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NANOSCALE MODIFICATION OF HARD COATINGS WITH ION IMPLANTATION

NANOVELIKOSTNA MODIFIKACIJA TRDNIH PREKRITIJ Z IONSKO IMPLANTACIJO

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The mechanical properties of new hard coatings based on a multilayer structure have been investigated at the nanometre scale. The multilayer structure consists of a nitrided layer on a steel substrate and a hard coating deposited by Physical Vapor Deposition and Ion Beam Assisted Deposition. In the present investigation the subsequent ion implantation was provided by $N2^+$ ions. This paper describes the use of the nano-indentation technique for a determination of the hardness and elastic modulus. The results are analyzed in terms of load-displacement curves, hardness, Young's modulus, unloading stiffness and elastic recovery. The analysis of the indents was performed with an Atomic Force Microscope. The analyzed AE signal was obtained by a scratch test designed for adherence evaluation. The coating is often in tensile stress with greater microhardness. The stress determination follows the conventional $\sin^2 \psi$ method, using an X-ray diffractometer. A variety of analytic techniques were used for the characterization, such as a scratch test, calo test, SEM, AFM, XRD and EDAX for engineering applications. The experimental results indicated that the mechanical hardness is elevated by the penetration of nitrogen, whereas the Young's modulus is significantly elevated.

Keywords: coatings, ion implantation, microstructure, adhesion, nanohardness

Mehanske lastnosti novih prekritij na podlagi večplastne strukture so bile raziskane v merilu nanometra. Večplastna struktura sestoji iz nitridne plasti na podlagi iz jekla, trdo prekritje pa je naneseno s fizikalnim nanosom par in nanosom z ionskim curkom. Uporabljena je tudi ionska implantacija z N_2-ioni. Opisana je uporaba nanoindentacije za določitev trdote in elestičnega modula. Rezultati so analizirani z upoštevanjem odvisnosti obremenitev – deformacija, trdote, Youngovega modula, razbremenitvene togosti in elastične poprave. Analiza indentacij je bila izvršena z mikroskopom na atomsko silo. Analizirani AE-signal je bil dobljen s preizkusom razenja, namenjen za določanje oprijetosti. V prekritju so pogosto natezne napetosti,,ima pa tudi veliko mikrotrdoto. Določitev napetosti je bila izvršena z metodo $\sin^2 \psi$ in uporabo rentgenskega difraktometra. Za karakerizacijo je bila uporabljana vrsta analitičnih tehnik, kot so preizkus razenja, calo-preizkus, SEM, AFM, XRD in EDAX za inženirsko uporabo. Eksperimentalni rezultati kažejo, da se mehanska trdota povečuje s penetracijo dušika, pri čemer je Youngov modul pomembno povečan.

Ključne besede: prekritje, ionska implantacija, mikrostruktura, oprijetost, nanotrdota

1 INTRODUCTION

The film-deposition process exerts a number of effects such as crystallographic orientation, morphology, topography, densification of the films. The optimization procedure for coated parts could be more effective, knowing more about the fundamental physical and mechanical properties of a coating. In this research we present the results of a study of the relationship between the process, composition, microstructure and nanohardness.

A duplex surface treatment involves the sequential application of two surface technologies to produce a surface composition with combined properties.[1] A typical duplex process involves plasma nitriding and a coating treatment of materials. In the paper we present the characteristics of hard coatings deposited by PVD (physical vapour deposition) and IBAD (ion beam assisted deposition). The synthesis of the TiN film by IBAD has been performed by the irradiation of Ar ions. Subsequent ion implantation was provided with N^{5+} ions. Ion implantation has the the capabilities of producing new compositions and structures unattainable by conventional means. Implantation may result in changes in the surface properties of a material.

Thin hard coatings deposited by physical vapour deposition (PVD), e.g., titanium nitride (TiN), are frequently used to improve tribological performance in many engineering applications.[2,3] In many cases a single coating cannot solve the wear problems.[4]

Conventional TiN and correspondingly alloyed systems show high hardness and good adhesion strength. However, these coatings have poor cracking resistance, especially in high-speed machining. The duplex surface treatment was used to enhance the adhesion strength and hardness of hard coatings.

In the nano-indentation technique, hardness and Young's modulus can be determined by the Oliver and Pharr method, where hardness (H) can be defined as: $H = P_{max}/A$, where P_{max} is the maximum applied load, and A is the contact area at maximum load.

In nano-indentation, the Young's Modulus, E, can be obtained from:

$$\frac{1}{E_r} = \frac{1-\nu^2}{E} + \frac{1-\nu_i^2}{E_i}$$

where v_i = Poisson ratio of the diamond indenter (0.07) and E_i = Young's modulus of the diamond indenter.

This paper describes the use of the nano-indentation technique for a determination of the hardness and elastic modulus. The depth of nanopenetration provides an indirect measure of the area of contact at full load and thus the hardness is obtained by dividing the maximum applied load with the contact area.[5]

2 EXPERIMENTAL

The substrate material used was high-speed steel type M2. Prior to deposition the substrate was mechanically polished to a surface roughness of 0.12 μm (R_a). The specimens were first austenized, quenched and then tempered to the final hardness of 850 HV. In order to produce good adhesion of the coating, the substrates were plasma nitrided at low pressure (1×10^{-3} Pa), prior to deposition of the coating. The PVD treatment was performed in a Balzers Sputron installation with a rotating specimen. The deposition parameters were as follows: Base pressure in the chamber was 1×10^{-5} mbar. During etching, the bias voltage was U_b = 1 kV and the current was I_d = 50 mA. During deposition the substrate temperature was T_s = 200 °C, the partial pressure of Ar was $P_{Ar} = 1 \times 10^{-3}$ mbar and the partial pressure of N_2 was $P_{N2} = 3 \times 10^{-4}$ mbar. Prior to entering the deposition chamber the substrates were cleaned.

The IBAD system consists of an e-beam evaporation source for evaporating Ti metal and 5-cm-diameter Kaufman ion source for providing argon ion beam. The base pressure in the IBAD chamber was 1×10^{-6} mbar. The partial pressure of Ar during deposition was $(3.1–6.6) \times 10^{-6}$ mbar and partial pressure of N_2 was $6.0 \times 10^{-6}–1.1 \times 10^{-5}$ mbar. The ion energy (E_{Ar} = 1.5–2 keV), ion beam incident angle (15°), and substrate temperature T_s = 200 °C, were chosen as the processing variables. The deposition rate was a_D = 0.05–0.25 nm/s. A quartz crystal monitor was used to gauge the approximate thickness of the film. After deposition, the samples were irradiated with 120 keV, N^{5+} ions at room temperature (RT). The Ion Source is a multiply charged heavy-ion injector, based on the electron cyclotron resonance effect (ECR). The implanted fluencies (ions) were in the range from 0.6×10^{17} to 1×10^{17} cm^{-2}.

A pure titanium intermediate layer with a thickness of about 50 nm was deposited first for all the coatings to enhance the interfacial adhesion to the substrates.

The mechanical properties on the coated samples were characterized using a Nanohardness Tester (NHT) developed by CSM Instruments. Nano-indentation testing was carried out with applied loads in the range of 10 mN to 20 mN. A Berkovich diamond indenter was used for all the measurements. The data was processed using proprietary software to produce load–displacement curves and the mechanical properties were calculated using the Oliver and Pharr method.

The scratch adhesion testing was performed using commercially available equipment (REVETEST CSEM) fitted with a Rockwell C diamond stylus (cone apex angle of 120 °C, tip radius 200 μm). Acoustic Emission (AE) is an important tool for the detection and characterization of failures in the framework of non-destructive testing. The analyzed AE signal was obtained by a scratching test designed for adherence evaluation. The detection of elastic waves generated as a result of the formation and propagation of micro-cracks.

X-ray diffraction studies were undertaken in an attempt to determine the phases present, and perhaps an estimate of the grain size from line broadening. The determination of phases was realized by X-ray diffraction using a PHILIPS APD 1700 X-ray diffractometer. The X-ray sources were from Cu$K\alpha$ with a wavelength of 15.443 nm (40 kV, 40 mA) at a speed of 0.9°/min. The surface roughness was measured using stylus-type (Talysurf Taylor Hobson) instruments. The most popular experimental XRD approach to the evaluation of residual stresses in polycrystalline materials is the $\sin^2 \psi$ method. The method requires a $\theta–2\theta$ scan for every ψ angle around the selected diffraction peak, in order to emphasize the peak shifts.

3 RESULTS

The nitrogen-to-metal ratio (EDX) is stoichiometric for the IBAD technology and something smaller from the PVD (0.98). For the sample with additional ion implan-

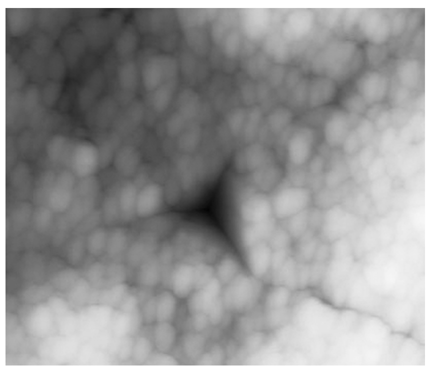

Figure 1: AFM image of crack paths from nano-indentation
Slika 1: AFM-posnetek smeri razpok pri nanoindentaciji

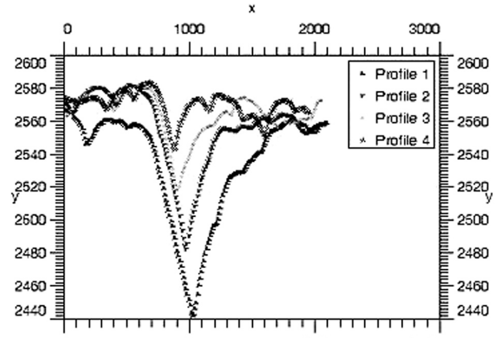

Figure 2: Cross-section of the indentation
Slika 2: Prerez nanoindentacije

tation, the value is significantly smaller (0.89). It is possibly diffused from the layer of the TiN to the interface.

All the results of the nanohardness are obtained with the Oliver & Pharr method and using a supposed sample Poisson's ratio of 0.3 for the modulus calculation The analysis of the indents was performed with an Atomic Force Microscope (**Figure 1**).

It can be seen, from the cross-section of an indent during indentation, that the indents are regularly shaped with slightly concave edges tipically seen where there is a significant degree of elastic recovery (**Figure 2**).

The nanohardness values and the microhardness are shown in **Table 1**.

Table 1: Surface nanohardness (load-10mN)
Tabela 1: Nanotrdota površine (breme 10 mN)

Unit	pn/IBAD	PVD	pn/PVD/II
GPa	21.6	32.6	42.6

For each adhesion measurement, the penetration (P_d), the residual penetration (R_d), the acoustic emission (AE) and the frictional force are recorded versus the normal load. The breakdown of the coatings was determined both by AE signal analysis and scanning electron microscopy. AE permits an earlier detection, because the shear stress is a maximum at a certain depth beneath the surface, where a subsurface crack starts. The critical loads are presented in **Table 2**.

Table 2: Critical loads for different type of coatings.
Tabela 2: Kritično breme za prekritja različne vrste

	pn/TiN(IBAD)	pn/TiN(PVD)
L_{c1}	–	23
L_{c2}	100	54
L_{c3}	138	108

The critical load L_{c1} corresponds to the load inducing the first crack on the coating. No cracks were observed on sample 1. The critical load L_{c2} corresponds to the load

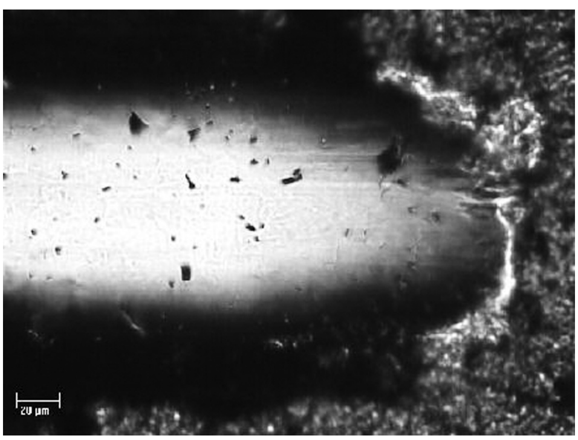

Figure 3: Delamination of coating
Slika 3: Luščenje prekritja

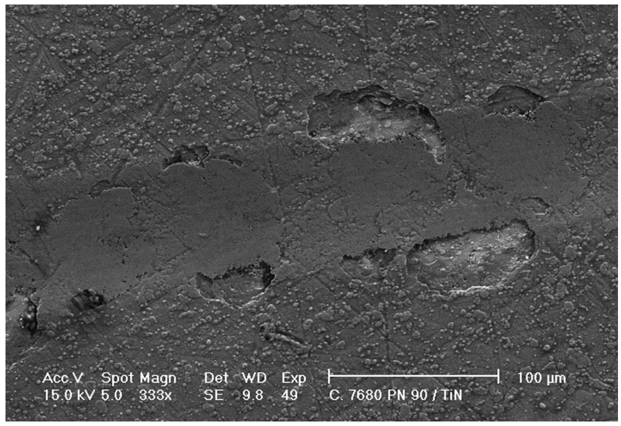

Figure 4: SEM morphology of scratch test pn/TiN(PVD).
Slika 4: SEM-morfologija preizkusa razenja pri pn/TiN (PVD)

inducing the partial delamination of the coating. The critical load L_{c3} corresponds to the load inducing the full delamination of the coating. In some places of hard coatings the cohesive failure of the coating and the delamination of the coating were observed (**Figure 3**).

It was found that the plasma-nitriding process enhanced the coating-to-substrate adhesion. In some places of the hard coatings cohesive failure of the coating and the delamination of the coating were observed (**Figure 4**).

The width of the column, for plane (422) is derived from the width of the diffraction peaks (Scherrer formula: $t = 0.9\ \lambda/(\beta \cos \theta/\lambda \cos \theta)$) of TiN, ($\beta = 0.154$ nm, $\theta = 62.5°$ and $\beta = 0.056$ rad), and it is 70 nm. Because of the low deposition temperature, it is possible that other planes also have a small width of the columns.

The stress determination follows the conventional $\sin^2 \psi$ method. The stress determination was performed using a PHILIPS XPert diffractometer. The (422) diffraction peak was recorded in a 2θ interval between 118° and 130°, with tilting angle: $\psi_o^1 = 0°$, $\psi_o^2 = 18.75°$, $\psi_o^3 = 27.03°$, $\psi_o^4 = 33.83°$, $\psi_o^5 = 40°$. A typical result for the compact film, with residual stresses $\sigma = –4.28$ GPa, was TiN(PVD).

4 DISCUSSION

A hardness increase is observed for implanted samples. This can be attributed to iron nitride formation in the near-surface regions. The standard deviation of the results is relatively important due to the surface roughness of the samples. Because the thickness of the TiN coatings presented here is sufficiently large, which for all coatings is about 2900 nm (TiN-PVD), the hardness measurements will not be affected by the substrate, as in the three-times thinner (900 nm TiN-IBAD).

The individual values of E are different for all the measurements. The errors related to the measurements and estimations were different and for duplex coating with ion implantation they are less than 4 %. Good

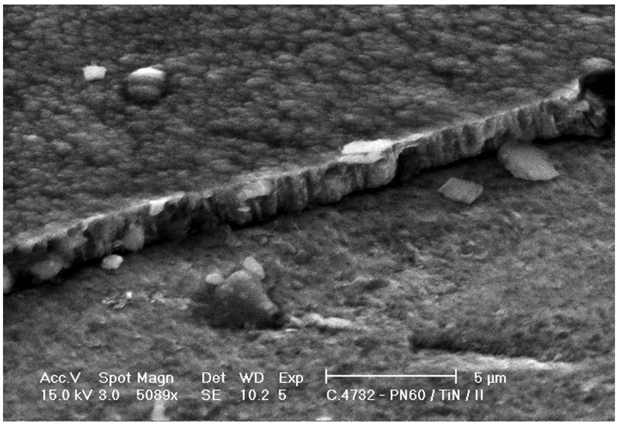

Figure 5: Surface morphology of duplex coating with ion implantation
Slika 5: Morfologija površine dupleksnega prekritja z ionsko implantacijo

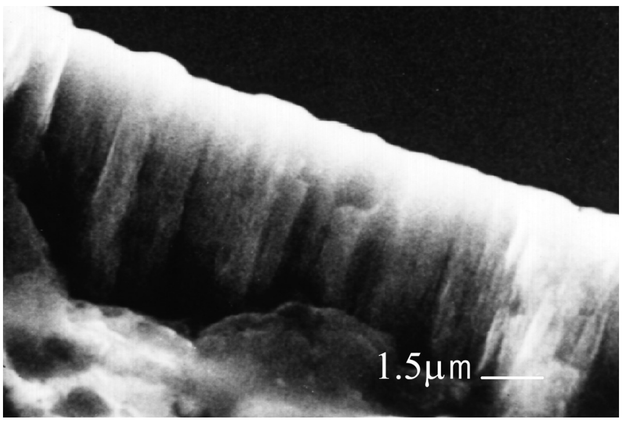

Figure 6: SEM of coating cross-section TiN (PVD)
Slika 6: SEM-prereza prekritja TiN (PVD)

agreement could be achieved between the E_c values and the nanohardness.

The topography of the TiN coatings was investigated using SEM (**Figure 5**).

The PVD coating process did not significantly change the roughness. For practical applications of IBAD coatings it is important to know that the roughness of the surface decreased slightly after the deposition (from R_a = 0.19 µm to R_a = 0.12 µm).

The formation of TiN by IBAD has its origin in a kinetically controlled growth. The nitrogen atoms occupy the octahedral sites in varying numbers according to the energy that these atoms possess to cross the potential barriers created by the surrounding titanium anions. The ion bombardment is believed to enhance the mobility of the atoms on the sample surface. The XRD analysis revealed the presence of only one phase, δ-TiN, and no evidence for other phases, such as Ti_2N, could be found. The ε-Ti_2N does not lead to an improvement in the tribological behavior.

The coating morphology was evaluated using the well-known structure zone model of Thornton. All the observed morphologies, **Figure 6**, are believed to be from a region of zone I (PVD) and from the border of region zone T (IBAD).

It has been suggested[5] that the transition from an open porous coatings with a low microhardness and rough surface, often in tensile stress to dense coating films with a greater microhardness, a smooth surface occurs at a well defined critical energy delivered to the growing film.

5 CONCLUSIONS

The experimental results indicated that the mechanical hardness is elevated by the penetration of nitrogen, whereas the Young's modulus is significantly elevated. Nitrogen-ion implantation leads to the formation of a highly wear resistant and hard surface layer.

Nitrogen implantation into hard TiN coatings increases the surface hardness and significantly reduces the tendency of the coatings to form microcracks when subjected to loads or stresses.

The above findings show that the deposition process and the resulting coating properties depend strongly on the additional ion bombardment.

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