/ceramic coating after static mechanical tests by application of transmission electron microscopy techniques. The coatings, were subjected to static mechanical test because it simulates the uploading in their real application (as a coatings for pumps elements which support artificial heart chambers).

2. Experimental

Thin and ultra- thin coatings are preferably produced by deposition from the gaseous phase (PVD-Physical Vapour Deposition and CVD- Chemical Vapour Deposition). PVD coating requires as the first step the vaporization of the basic material- the target. CVD coating starts from mixtures of reactive gases. In contrast to CVD techniques, the PVD processes are generally characterized by lower coating temperatures, a wide range of possible coating and substrate materials, and the higher purity of the deposited coatings. Besides an optimized microstructure, the adhesion of a coating on a substrate is the most crucial property for a coating defining its durability in industrial applications. One of the techniques combining classical evaporation with plasma activation is the Pulsed Laser Deposition (PLD) technique. The target evaporation (ablation) and vapor activation take place by means of a high-energetic focused pulsed laser beam. The high- energetic vapour (plasma) flux allows deposition of highly adhesive coatings even at room temperature. In addition the industrially- scaled room- temperature PLD deposition process was linked with other vacuum coating technique- magnetron sputtering and ion- assisted deposition to combine the advantages of these techniques.

The hybrid PLD with titanium and carbon targets (99, 9at. %) was used for coatings deposition also in presented work. Single layered TiN coatings were deposited using Ti target in nitrogen atmosphere. Multilayer Ti/TiN coatings were deposited using Ti target and sequential gas atmosphere change in between argon for Ti phase deposition to nitrogen for TiN phase deposition. Multilayer TiN/Ti/a-C:H coatings were deposited using both sequential atmosphere change (nitrogen for TiN and argon for a-C:H) and sequential target change (Ti for TiN and C for a-C:H). The details of deposition process is described elsewhere (J. M. Lackner, 2006).

Analyzed coatings were deformed by pushing a diamond indenter with 20 m tip radius under 1N load into it. The test simulates the mechanical interaction by which elements are uploaded in their real application (as a coatings for pumps elements which support artificial heart chambers). The microstructure of as deposited coatings as well as coatings after mechanical tests was characterized using TECNAI G^2 F20 FEG (200kV) transmission electron microscope (TEM). Phase analysis was performed by electron diffraction pattern and confirmed by identification of high resolution images (HRTEM). Energy Dispersive X-Ray technique (EDS) was done for chemical analysis. Thin foils for TEM analysis have been prepared from a section of mechanically deformed place by the Focused Ion Beam technique (FIB). The FIB technique together with in-situ OmniProbe micro- manipulator allowed to receive foil directly from the place of interest, in this particular case from deformed part of coating after mechanical test.

3. Results and discussion

3.1 TEM analysis of microstructure of single layered coatings

3.1.1 As deposited coatings

The as deposited single layered a-C:H coatings was characterized by totally amorphous structure (Fig. 1). The atom arrangements in amorphous materials are still relatively poorly understood. An amorphous material is one where the locations of the neighboring atoms are defined by a probability function, so they average inter- atomic distance vary significantly.

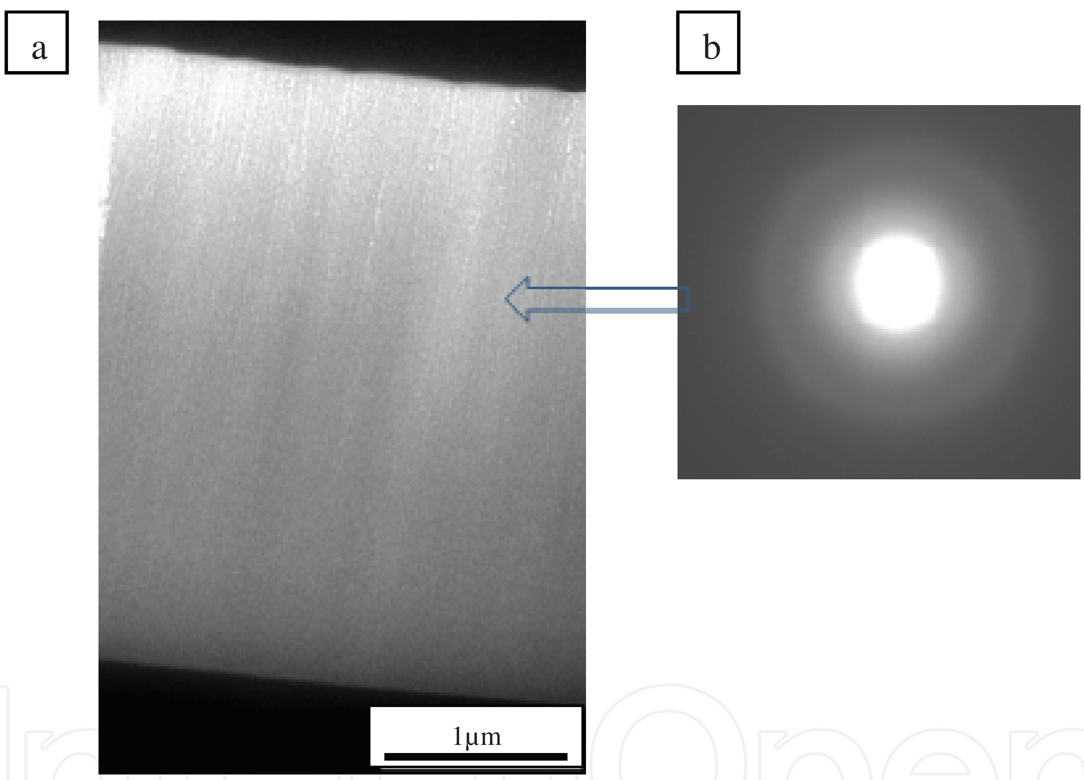

Fig. 1. Microstructure analysis of single layered amorphous carbon coating done on a cross-section by TEM technique; a). TEM Bright Field; b). electron diffraction pattern.

As a result a diffraction pattern from an amorphous material looks similar to that from polycrystalline material, but rings are broad and diffused. Aside from first ring representing distribution of "nearest neighbours" usually also similar but fainter second ring representing "next nearest neighbours" is present.

In the case of crystalline materials, like TiN, thin ceramic PVD coatings deposited at low temperatures are generally characterized by columnar structure with microcracks, pinholes and transient grain boundaries (Fig. 2a). Due to high compressive residual stress in the single layer TiN coating, microcrack-like features are forming along the column boundaries. (Fig. 2b) They consist of accumulation and pile-up of dislocations between the columns, as proved by high resolution imaging. According to literature, microcracks are nucleated in crystalline materials by three different mechanisms: dislocation pile-ups, twin intersections, and strain incompatibility (Gwidon & W. Stachowiak, 2005). In present material all these mechanisms are probably operating simultaneously.

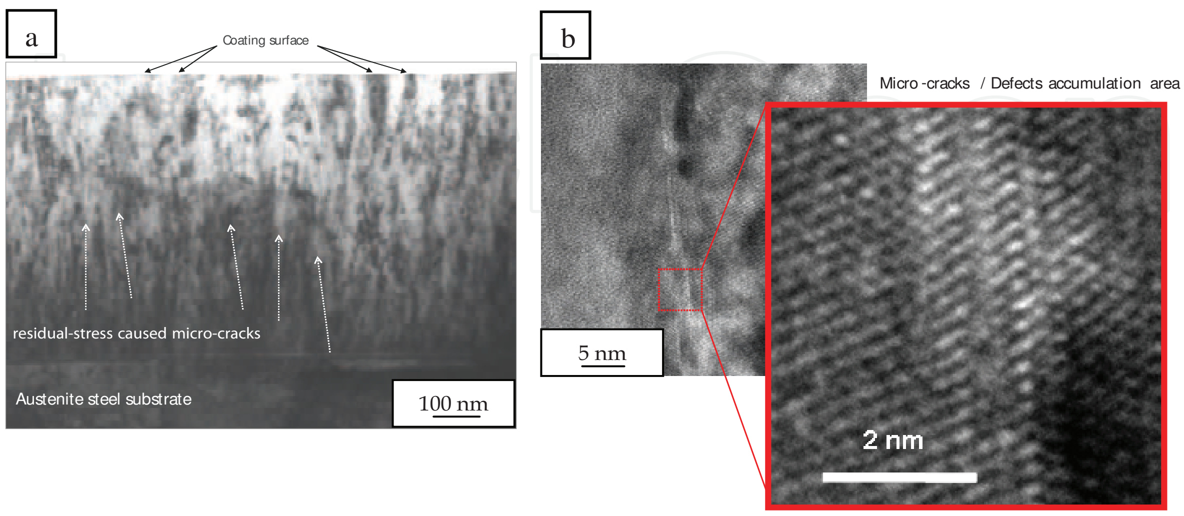

Fig. 2. Microstructure analysis of single layered TiN coating done on a cross- section by TEM technique; a). TEM Bright Field; b). high resolution image (HRTEM) of microcrack at columnar boundary.

The increase TiN single layered coating/substrate adhesion is achieved by inserting, a thin metallic Ti buffer layer (~150nm) between substrate and the coatig (Fig. 3).

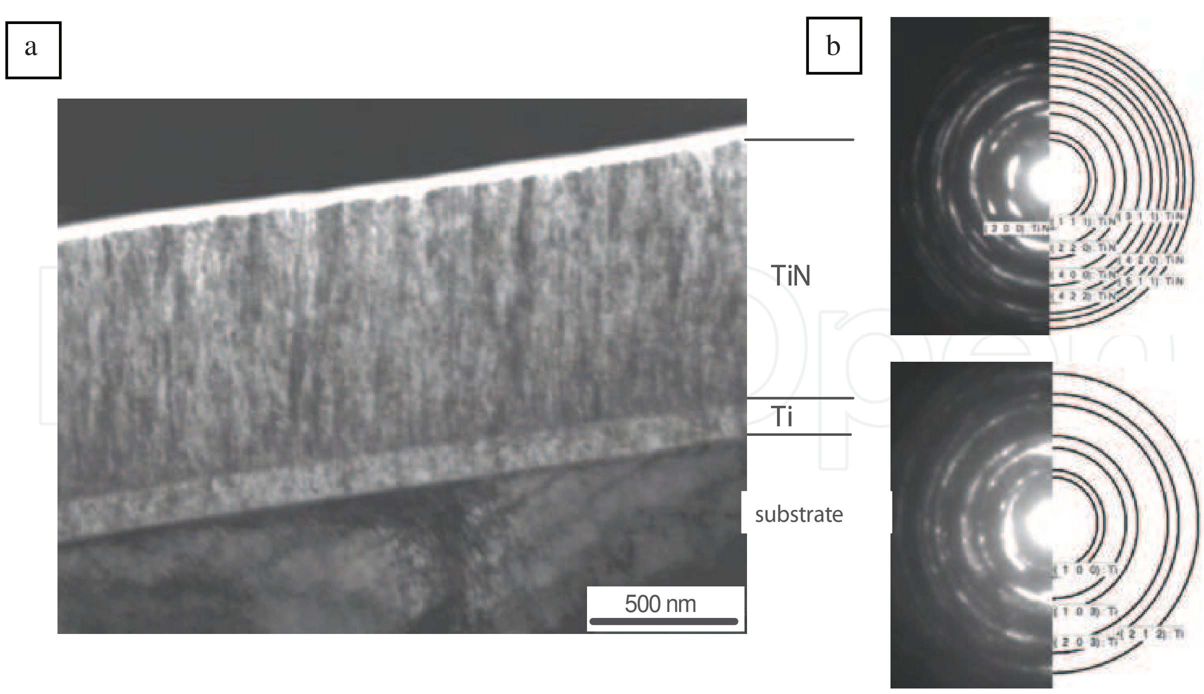

Fig. 3. Microstructure analysis of single layered TiN coating with Ti additional buffer layer done on a cross- section by TEM technique; a). TEM Bright Field; b). phase analysis done by electron diffraction pattern (SAEDP).

The ring patterns of selected area electron diffraction patterns confirmed that it belong to cubic (TiN) and hexagonal (Ti) systems. The presence of large number of fine spots in these rings indicate that layers are formed from extremely fine crystallites. Metallic buffer layer may prevent contact of substrate with environment by sealing cracks. Energy of brittle cracking in ceramic layer may be compensated by energy of plastic deformation of buffer.

3.1.2 Coatings after mechanical test

Above described coatings were subjected to mechanical test. The test simulated the condition by which coatings are uploaded in their real application. The test was static and based on pushing diamond indenter into the coating with 1N of the applied load (Fig. 4).

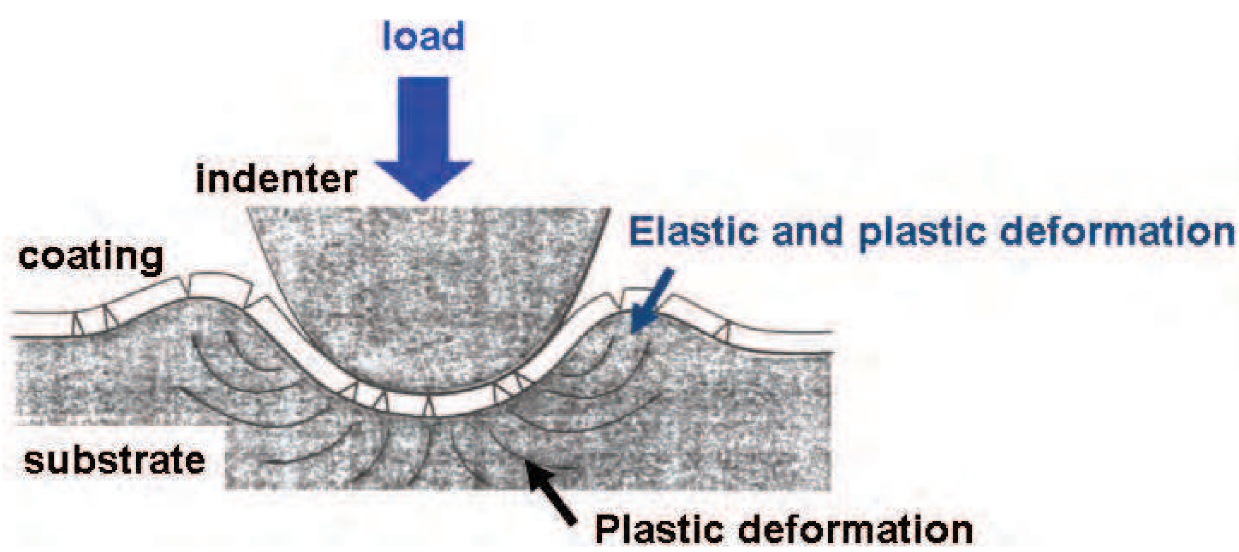

Fig. 4. Theoretical scheme of mechanical test by which analyzed coatings were subjected (R. F. Bunshah, 2001).

Reaction of coatings to the mechanical load during application is as follows: at the beginning elastic deformation dominates and next plastic deformation takes over. Because of ionic or covalent bonding, which characterize ceramic materials, plastic deformation is limited. As the dislocations are locked, brittle cracking is dominating.

First described material was amorphous carbon single layer coating after static mechanical test (Fig. 5).

Carbon, single layered coating turned out very brittle, as expected. During static mechanical test, substrate deformed plastically, while coating deformation was limited. It deformed elastically and just after that brittle cracks occured. The test caused coating delamination from the substrate. The adhesion was relatively weak.

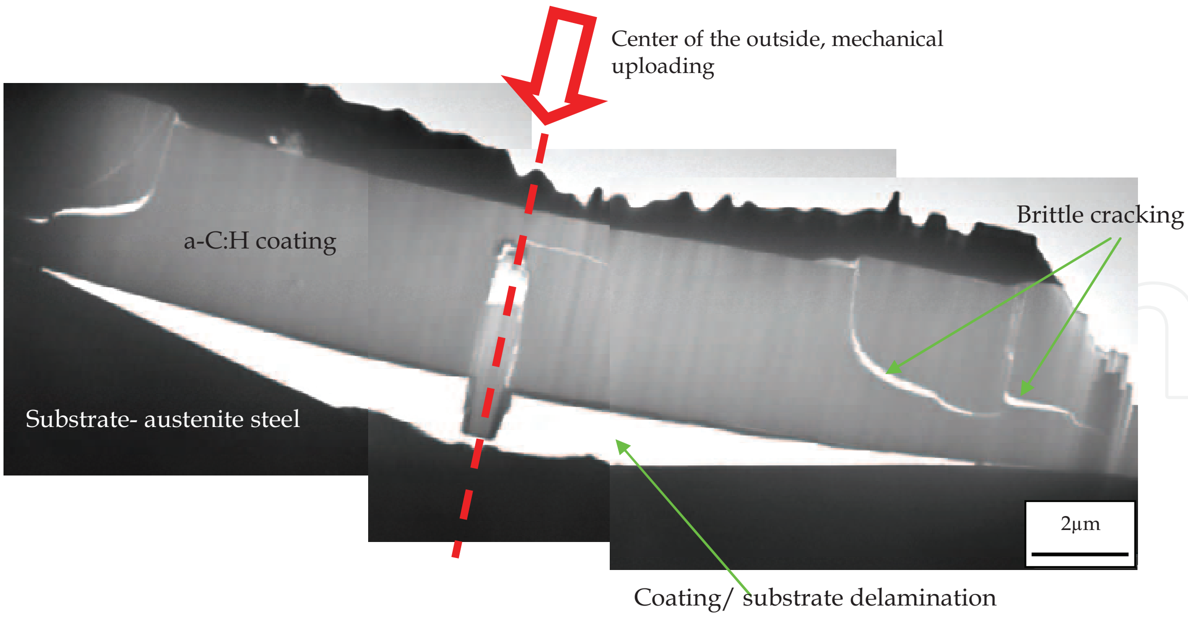

Fig. 5. Microstructure analysis of single layered a-C:H coating on a cross- section, after mechanical test, done by TEM technique.

Static mechanical test performed on TiN single layered coating with Ti buffer layer, caused serious deformation of coating (Fig. 6)

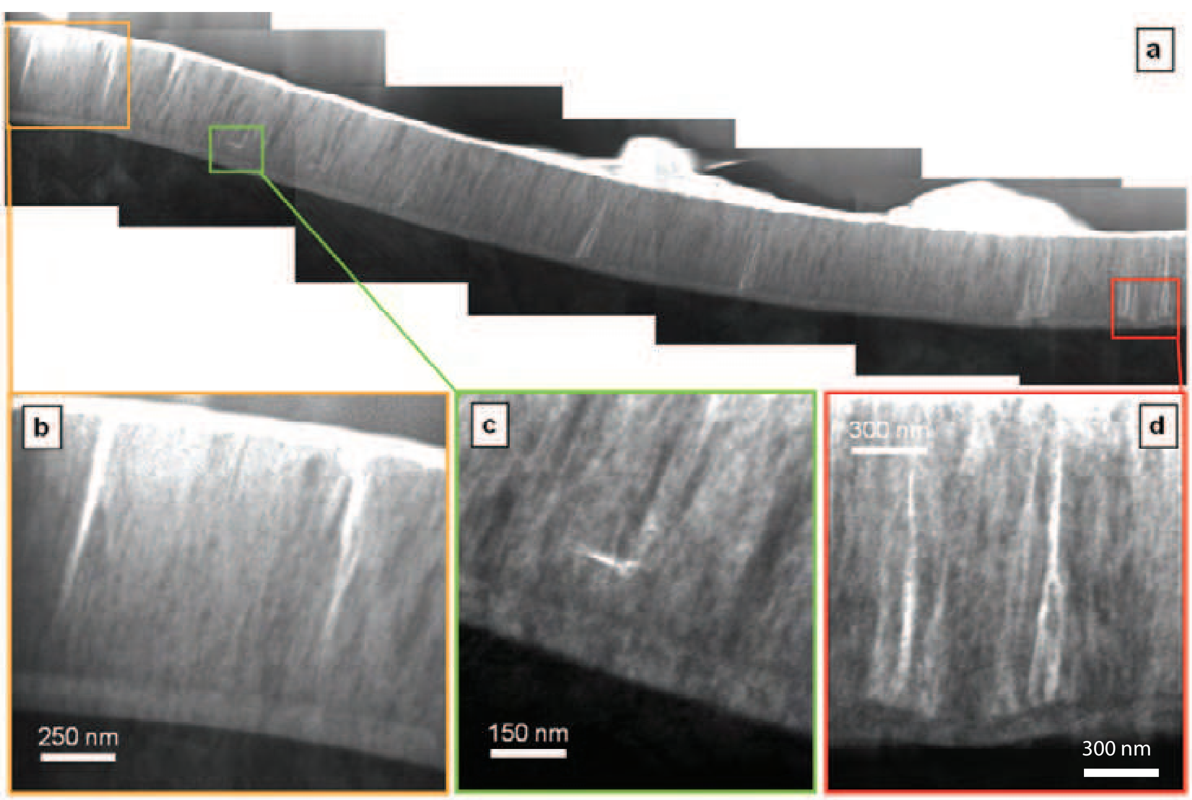

Fig. 6. Microstructure analysis of single layered TiN coating with Ti buffer layer on a cross-section, after mechanical test, by TEM technique.

TiN layer brittle cracked (Fig. 6). Cracking in ceramic crystalline materials mainly depends on the crystallographic plane which is the most responsible for cracking propagation as presents on the scheme (Fig. 7).

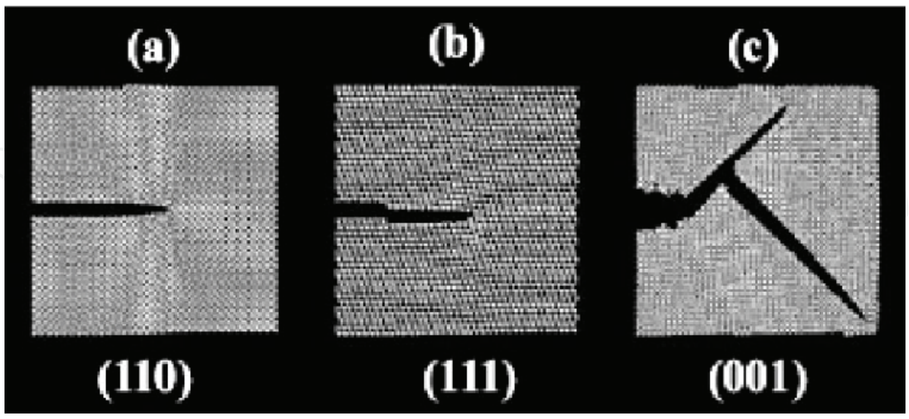

Fig. 7. Schemes of cracking character in dependence on the crystallographic plane on which it may be realized (C. L. Rountree et al. 2002).

Normally the process occurs on the most packed planes. If cracking is propagating along {110} planes the cleavage like cracking is visible. In case of cracks on {111} planes, steps like line is formed. Finally on {001} planes, branches like pattern is visible. Titanium nitride is characterized by face center cubic (fcc) structure. The most packed plane for fcc is {111} on which cracking is the most probable.

High resolution analysis of crack path performed through the TiN layer revealed that cracking was propagating along {111} plane (Fig. 8).

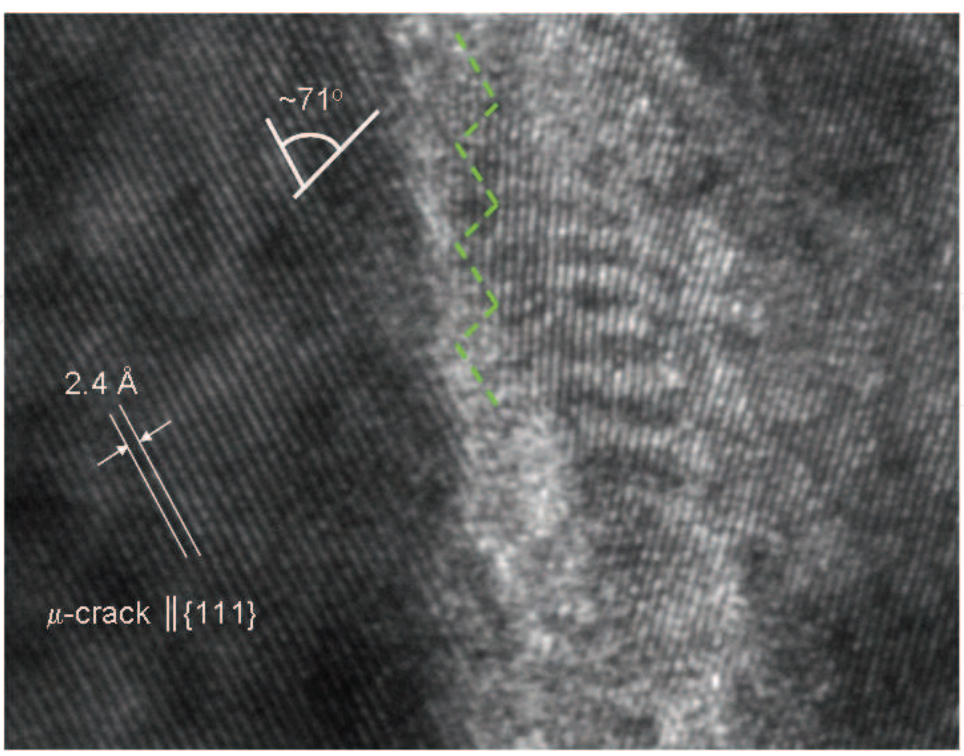

Fig. 8. HRTEM image of crack propagating through the TiN layer.

The steps like line was formed (Fig. 7b). The angle in between steps was ~71^0. Calculation of the distance in between lattice fringes and the angle consideration informed about the most plausible plane for cracking.

The presence of Ti thin buffer layer allowed to stop crack propagation through coating. Energy of brittle cracking in TiN layer transformed into the energy of plastic deformation in Ti at the interface (Fig. 9).

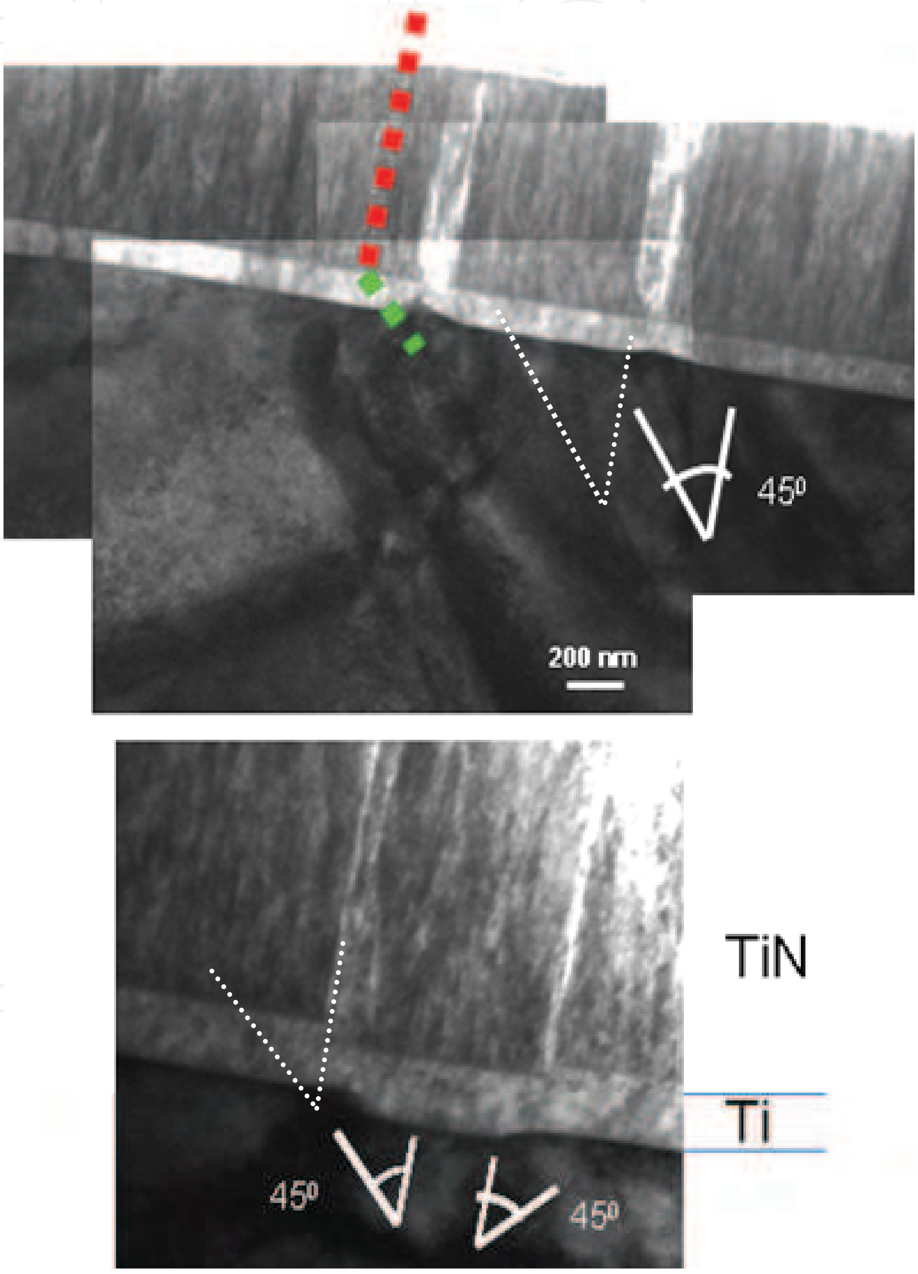

Fig. 9. Bright field image of crack propagating through the TiN layer and plastic deformation in Ti layer obtained by TEM.

The 45^0 it is a typical angle of metallic, polycrystalline materials plastic deformation. The presence of Ti phase (buffer layer) did not allow the substrate to contact with outside environment. It prevents also against catastrophic coating delamination.

3.2 TEM analysis of microstructure change of multilayer coatings

3.2.1 Coatings before mechanical test

As- deposited multilayered Ti/TiN coatings were characterized by strongly defected columnar crystallites (Fig. 10).

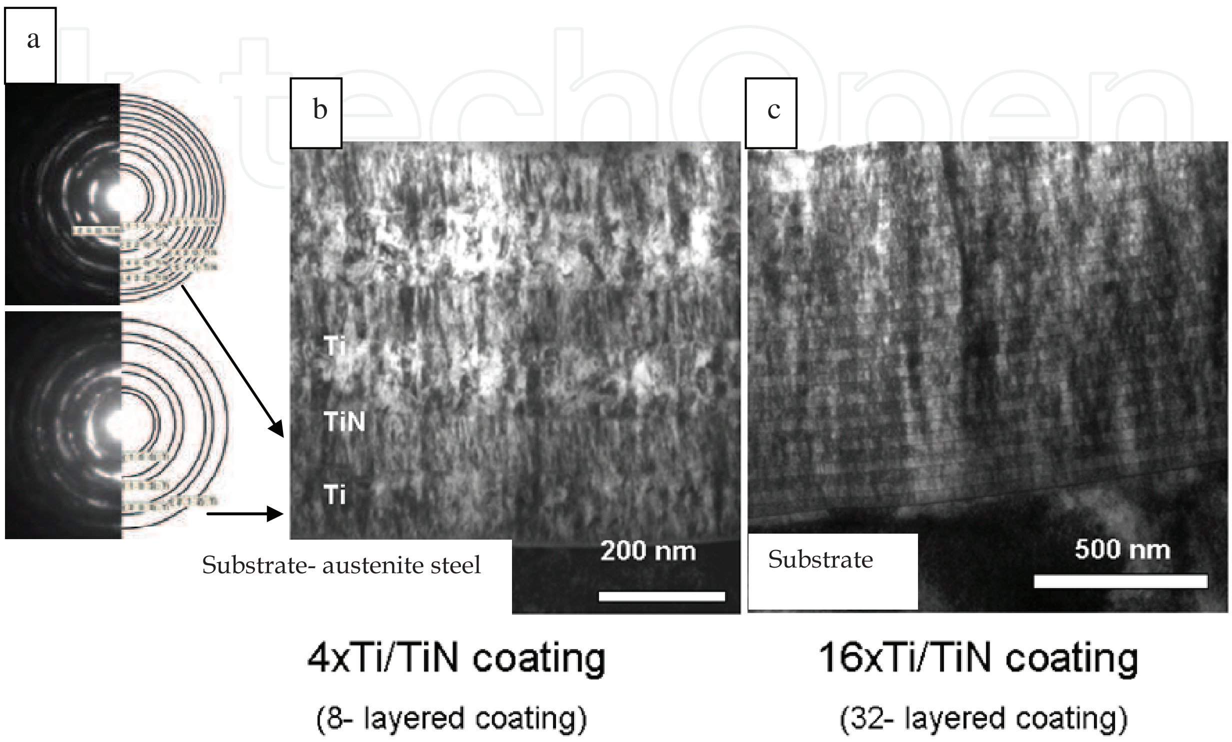

Fig. 10. Microstructure analysis of multilayered Ti/TiN coatings done on a cross- section by TEM technique; a). phase analysis done by diffraction patterns; b). 8- layered coating; c). 32- layered coating.

The same diffraction contrast, which goes through several interfaces, indicates that there are crystallographic relations in between individual layers. The first metallic buffer layer (in connection to the substrate) was characterized by much smaller crystallites then following sub- layers of the same phase.

The second group of multilayers was based on two ceramic phases: titanium nitride and amorphous carbon. To control the damage process of TiN/a-C:H multilayer coatings, small amount of metallic phase was inserted into the coating at each interface. To increase the adhesion properties of coating, metallic Ti buffer layer was deposited as a first layer on the substrate as well (Fig. 11).

The presence of carbon layers placed in a sequence with TiN ones is evident also from the line scan (Fig. 11b). Line scan confirmed presence of very thin metallic Ti layers at each TiN/a-C:H interface. It is with a good agreement with the deposition process. Energetic lines of Ti and N are very close to each other. Theoretical peak deconvolution is the only way to separate these two elements in EDS analysis. It was possible to do by confirmation phase analysis by electron diffraction pattern, and by HRTEM images. It will be presented in the 3. 2. 2 section -“Coatings after mechanical test”.

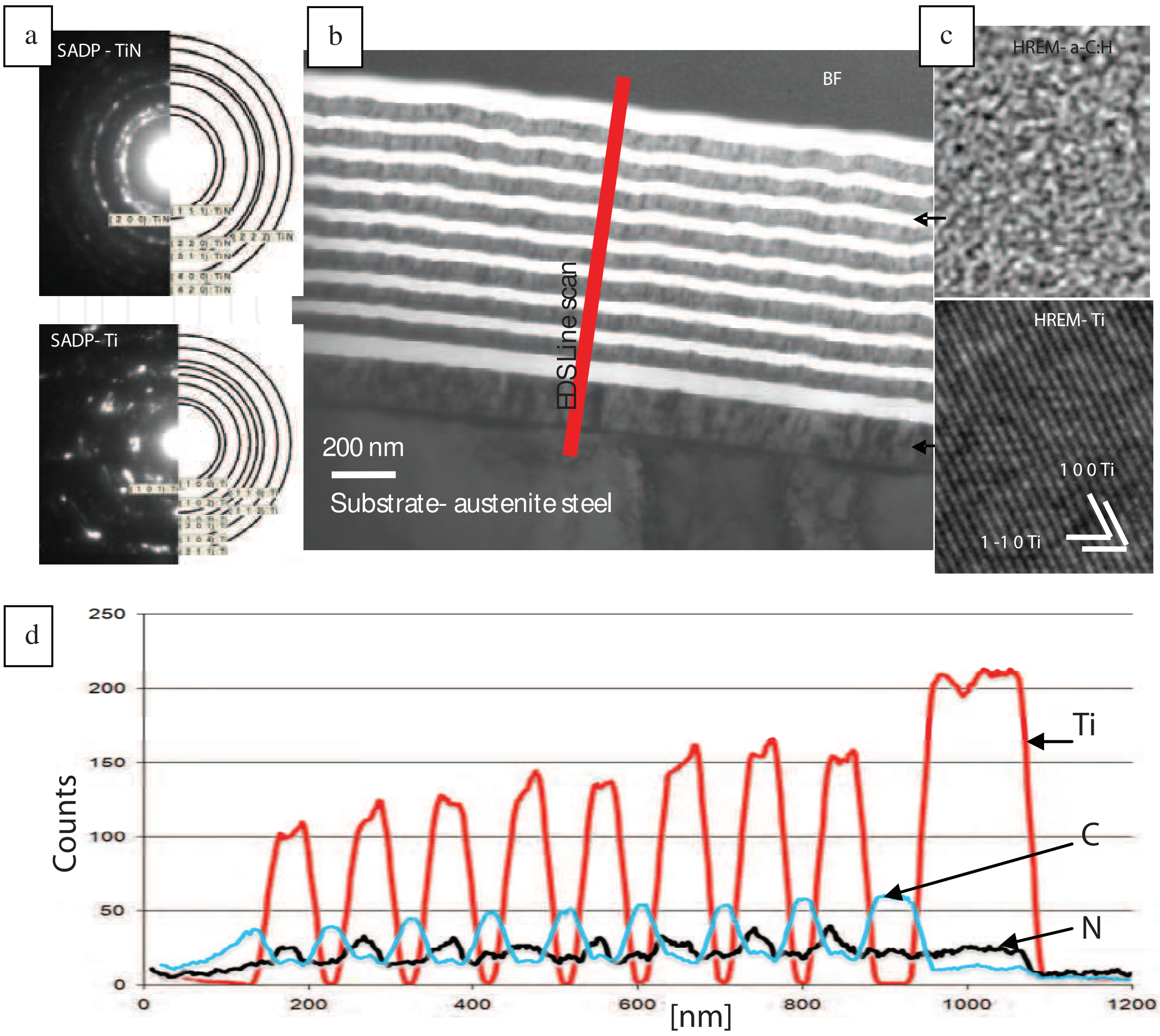

Fig. 11. Image of the TiN/Ti/a-C:H multilayer coating done by transmission electron microscopy; a). phase analysis done by SAEDP; b). bright field image and phase analysis of 8xTiN/Ti/a-C:H coating done by electron diffraction pattern analysis and high resolution; c). HRTEM images of a-C:H and Ti buffer; d). qualitative chemical analysis done by EDS (Energy Dispersive X-ray Spectroscopy) (line- scan along the line marked in the Fig. 11b).

3.2.2 Coatings after mechanical test

Both types of multilayer coatings were subjected to static mechanical tests. The tests were based on pushing diamond spherical indenter into the coatings with 1N of the applied load. Ti/TiN multilayer coatings after mechanical test were taken first under consideration focusing on microstructure change after mechanical test (Fig. 12).

The multilayer Ti/TiN coating was strongly deformed. Deformation lines appeared at an constant angle to the crystallites growth. Deformation lines were formed at 45^0 to the crystallites growth, which is a typical angle of plastic deformation for metallic polycrystalline materials (Fig. 13).

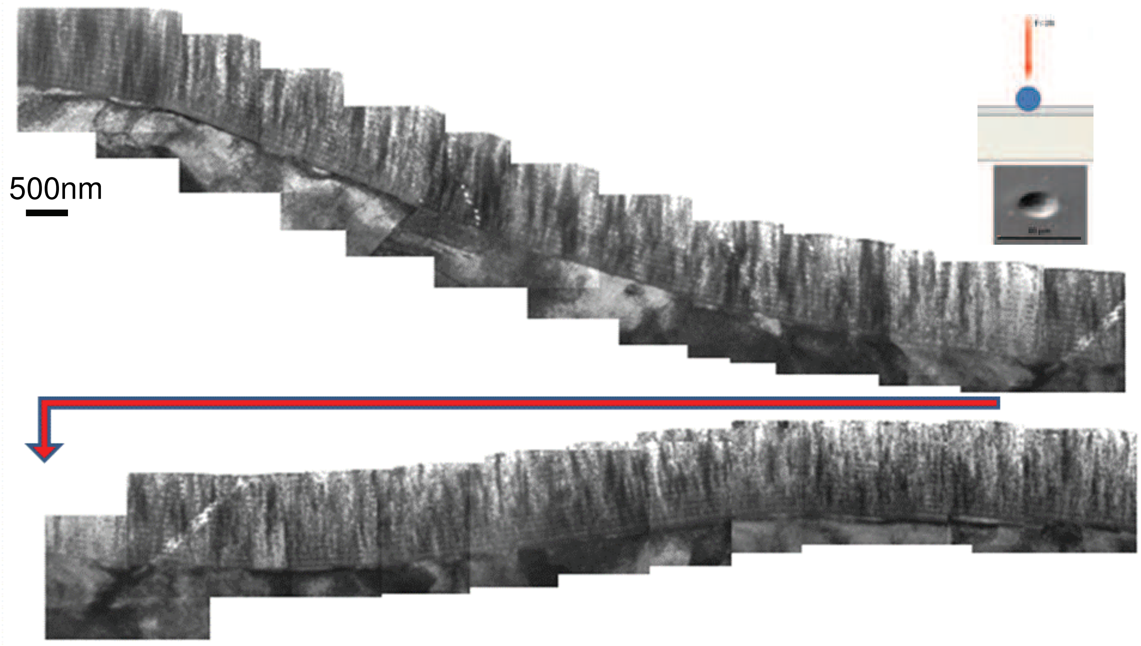

Fig. 12. Microstructure analysis of multilayered Ti/TiN coatings after static mechanical test done on a cross- section by TEM technique.

Fig. 13. Microstructure analysis of multilayered Ti/TiN coatings after static mechanical test done on a cross- section by TEM technique (higher magnification of the Fig. 12).

Detail analysis of deformation lines exhibited plastic deformation in metallic (Ti) layers and brittle cracking in ceramic (TiN) phase (Fig. 14)

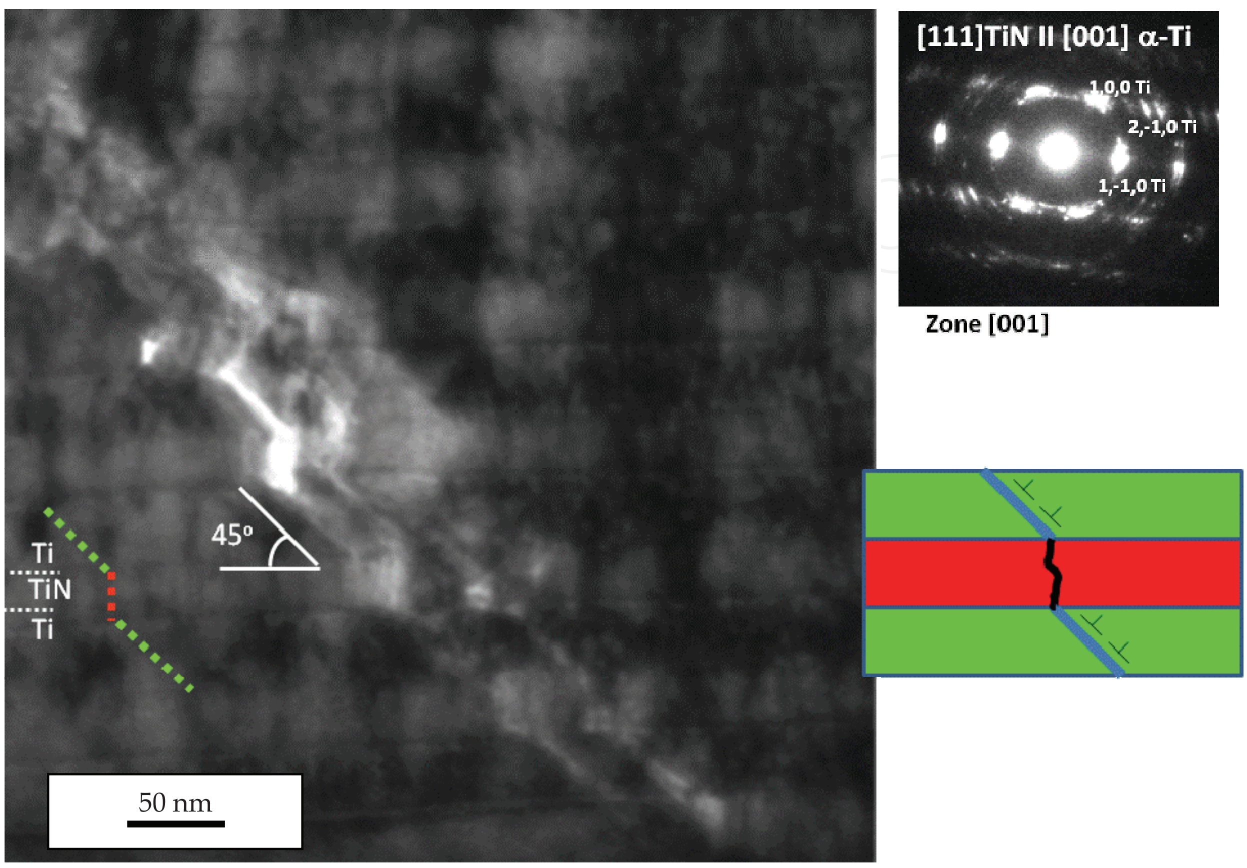

Fig. 14. Microstructure analysis of multilayered Ti/TiN coatings after static mechanical test done on a cross- section by TEM technique (detail analysis of deformation line).

Titanium metallic layers deformed plastically by slip systems while ceramic TiN brittle cracked. The character of the total deformation line suggested domination of plastic deformation in the total coating.

On one side, the presence of metallic sub- layers is crucial; they may stop crack propagation through the coating or decrease the energy of cracking; on the other side, the decrease of their amount and the increase of the hard phase, keeping constant the total thickness of coating. It may have an influence on the increase of mechanical properties, like hardness increase. One could ask, if the metallic phase reduction allow to keep control over wear. Two types of multilayer coatings have been suggested. The first with 1:2 ratio (the amount of ceramic phase two times higher than metallic one) and the second 1:4 ratio (the amount of ceramic phase four times higher than metallic ones). The advantage of multilayer coatings is fact that they contain metallic inter- layers. They are responsible for stopping cracks propagation. Their presence reduces the risk that substrate would have sudden contact with outside environment. It may suggest that these coatings would have much better corrosion properties. The characterization of the coatings with different ratio has been done in the use of transmission electron microscopy, on the cross- section (Fig. 15).

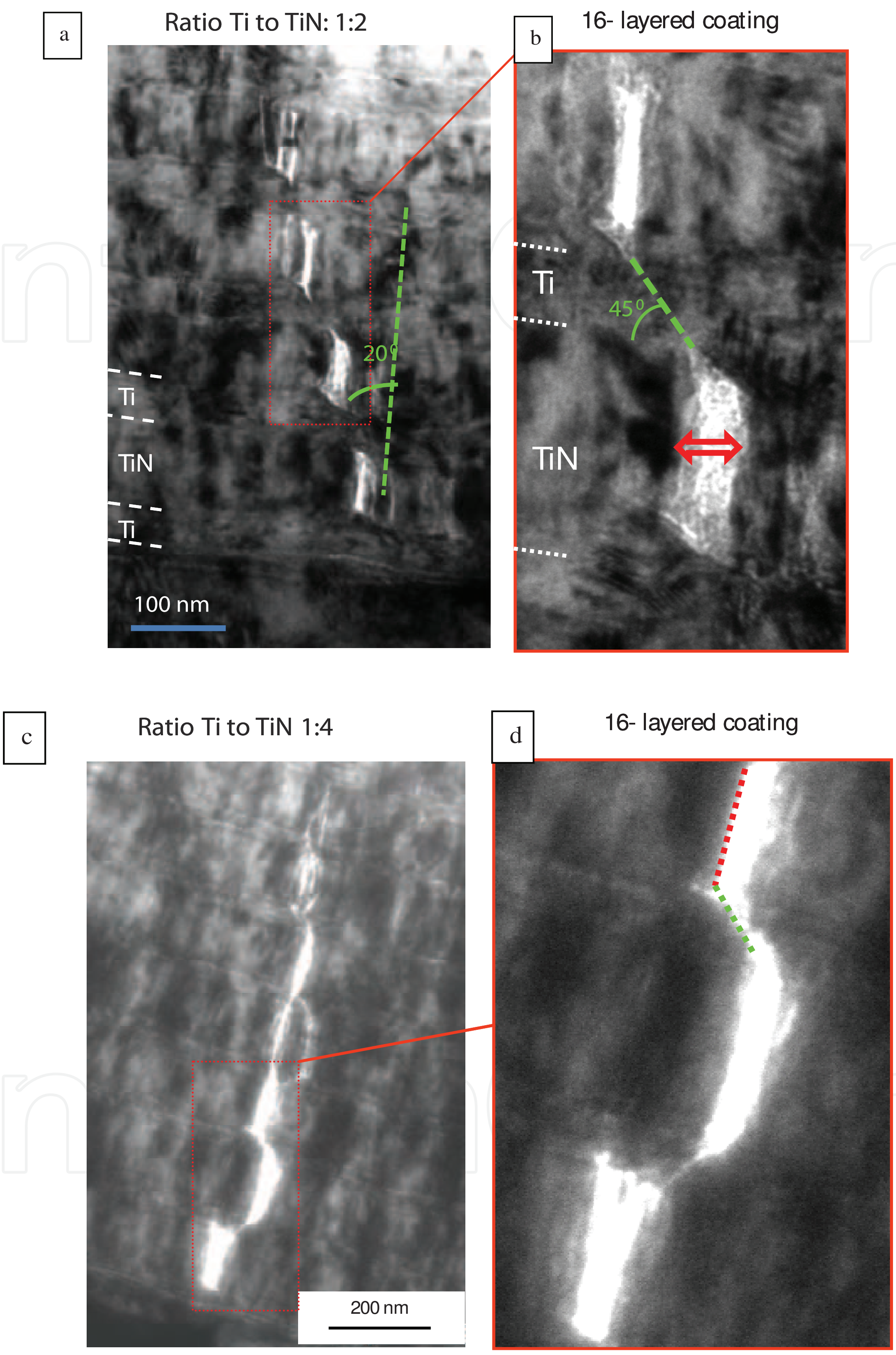

Fig. 15. Microstructure analysis of multilayered Ti/TiN coatings with different Ti to TiN ratio after static mechanical test done on a cross- section by TEM technique; a). ratio 1:2; b). higher magnification of the crack propagation through the coating with the 1:2 ratio; c). ratio 1:4; d). higher magnification of the crack propagation through the coating with the 1:4 ratio.

Ceramic inter- layers brittle cracked under the applied load, while metallic ones plastically deformed in slip systems. Plastic deformation of metallic Ti layers did not allow to contact both brittle cracked areas. The character of the total deformation line was intermediate in between plastic deformation and brittle cracking domination. The angle between the direction of crystallites growth was about 20^0. In the case of multilayer coating, where the amount of ceramic phase was four times higher than metallic one, character of the total deformation line in general was perpendicular to the substrate. Higher magnification showed that the metallic inter- layers played still its own role, not to allow to the contact of the substrate with outside environment by plastic deformation in slip system.

Second described multilayer system was TiN/Ti/a-C:H coating which was subjected to mechanical test (Fig. 16).

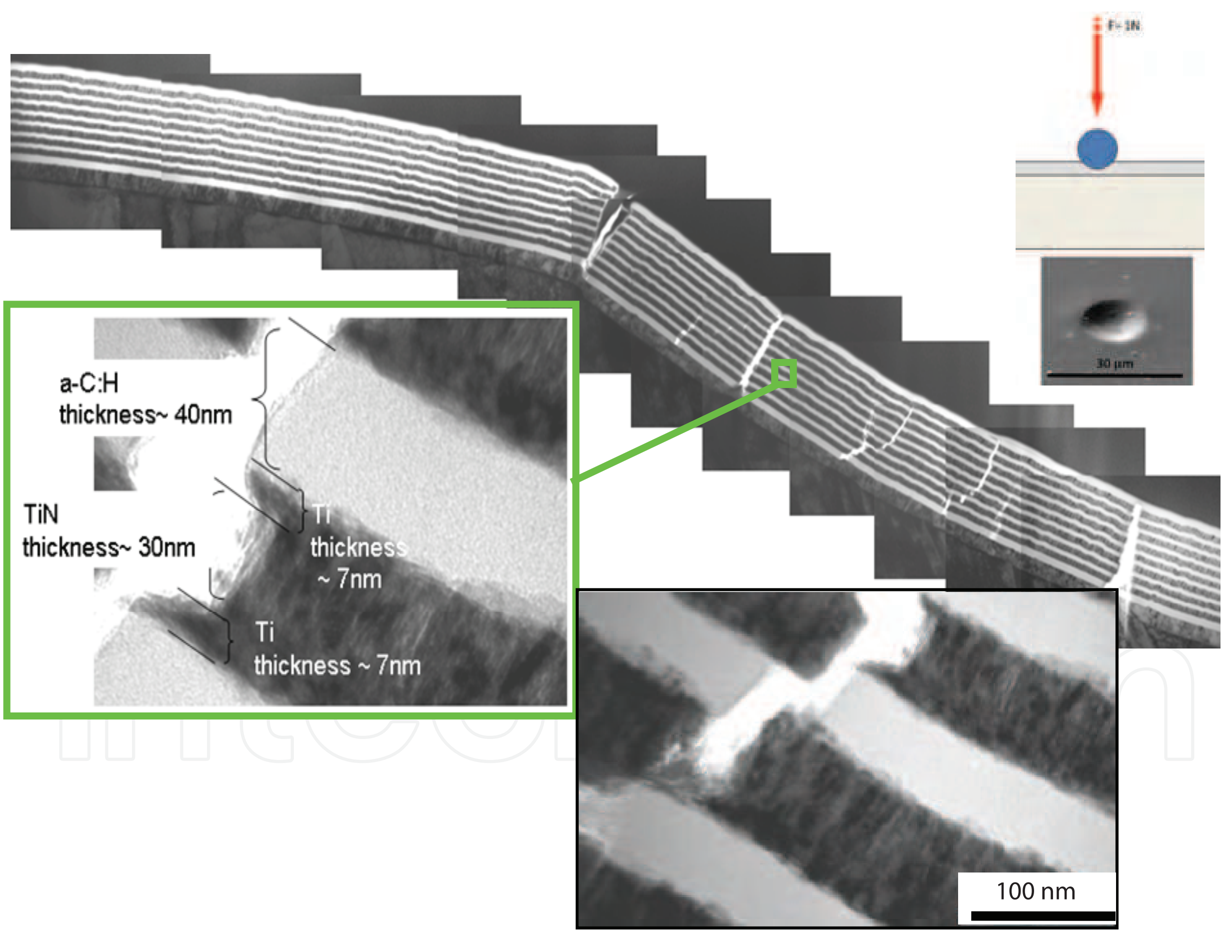

Fig. 16. Microstructure analysis of deformed a-C:H/TiN multilayer coating; a). topography of the coating after the done by SEM technique; b). bright filed analysis of deformed coating at the cross-section by TEM technique.

The presence of thin metallic layers at interfaces and their important role in damage process of described multilayer system was confirmed by bright field and high resolution TEM analysis (Fig. 17).

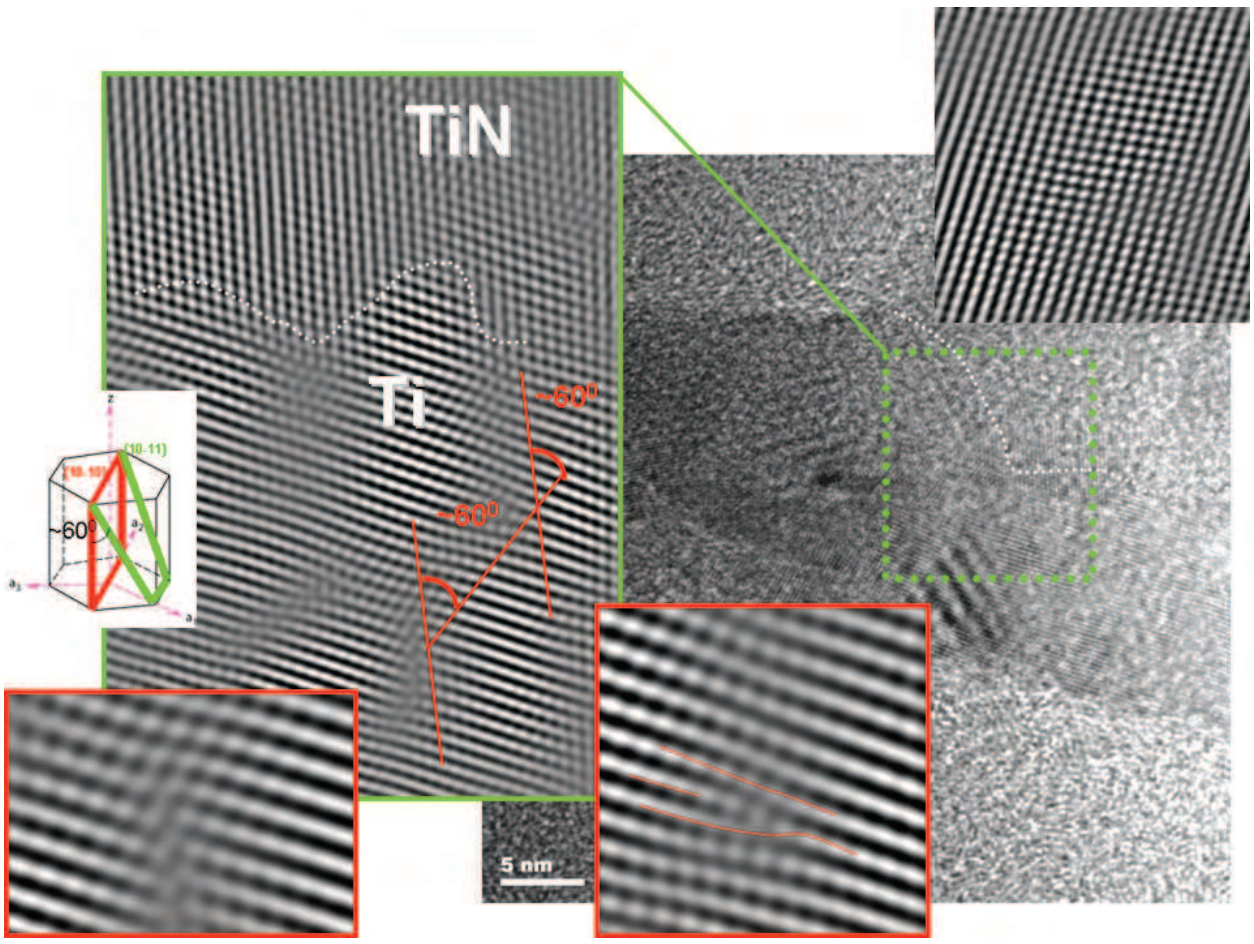

Fig. 17. Microstructure analysis of deformed TiN/Ti/a-C:H multilayer coating by high resolution technique.

Ceramic TiN, as well as a-C:H layers brittle cracked while very thin metallic layers plastically deformed. Plastic deformation propagated at 45^0 to crystals growth. The presence of plastically deformed Ti layers at interfaces as well as presence of Ti buffer layer (first layer from the substrate) play an important role in a damage process control. In zones where the impact of the external force was big, cracks were formed perpendicular to the substrate (normal behavior of brittle coatings), while in areas where the load was lower the deformation lines formed at 45^0 (Fig. 16). The multilayer TiN/Ti/a-C:H type coating may help diverting perpendicular cracks to tilted cracks without losing much of coating hardness and get some control over the coating damage. HRTEM analysis of the individual Ti crystallites visualized the presence of crystallographic planes on which deformation was realized (Fig. 17).

Titanium is characterized by hexagonal structure. The most probable planes for plastic deformation for hexagonal metals is: {10-10}, {10-11} and {0001}. The angle in between {10-10} and {10-11} is 60^0. Filtrated HRTEM image (after twin-oval-mask application on the fast fourier transform) exhibited blurred lines in the area of individual Ti crystallite. The lines formed angle of ~60^0. It informed which crystallographic planes were the most responsible for plastic deformation of titanium. Fourier masking can remove unwanted noise or enhance periodic elements of an image. The typical sequence for using masking is to perform a Fourier transform on a real- space image, mask off the desired frequencies in frequency space, and finally perform an inverse Fourier transform on the masked image (DigitalMicrograph, 1996-2003).

4. Summary

The as deposited single layered TiN and multilayered Ti/TiN coatings were characterized by columnar microstructure and high dislocation density. Carbon phase as single layered coating as well as in multilayer TiN/Ti/a-C:H system was amorphous. Coatings after mechanical tests were strongly deformed i. e. showed presence of cracks. In Ti/TiN multilayer system under the applied load characteristic deformation lines appeared. Deformation line consisted of plastic deformation in metallic layers and brittle cracks in ceramic layers. Deformation occurred at 45^0 to crystals growth. It is a typical angle for plastic deformation of metallic, multi- crystalline materials. Cracking in crystalline layers (TiN) were propagating along the most packed {111} planes. In the case of TiN/Ti/a-C:H multilayer system ceramic TiN and a-C:H layers were cracked, metallic Ti layers, presented at each interface, deformed plastically. The presence of metallic phase lead to deviation of direction of small cracks resulting in improving an overall coating cracks resistance.

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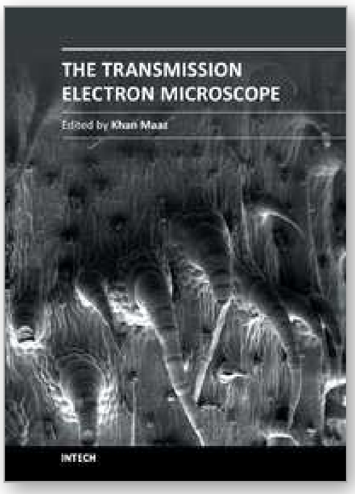

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University Campus STeP Ri
Slavka Krautzeka 83/A
51000 Rijeka, Croatia
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