Archives of Materials Science and Engineering

Volume 63
Issue 2
October 2013
Pages 53-57

International Scientific Journal published monthly by the World Academy of Materials and Manufacturing Engineering

Multiscaled analysis of wear mechanism of titanium and carbon basis multilayer coatings

L. Major [a], J.M. Lackner [b], B. Major [a,*]

[a] Institute of Metallurgy and Materials Science, Polish Academy of Sciences PAN in Cracow, ul. W. Reymonta 25, 30-059 Kraków, Poland

[b] Joanneum Research Forschungs-GmbH, Materials - Functional Surfaces, Leoben, Franz-Pichler-Straße 30, 8160 Weiz, Austria

* Corresponding e-mail address: b.major@imim.pl

Received 04.06.2013; published in revised form 01.10.2013

ABSTRACT

Purpose: The wear mechanisms of Ti/TiN and (TiN/Ti/a-C:H) multilayer coatings were investigated. Coatings were deposited using the hybrid Pulsed Laser Deposition technique (PLD) on austenitic stainless steel. The microstructure investigations were performed with the TECNAI G2 SuperTWIN FEG (200kV) transmission electron microscope. Ceramic TiN and a-C:H layers showed brittle cracking, while very thin metallic Ti layers were deformed plastically. The presence of metallic phase led to the cracking resistance and increased an energetic cost of propagating cracks.

Design/methodology/approach: Ti/TiN and (TiN/Ti/a-C:H) multilayer coatings were deposited on austenitic stainless steel (316L) using the hybrid PLD (Pulsed Laser Deposition + magnetron sputtering) equipped with high purity titanium target (99.9% at. Ti) and carbon target. Microstructure was analyzed on thin foils prepared using the FEI Dual BeamTM FIB system equipped with an Omniprobe lift-out technique. Foils were cut perpendicularly both to coating surface and wear path. The microstructure observations were performed using TECNAI F20 SuperTWIN (200kV) transmission electron microscope.

Findings: The wear mechanism of the multilayer coating was realized through brittle cracking of ceramic layers and plastic deformation of metallic ones.

Research limitations/implications: Optimization of layer thickness and modulation; application of advanced deposition and diagnostic methods.

Practical implications: Switching from mono- to multi-layered coatings allows changing the mechanism of wear from through-coating cracking leading to catastrophic delamination to more gradual layer-by-layer coating removal. The farther wear decrease should be sought at lower multilayer period.

Originality/value: Design and fabrication of Ti/TiN and (TiN/Ti/a-C:H) multilayer coatings revealing an improved behavior in service systems subjected to wearing. Multiscale microstructure diagnostics of multilayer coatings.

Keywords: Multilayer coatings; Microstructure; TEM diagnostics; Wear mechanism

Reference to this paper should be given in the following way:

L. Major, J.M. Lackner, B. Major, Multiscaled analysis of wear mechanism of titanium and carbon basis multilayer coatings, Archives of Materials Science and Engineering 63/2 (2013) 53-57.

METHODOLOGY OF RESEARCH, ANALYSIS AND MODELLING

1. Introduction

Coatings produced by different technologies [1] are more and more frequently used to protect surface of mechanical parts exposed to wear loads [2,3]. The ceramic hard coatings like TiN and DLC are of special interest due to their corrosion resistance and high hardness [1-4]. The success of TiN coatings in extending cutting tools lifetime realized nearly half century ago still keep strong interest in further improvement in this field [5]. Aside from testing different deposition techniques and conditions [1], the progress was seen in elaboration of still harder or more heat resistant coatings realized either with new materials like (Ti,Al)N or (Cr,Si)N or with multilayer TiN/Ti or CrN/Cr coatings [6,7].

Experimenting with multilayer ceramic/metallic coating has been aimed at alleviating the problem of catastrophic delamination of large tool areas during material cutting [8]. Such delamination might be caused by several reason among which as the most important one may name: (i) brittleness of columnar coatings augmented by high stress level introduced during deposition leading to vertical cracking along the crystallites boundaries, (ii) weak adhesion compromised by always present native oxides on steel substrates. Both these reason are closely interrelated, as weak adhesion will strongly contribute to enlargement of cracked area. It has been expected that in the multilayer coatings consisting of alternating ceramic and metallic layers cracks formed at the surface would soon be stopped in next plastically deformed metallic layer. As a result the wear of such multilayer coating would proceed in number of steps corresponding to number of layers and in the effect minimizing the substrate barred area, i.e. the overall wear [9,10].

The above concepts have solid backing in mechanisms of crack propagation in solid matter but generally lack in detail direct experimental verification like transmission electron microscopy (TEM) observations. The previous experiments with monolayer TiN coating helped to confirm only that the through-coating inter-crystallite vertical crackings are a dominating feature in their microstructure even already after their deposition [10,11]. The start of the wear both enlarge and increase number of these vertical cracks as well as opens some inclined to the surface through-crystalline. In effect wear starts in breaking away small pieces from the TiN surface producing “broken-teeth” grove morphology, which is soon dominated by opening the vertical cracks leading to catastrophic coating delamination. The damage of ceramic/ceramic like TiN/CrN or TiN/Ti(C,N) multilayer coatings proceeds by they cracking at the interfaces [11], but there is no similar observations of the ceramic/metallic multilayers. Therefore the aim of the present work was to document the microstructure changes caused in Ti/TiN multilayer coating, i.e. in the wear grove formed during the ball-on-disc test using transmission electron microscopy technique.

The other suggested material for wear resistant coatings is amorphous carbon [2]. The diamond like carbon coatings (DLC or a-C:H) are characterized by very low friction coefficient and biological inertness [4]. There is a tendency to connect the properties of different type of materials in multilayered composition [1,12]. The TiN/Ti/a-C:H multilayer coatings might be applied for pump parts supporting, namely, medical systems. The detailed microstructure description of wear mechanisms in coatings, particularly in multilayer systems are lacking. To enhance the cracking resistance properties of coatings it is a high need to increase an energetic cost of propagating cracks. To do that, the multilayer systems where metallic layers are placed in the sequence with ceramic ones are suggested [10,11]. Deformation lines propagating through the multilayer coating contain plastic deformation in metallic layers and brittle cracking in ceramic ones. Brittle cracking in ceramics may be stopped at the interface. Anyway, there are some sorts of application where it is a need to decrease the metallic phase as much as it is possible. Namely, restrictions are high for tribological coatings used in medicine. They should have high mechanical properties as well as should be bio-compatible. The metallic phase must be limited due to possibilities of metalosis; the metal ions interaction with human organism.

The above concepts have solid backing in mechanisms of crack propagation in solid matter but generally lack in direct experimental verification like transmission electron microscopy observation. The previous experiments with monolayer TiN coating helped to confirm only that the through-coating inter-crystallite vertical cracking are a dominating feature in their microstructure even already after their deposition [10,11]. The start of the wear both enlarge and increase number of these vertical cracks as well as opens some inclined to the surface through-crystalline. In effect wear starts in breaking away small pieces from the TiN surface producing “broken-teeth” grove morphology, which is soon dominated by opening of the vertical cracks leading to catastrophic coating delamination. The damage of ceramic/ceramic like TiN/CrN or TiN/Ti(C,N) multilayer coatings proceeds by they cracking at the interfaces [11], but there is no similar observations of the ceramic/metallic multilayers.

The goal of the presented paper was to describe the microstructure changes of multilayer metal/ceramic and ceramic phase/ceramic phase with very small amount of metallic phase (TiN/Ti/a-C:H) after wear mechanical tests by application of transmission electron microscopy examinations.

2. Experimental

2.1. Ti/TiN multilayer coatings

The Ti/TiN multilayer coatings were deposited on austenitic stainless steel (316L) using alternate reactive and non-reactive magnetron sputtering of a high purity titanium target (99.9 at.% Ti). The deposition system was described in detail elsewhere [13]. The Ti/TiN coating was deposited in a way that first the substrate was covered with a layer of titanium and next TiN of equal thickness. The cycle was repeated four times producing multilayer of Λ=250 nm nominal period.

The wear test of the coating was performed using ball-on-disc test with Al_2O_3 ball under the load of 1N for 2000 cycles. The effect of ball action on coating microstructure was analyzed by cutting thin foils from the wear grove with the FEI Dual Beam™ FIB system equipped with an Omniprobe lift-out technique. The foils were cut perpendicularly both to coating surface and wear path. The microstructure observations were performed using TECNAI F20 SuperTWIN (200kV) transmission electron microscope.

Results

The microstructure observation confirmed that the coating consist of alternating layer of around 120 nm thickness of fine columnar crystallites (Fig. 1). The slightly finer size as well as higher defect density of TiN layers than Ti results in lighter contrast on the latter as separately confirmed by analysis of selected area diffraction patterns (Fig. 2). The observations also showed that the grove formed after multiple passes of the Al_2O_3 ball was partially caused by thinning down of the coating and partially by pushing-in of the substrate (Fig. 1). At the grove side the substrate/coating interface presented a wavy lowering of the profile, while at the grove centre presence of steps of $\Lambda/4$ height was noted. At the same time the coating thickness decreased from 6 to 5 layers at the side and at the center part respectively (Fig. 1). A more detailed investigation of the wear grove center part and especially of the parts of the specimen of smaller thickness proved that TiN layers contain number of separate or multiple vertical cracks, while Ti layers are practically free of them (Figs. 2, 3). The accumulation of cracks usually results in relatively small of up to ~$\Lambda/10$ vertical relocation of blocks of TiN layer, which are only partially absorbed by Ti layer (Fig. 3). The high resolution electron microscopy observations confirmed that the cracks opened in the TiN layers are closed soon after immersing in the Ti layer. The inverse fast Fourier transform of (1,-1,0) and (1,0,1) beams helped to show that in Ti layer close to crack tip defects (as marked with squares) are accumulated to higher extent than in other areas. It confirms that the Ti layers are capable of stopping cracks via-plastic deformation.

a)

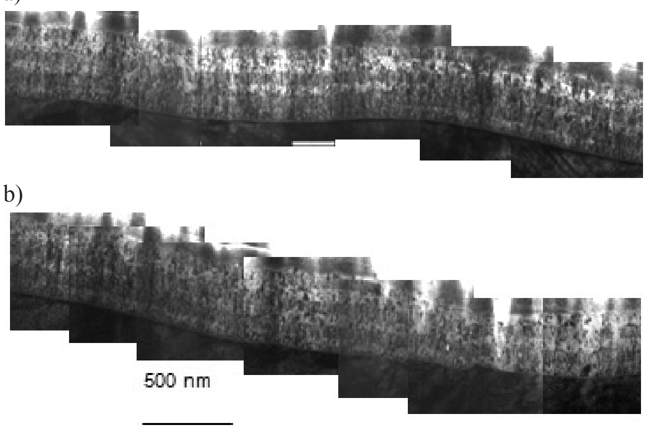

Fig. 1. The low-magnification image of *cross-section* microstructure of the wear track: (a) side and (b) centre

Discussion and concluding remarks on Ti/TiN multilayer coatings

The microstructure observation of the areas below the wear grove indicated, that in present system, i.e. Ti/TiN on stainless steel, the multiple passes of the Al_2O_3 ball results in plastic deformation of the substrate even before coating delamination. The lining of grove with remnants of the coating was realized through brittle and plastic deformation of the TiN and Ti layers, respectively. It is of interest that the plastically deformed Ti layers preserved their thickness from as-deposition stage, i.e. any necking-like behavior was absent. This observation indicates that the fine graining together with some contamination from argon and nitrogen from deposition of Ti layer increased its strength above that of stainless steel substrate.

The cracks observed in TiN were mostly in-between the columnar crystallites. That type of inter-crystalline cracking of the metallic nitride layer like CrN was already proposed as a dominating feature during wear of ceramic - metallic multilayer coatings [8,10]. However, the present experiment proved that for thicknesses of ceramic layers approaching the 100 nm not only the top one like in the discussed model but also those located deeper in the coating are severely cracked. In such situation the so much anticipated change of wear mechanism from the one dominated by "through coating cracking" to "localized cracking" leading to layer-by-layer wear of such coating is compromised in a way that during the wear the newly exposed hard ceramic layers are already weakened by multiple cracks. The above problem, i.e. cracking of the non-exposed to wear layer, could be probably avoided by still lowering of the thickness of the ceramic layer as in that range the TiN layer could easily adjust to such elastic shape deformation [9].

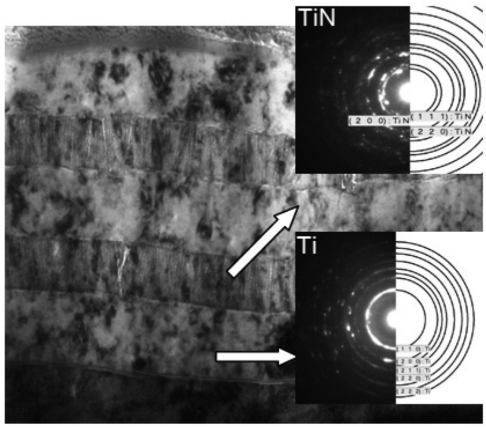

Fig. 2. The higher magnification microstructure of the wear grove centre with the selected area electron diffractions obtain from the TiN and Ti layers

The performed experiment proved that switching from mono- to multi-layer coatings indeed allows to change the mechanism of wear from through-coating cracking leading to catastrophic delamination to more gradual layer-by-layer coating removal. The farther wear decrease should be sought at lower multilayer period.

2.2. TiN/a-C:H multilayer coatings

The hybrid PLD (Pulsed Laser Deposition + magnetron sputtering) equipped with high purity titanium target (99.9% at.Ti) and carbon target were used for multilayer coatings deposition. The details of deposition process is described elsewhere [13]. Analyzed coatings were studied via 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 of the coatings. Thin foils for TEM analysis have been prepared from a section of mechanically deformed place by the Focused Ion Beam technique (FIB).

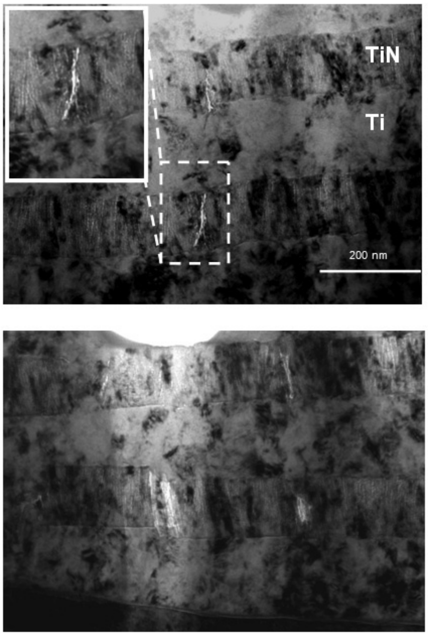

Fig. 3. The microstructure of the TiN layer with: cracks contain within it or forming a step at Ti/TiN interface

Results

In the presented paper two ceramic phases form a multilayer system. To control the damage process of TiN/a-C:H multilayer coatings small amount of metallic phase was inserted into the coating. Metallic Ti buffer layer was deposited as a first layer on the substrate, to increase the adhesion properties of the coating (Figs. 4, 5).

The presence of carbon layers placed in a sequence with TiN ones is evident from the line scan (Fig. 4). Line scan confirmed presence of very thin metallic Ti layers at each a-C:H/TiN interfaces. It is with a good agreement with the deposition process. The presence of thin metallic layers at interfaces and their important role in damage process of described multilayer system was also confirmed by bright field and high resolution TEM analysis which were done after mechanical test (Fig. 5).

TiN ceramic layers as well as a-C:H layers, brittle cracked while very thin metallic layers plastically deformed. Plastic deformation propagated at 45° to crystals growth. 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 control of damage process. In some areas 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° (Fig. 5). The multilayer TiN/Ti/a-C:H system may help diverting perpendicular cracks to angled cracks without losing much of coating hardness and get some control over the coating damage.

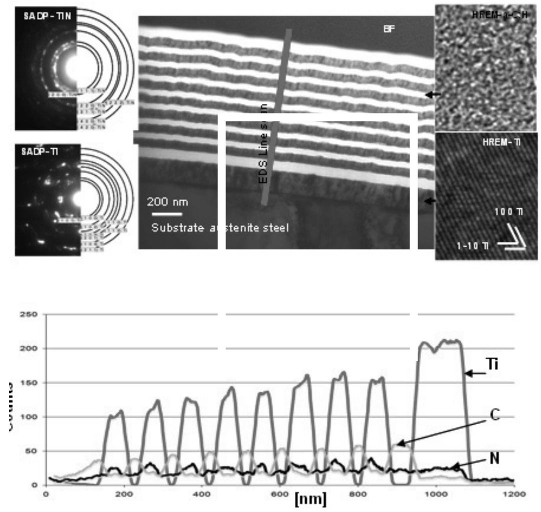

Fig. 4. Image of the a-C:H/TiN multilayer coating done by transmission electron microscopy; bright field image and phase analysis of 8xTiN/Ti/a-C:H coating done by electron diffraction pattern analysis and high resolution; qualitative chemical analysis done by EDS (Energy Dispersive X-ray Spectroscopy) (line- scan along the line marked)

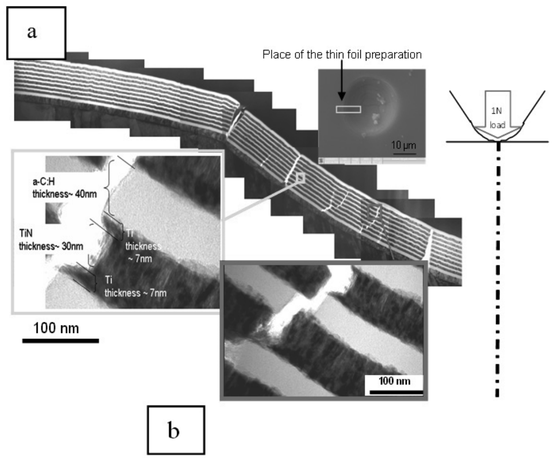

Fig. 5. Microstructure analysis of deformed a-C:H/TiN multilayer coating; topography of the coating done by SEM technique; b) bright filed analysis of deformed coating at the cross-section done by TEM technique

Discussion and concluding remarks on TiN/a-C:H multilayer coatings

As deposited coatings were characterized by crystalline/amorphous multilayer. The TiN layers reveal columnar microstructure and high defects densities (dislocations). The carbon layers were amorphous. Coatings after mechanical tests were strongly deformed i.e. showed presence of cracks. Ceramic TiN and a-C:H layers were cracked. Cracks in crystalline layers (TiN) were propagating along the most packed {111} planes. Metallic Ti layers, presented at each interface, deformed plastically. Deformation was done at 45^o to crystals growth. It is a typical angle for plastic deformation of metallic, multi- crystalline materials. The presence of metallic phase leads to deviation of direction of small cracks resulting in overall coating cracks resistance.

Acknowledgements

Financial support of this work by the Research Project of National Science No: 3066/B/T02/2011/40.

JOANNEUM RESEARCH Forschungsges.m.b.H., Institute for Surface Technologies and Photonics, Functional Surfaces, Austria; for coatings deposition-Polish- Austrian exchange project PL 12/2010-Prof. Jerzy Morgiel for discussion.

References

[1] A.D. Dobrzańska-Danikiewicz, The development perspectives of physical vapour deposition technologies, Journal of Achievements in Materials and Manufactures Engineering 54/1(2012)103-109.

[2] R.F. Bunshah, Handbook of hard coatings, William Andrew Publishing, New Jersey, 2001.

[3] D.S. Rickerby, A. Matthews, Advanced surface coatings; handbook of surface engineering, Chapman and Hall Publishing, New York, 1991.

[4] V. Kumar, A.A. Bergman, A.A. Gorokhovsky, A.M. Zaitsev, Formation of carbon nanofilms on diamond for all-carbon based temperature and chemical sensor application, Carbon 49 (2011) 1385-1394.

[5] A.D. Dobrzańska-Danikiewicz, K. Gołombek, D. Pakuła, J. Mikuła, M. Staszuk, L.W. Żukowska, Long-term development directions of PVD/CVD coatings deposited onto sintered tool materials, Archives of Materials Science and Engineering 49/2 (2011) 69-96.

[6] M. Polok-Rubiniec, L.A. Dobrzański, Comparison of the CrN and TiN/(Ti,Al)N PVD coatings deposited onto plasma nitrided steel, Archives of Materials Science and Engineering 54/2 (2012) 78-85.

[7] Li Chen, S.Q. Wang, S.Z. Zhou, Jia Li, Y.Z. Zhang, Microstructure and mechanical properties of Ti(C,N) and TiN/Ti(C,N) multilayer PVD coatings, International Journal of Refractory Metals and Hard Materials, 26 (2008) 456-460.

[8] M. Stueber, H. Holleck, H. Leiste, K. Seemann, S. Ulrich, C. Ziebert, Concept for the design of advanced nanoscale PVD multilayer protective thin films, Journal of Alloys and Compounds 483 (2009) 321-333.

[9] J.A. Smolik, The wear mechanism of hybrid layer "PN+CrN" during the hot forging process, Journal of Achievements in Materials and Manufactures Engineering 49/2 (2011) 215-223.

[10] Ł. Major, M. Kot, J.M. Lackner, The effect of metallic inter-layers on multilayer ceramic/metal coatings properties, Materials Science 3/175 (2010) 445-448.

[11] Ł. Major, J. Morgiel, TEM analysis of wear of Ti/TiN multi-layer coatings in ball-on-disc test, Key Engineering Materials 409 (2009) 123-127.

[12] L.A. Dobrzański, E. Jonda, K. Labisz, Comparison of the abrasion wear resistance of the laser alloyed hot work tool steels, Archives of Materials Science and Engineering 55/2 (2012) 85-92.

[13] J.M. Lackner, Industrially-scaled hybrid pulsed laser deposition at room temperature, Publishing House Orekop, Cracow, 2005.