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CHARACTERIZATION OF DUPLEX HARD COATINGS WITH ADDITIONAL ION IMPLANTATION

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Preliminary Note – Prethodno priopćenje

In this paper, we present the results of a study of TiN thin films which are deposited by a Physical Vapour Deposition (PVD) and Ion Beam Assisted Deposition (IBAD). In the present investigation the subsequent ion implantation was provided with N^{2+} ions. The ion implantation was applied to enhance the mechanical properties of surface. The thin film deposition process exerts a number of effects such as crystallographic orientation, morphology, topography, densification of the films. The evolution of the microstructure from porous and columnar grains to densel packed grains is accompanied by changes in mechanical and physical properties. A variety of analytic techniques were used for characterization, such as scratch test, calo test, Scanning electron microscopy (SEM), Atomic Force Microscope (AFM), X-ray diffraction (XRD) and Energy Dispersive X-ray analysis (EDAX).

Key words: steel, coating, super hard, ion implantation, nanohardness

Karakterizacija dupleks tvrdih prevlaka sa dodatnom ionskom primjenom. U ovom radu pretstavljaju se rezultati istraživanja TiN tankih filmova, nanešenih fizičkim odlaganjem iz parne faze i te podržani ionskim snopom. U ovom istraživanju je izvršena i naknadna ionska primjena sa N^{2+} ionima. Ionska primjena je sprovedena radi poboljšanja mehaničkih svojstava površina. Proces nanošenja tankih filmova karakterizira veliki broj učinaka, kao što su: kristalografska orijentacija, morfologija, topografija, gustoća filma. Razvoj mikrostrukture od porozne i stubaste u zrnastu gusto pakovanu, se dešava uz istovremenu promjenu mehaničkih i fizičkih svojstava. Za karakterizaciju su rabljene različite analitičke tehnike, kao što su test zaparavanja, kalo test, skenirajući elektronski mikroskop (SEM), mikroskop atomskih sila (AFM), rentgenska difrakcija X zraka (XRD) i energijska disperzivna analiza X zraka (EDAX).

Ključne riječi: čelik, prevlake, supertvrdoća, ionska primjena, nanotvrdoća

INTRODUCTION

The various deposition techniques of coatings and process parameters differ widely in morphology and microstructure, in phases, grain size, texture, defects, impurity content, state of stress, and their mechanical and tribological properties.

Ion bombardment during physical vapour deposition (IBAD) has more independent parameters than classic plasma based technique (PVD). The film deposition process exerts a number of effects such as crystallographic orientation, morphology, topography, densification of the films [1].

However, the adhesion, structure and durability of coatings on various substrates can

be substantially improved by irradiating the substrates and the condensing film with ions and energetic neutrals in the energy range of several electron volts [2]. One of the most widely used physical vapour deposited coatings for engineering components is TiN.

The adhesion strength transmits the surface loads into the component and takes up the stresses that arise because of the different properties of coating and substrate. The nitrided layers are a key issue in duplex coating processing [3]. IBAD, can be used to control the preferred orientation and the properties of the TiN film. IBAD has more independent parameters than a PVD technique and it is possible to study the effect of deposition parameters on the structure of grown films.

The tribological performance of a component is governed by its design, environment, contact conditions and the materials of which it is composed [4]. The adhesion strength transmits the surface loads into the component and takes up the stresses that arise because of the different properties of coating and substrate. The three basic points that are considered fundamental to studies of friction are the surface area and nature of the intimate asperity contacts, the surface adhesion and shear strength, and the nature of deformation and energy dissipation occurring at the asperity junctions [5].

Characteristics of surface layer structure as well as important properties were investigated. A variety of analytic techniques were used for characterization, such as scratch test, calo test, SEM, AFM, XRD and EDAX.

EXPERIMENTAL PROCEDURE

The substrate material used was high speed steel type S 6-5-2. High-speed steel's microstructure consists

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of large primary carbide particles, disappeared in tempered martensitic matrix containing a much finer dispersion of secondary carbides.

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. The used sputtering system allowed an ultimate pressure of about 5Pa.

The PVD treatment was performed in a Balzers Sputron installation with rotating specimen. The deposition parameters were as follows: Base pressure in the chamber was 1×10^{-5} mbar, bias voltage U_b=1kV, discharge current I_d=50mA, substrate temperature T_s=200 °C, target to substrate distance d_s–t=120 mm. The partial pressure of Ar during deposition was $P_{Ar}=(3,1–6,6)\times10^{-6}$ mbar and partial pressure of N_2 was $P_{N2}=6,0\times10^{-6}$–$1,1\times10^{-5}$ mbar. Deposition rate a_D=0,1 nm/s. Prior to entering the deposition chamber the substrates were cleaned. The coatings (IBAD), were deposited with ion beam bombardment in a DANFYSIC chamber. The base pressure in the vacuum chamber was 10^{-4} Pa for all experiments. System has Kaufman-type ion source, sample holder and quartz crystal thickness monitor. A pure titanium intermediate layer with a thickness of about 50nm has been deposited first for all the coatings to enhance the interfacial adhesion to the substrates. The ion energy (E_{Ar}=1,5–2 keV), ion beam incident angle (15°), target to substrate distance d_s–t=360 mm, and substrate temperature T_s=200 °C, were chosen as the processing variables. Deposition rate a_D=0,05–0,25 nm/s. Quartz crystal monitor was used to gauge the approximate thickness of the film. After deposition, the samples were irradiated with 120 keV N^{2+} ions at room temperature (RT). N^{2+} ions were supplied by an electron cyclotron resonance (ECR) ion source. The implanted fluencies were in the range from $0,6\times10^{17}$ to 1×10^{17} ions/cm^2

The mechanical properties on coated samples were characterized using a Nanohardness Tester (NHT) developed by CSM Instruments. The NHT is especially suited to load and penetration depth measurements at nanometer length scales. The maximum indentation depth was fixed at one tenth of the coating thickness.

The analyzed AE signal was obtained by a scratching test designed for adherence evaluation. Acoustic Emission (AE) is an important tool for the detection and characterisation of failures in the framework of non-destructive testing. The analysed AE signal was obtained by a scratching test designed for adherence evaluation. Scratch tests were performed under controlled conditions with a device that consisted of a loaded probe with a diamond indenter moving linearly along the sample with a constant speed and continuously increasing force. The steadily increasing contact load causes tensile stress behind the indenter tip and compressive stress ahead of the cutting tip. Detection of elastic waves generated as a result of the formation and propagation of micro cracks. The AE sensor is insensitive to mechanical vibration frequencies of the instrument. This enables the force fluctuations along the scratch length to be followed, and the friction coefficient to be measured. The scratch tester equipment with an acoustic sensor (CSM-REVETEST) was used.

The stress determination follows the conventional $\sin^2\psi$ method, using a PHILIPS XPert diffractometer.

In the nanoindentation technique, hardness and Young's modulus can be determined by the Oliver and Pharr method [6], where hardness (H) can be defined as: $H=P_{max}/A$, where P_{max} is maximum applied load, and A is contact area at maximum load. In nanoindentation, the Young's Modulus, E, can be obtained from: $1/E_r=(1-\nu^2)/E+(1-\nu^2)/E_r$, where ν_i=Poisson ratio of the diamond indenter (0.07) and Ei=Young's modulus of the diamond indenter. Therefore, in recent years, a number of measurements have been made in which nanoindentation and AFM have been combined. Indentation was performed with CSM Nanohardness Tester. 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 by Atomic Force Microscope. The stress determination follows the conventional $\sin^2\psi$ method, using an X-ray diffractometer.

RESULTS AND ANALYSIS

The analyzed nitrogen-to-metal ratio of the deposited films, with EDAX, is given in the Table 1.

The nitrogen to metal ratio, EDX, is stoichiometries for IBAD technology and something smaller from PVD. For sample with additional ion implantation, value is significantly different, smaller.

Table 1 **Atomic ratio N/Ti in coating**

	Coating	Ratio N/Ti (atomic)
1	IBAD	1,00
2	PVD	0,98
3	PVD/III	0,89

It is possibly diffused from the layer of TiN to the interface. The TiN coatings only show a golden surface and after ion implantation the colour is dark golden.

Vickers microhardness and nanohardness measurements of samples are given in Table 2.

Table 2 **Surface microhardness ($HV_{0.03}$) and nanohardness (load-10mN).**

	Unit	pn/IBAD	PVD	pn/PVD/II
Av.	Vickers	2 007	3 028	3 927
Av.	GPa	21,6	32,6	42,6

The maximum nanohardness of coating measured by Berkovich indenter is about 42,6 GPa. All the results of nanohardness are obtained with the Oliver & Pharr method and using a supposed sample Poisson's ratio of 0,3 for modulus calculation. A hardness increase is observed for implanted samples. This can be attributed to iron nitride formation in the near surface regions.

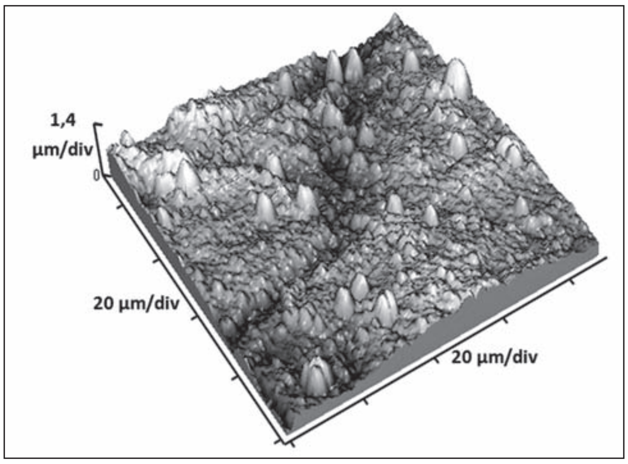

Figure 1 AFM image of a TiN coating implanted with nitrogen

Typical surface image measured by AFM (Veeco dc II) is presented on Figure 1.

For the practical applications of IBAD coatings, it is important to know that the roughness of the surface decreased slightly after deposition (from Ra=0,19 μm to Ra=0,12 μm).

The nanoindentation elastic modulus was calculated using the Oliver–Pharr data analysis procedure. The individual values of E are the different for all measurements, Figure 2.

The errors related to the measurements and estimations were different and for duplex coating with ion implantation is less than 4 %. Good agreement could be achieved between the E_c values and nanohardness.

For each measurement, the penetration (Pd), the residual penetration (Rd), 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 optical and scanning electron microscopy. AE permits an earlier detection, because the shear stress is a maximum at certain depth beneath the surface, where a subsurface crack starts. The critical load Lc3 corresponds to the load inducing the delamination of the coating, Figure 3.

Coating is often in tensile stress with greater microhardness. During TiN film growth, titanium atoms are firstly piled, as compact as possible, depending on the local conditions. The nitrogen atoms occupy the octahedric sites in varying number according to the energy

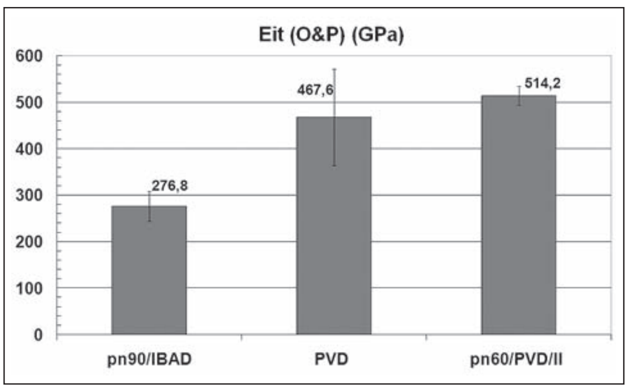

Figure 2 Young's elastic module.

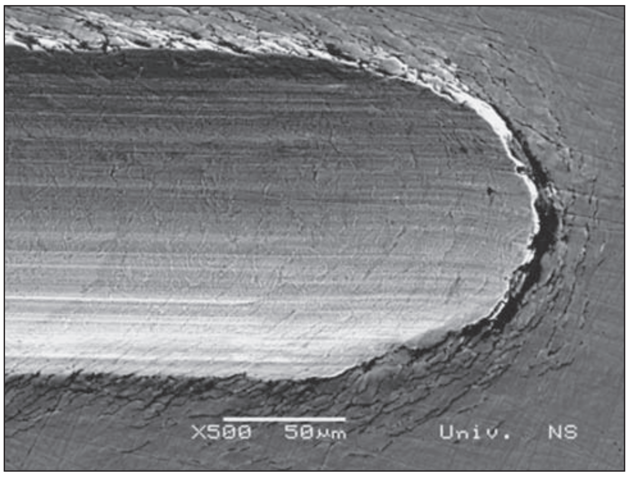

Figure 3 Delamination of coating

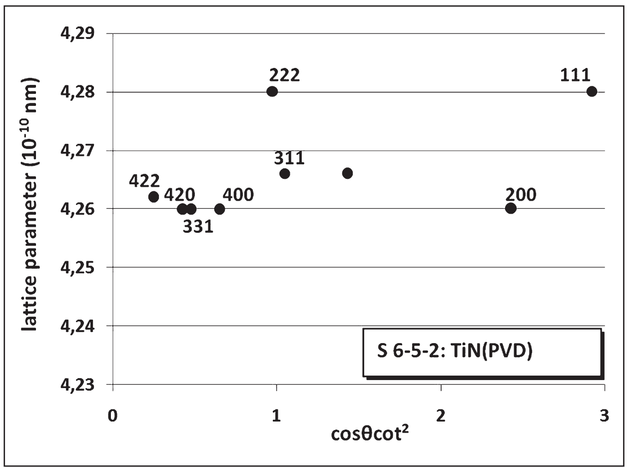

Figure 4 The Cohen-Wagner plot, lattice parameters a_{hkl} vs.cosθcot²θ.

that these atoms possess to cross the potential barriers created by the surrounding titanium anions.

The tribological behaviour of the coatings was studied also by means of pin-on-ring contact configuration in dry sliding conditions, described elsewhere [7].

The simplest form of X-ray diffraction (XRD) characterization of thin film microstructure is Cohen-Wagner plot. A typical result for compact film, with residual stresses σ = -4,28Gpa, is shown in Figure 4.

The anisotropy of lattice parameters, a_{hhh}>>a_{hoo}, is characteristic for compact film.

The width of column is derived from the width of the diffraction peaks (Figure 5), (λ=0,154nm, θ=62.5° and β=0,056rad), and it is 70 nm.

The (422) diffraction peak was recorded in a 2θ interval between 118° and 130°, with tilting angle. It is observed an increase in micro hardness with the (200) orientation degree [8]. These results are in agreement with those obtained in other paper [9]. The coating morphology was evaluated using the well-known structure zone model of Thornton. All observed morphologies are believed to be from region of zone I (PVD) and from the border of region zone T (IBAD). It has been suggested [10], that the transition from open porous coatings with low micro hardness and rough surface, often in tensile stress, to dense coatings films with greater micro hard-

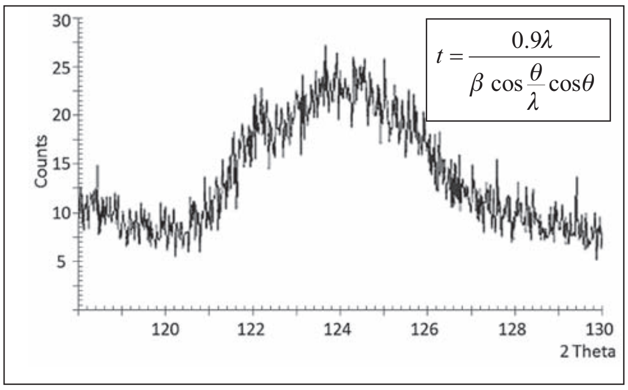

Figure 5 XRD diffraction peak of TiN(422)

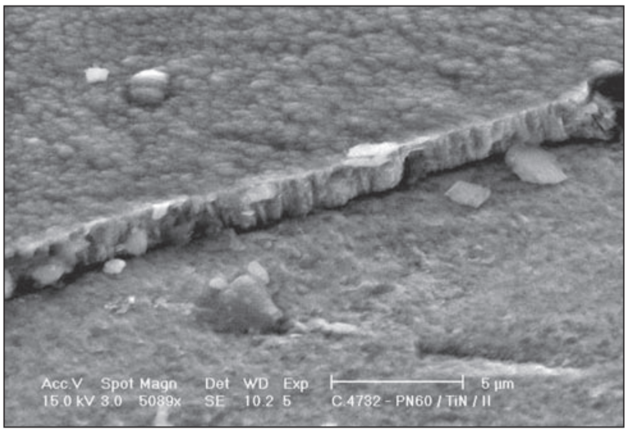

Figure 6 Surface morphologies of TiN(PVD) implanted with nitrogen

ness, smooth surface occures at a well defined critical energy delivered to the growing film. The microstructure of the TiN film, Figure 6, shows a columnar structure reaching from the substrate to the coating surface.

The specimen for these investigation was broken and the fracture surfaces were inspected.

CONCLUSIONS

Deposition of TiN on plasma nitrided steel by IBAD process was successfully used to produce a hard surface. It was found that the plasma-nitriding process enhanced the coating to substrates adhesion.

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

Coatings developed under this project should demonstrate performance that exceeds that of PVD coatings.

Nitrogen implantation into hard TiN coatings significantly reduces the tendency of the coatings to form micro cracks when subjected to loads or stresses.

The present coating method can produce dance structures and the high critical load values can be achieved.

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

Acknowledgments

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Note: The responsible translator for the English language is Pal Terek, University of Novi Sad, Serbia