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NANO CHARACTERIZATION OF HARD COATINGS WITH ADITIONAL ION IMPLANTATION

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Abstract: *In the paper are presented characteristics of hard coatings, type TiN, produced by classic technology PVD (physical vapour deposition) and IBAD (ion beam assisted deposition). Wear resistance and exchanges of friction coefficient was measured with on line test using special designed tribology equipment. Following the tests, the wear zone morphology and characteristics of surface layer structure as well as important properties were investigated. In the nanoindentation technique, hardness and Young's modulus can be determined by the Oliver and Pharr. 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. A variety of analytic techniques were used for characterization, such as scratch test, calo test, SEM, AFM, XRD and EDAX.*

Keywords: *nano, coating, super hard, ion implantation, wear.*

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 are 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 the coating treatment of materials. In the paper are presented 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 irradiation of Ar ions. Subsequent ion implantation was provided with N^{5+} ions. Ion implantation has the capabilities of producing new compositions and structures unattainable by conventional means. Implantation may result in changes in the surface properties of a material [1].

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].

In many cases single coating cannot solve the wear problems [3].

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 adhesion strength and hardness of hard coatings.

In the nanoindentation technique, hardness and Young's modulus can be determined by the Oliver and Pharr method, where hardness (H) can be defined as: $H = \frac{P_{max}}{A}$, 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:

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

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

This paper describes the use of the nanoindentation technique for determination of hardness and elastic modulus. The depth of nanopenetration provides an indirect measure of the area of contact at full load and thus hardness is obtained by dividing the maximum applied load with the contact area [4].

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 rotating specimen. The deposition parameters were as follows: Base pressure in the chamber was 1×10^{-5} mbar. During etching, bias voltage was U_b=1 kV, current I_d=50 mA. During deposition substrate temperature was T_s=200 °C, partial pressure of Ar was $P_{Ar}= 1\times10^{-3}$ mbar and partial pressure of N_2 was $P_{N2}=3\times10^{-4}$ 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. 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. 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^{5+} ions at room temperature (RT). The Ion Source is a multiply charged heavy ion injector, based on the electron cyclotron resonance effect (EC.R). The implanted fluencies were in the range from 0.6×10^{17} to 1×10^{17} ions/cm^2.

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 mechanical properties on coated samples were characterized using a Nanohardness Tester (NHT) developed by CSM Instruments, Nanoindentation testing was carried out with applied loads in the range of 10 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.

Scratch adhesion testing was performed using commercially available equipment (REVETEST CSEM) fitted with a Rockwell C diamond stylys (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. Detection of elastic waves generated as a result of the formation and propagation of micro cracks.

The tribological behavior of the coatings was studied by means of pin-on-ring contact configuration in dry sliding conditions, described elsewhere [5].

X-ray diffraction studies were undertaken in an attempt to determine the phases present, and perhaps an estimate of grain size from line broadening. The determination of phases was realized by X-ray diffraction using PHILIPS APD 1700 X-ray diffractometer. The X-ray sources were from CuKα with wavelength of 15.443 nm (40 kV, 40 mA) at speed 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 θ-2θ scan for every ψ angle around the selected diffraction peak and, in order to emphasize the peak shifts.

3. RESULTS

The nitrogen to metal ratio (EDX), is stoichiometries for IBAD technology and something smaller from PVD (0.98). For sample with additional ion implantation, value is significantly different, smaller (0.89). It is possibly diffused from the layer of TiN to the interface.

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 The analysis of the indents was performed by Atomic Force Microscope (Figure 1).

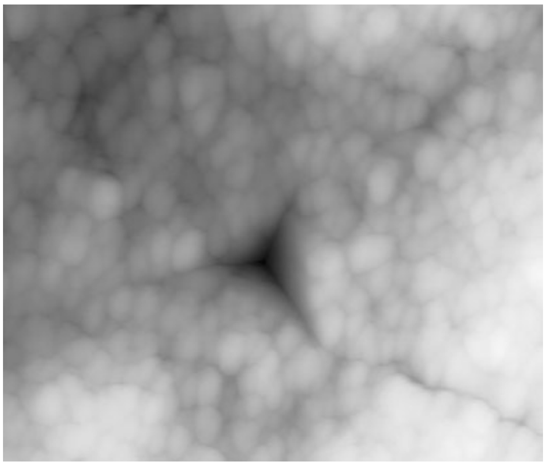

Figure 1. AFM image of crack paths from nanoidentation

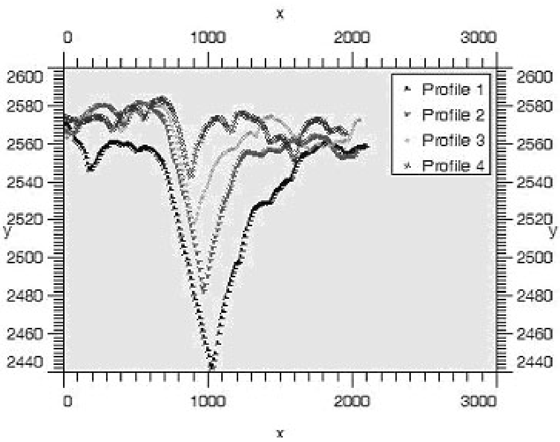

Figure 2. Cross section of the indentation

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

The nanohardness values and micro hardness are shown in Table 1.

Table 1. Surface mamohardness (load-10mN)

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

For each adhesion 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 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. Critical loads are presents in Table 2.

Table 2. Critical loads for different type of coatings

	pn/TiN(IBAD)	*pn/TiN(PVD)*
Lc1	-	23
Lc2	100	54
Lc3	138	108

The critical load Lc1 corresponds to the load inducing the first crack on the coating. No cracks were observed on sample 1.The critical load Lc2 corresponds to the load inducing the partial delamination of the coating. The critical load Lc3 corresponds to the load inducing the full delamination of the coating. In some places of hard coatings cohesive failure of the coating and the delamination of the coating were observed, (Figure 3).

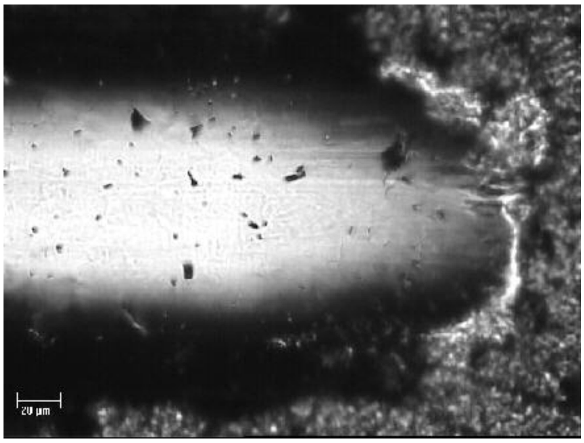

Figure 3. Delamination of coating

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

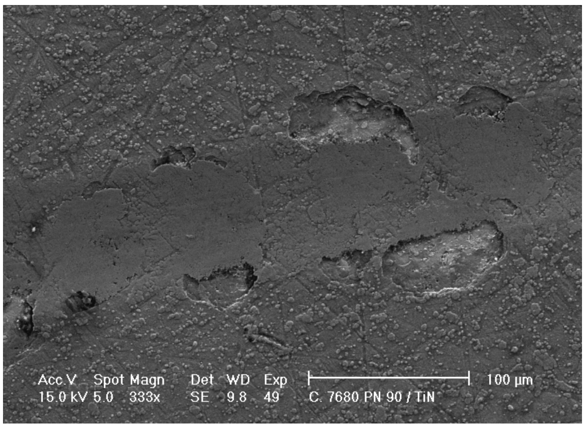

Figure 4. SEM morphology of scratch test pn/TiN(PVD).

The friction coefficient of sample with duplex coating with additional ion implantation, is presented in Figure 5.

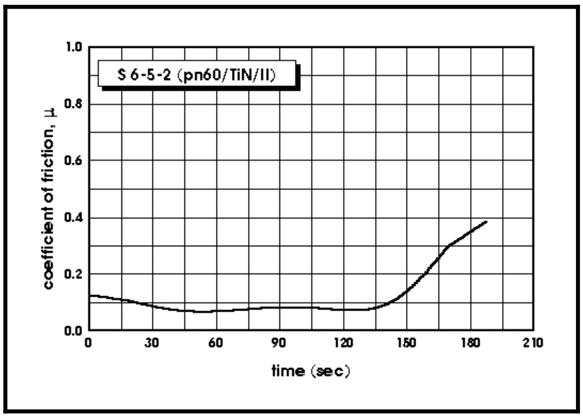

Figure 5. Friction Coefficient of pn/TiN/II.

The curves of friction coefficient are clearly reproducible and distinctively show a lower rise in friction coefficient for the composite (plasma nitrided/TiN) coated specimens and much lower for sample with additional ion implantation (under 0.1).

The reduction of strength, caused by high contact temperature, and high contact pressure in the contact zone, increases local deformability, thus produce enlarging of wear zone. When one considers the intimate contact of two sliding surfaces where hard particles are either present or formed during sliding, abrasive wear can occur as a consequence of both plastic deformation and fracture mechanisms. Damage to the coating surface is superficial (only a small polishing effect on TiN asperities can be seen and steel substrate is not exposed) by comparison with that inflicted by the other pin materials. At the worn zone are presented traces of adhered products of wear debris from counter-material. This adhered wear debris promotes new condition for wear at the tribological contact and influence on decreasing the wear and friction coefficient. When the steel counterface pin material is a softer material such as mild steel, under low-humidity conditions at low contact loads and speeds, the TiN wear mechanism reverts to regime with minimal damage to the coating, high steel wear and transfer of steel oxides to the TiN. As known, the sliding process is accompanied with the thermal effects. This is most common tribological contact condition and is often combined with high contact stress [6]. The significant part of the mechanical energy is converted into thermal energy. However, this thermal energy is inappropriate and the converted heat would be able to consider as a waste heat with negative environmental consequences.

The wear resistance of the TiN coating was obviously improved by the presence of a nitride interlayer. Such an improvements is probably due to the adequate bonding between the nitrided layer and substrate. Energy depressive analyze with X-ray (EDAX), of the transfer layer showed that the transfer layer consists of small amount of counter material (adhesive wear), Figure 6.

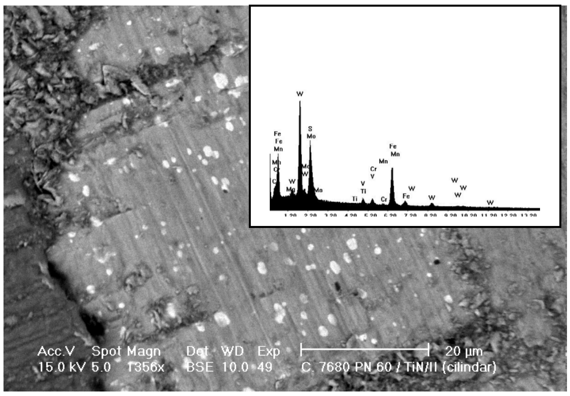

Figure 6. SEM micrograph of part with wear debris and EDAX image of wear debris.

Adhesive wear plays the predominant part in failure due to wear. Experience shows that every tribological system can be optimized by selecting the right coating.

The width of column, for plane (422), is derived from the width of the diffraction peaks (Scherrer formula):

$$t = \frac{0.9\lambda}{\beta \cos\frac{\theta}{\lambda}\cos\theta}$$

of TiN, (λ=0.154nm, θ=62.5^o and β=0.056rad), and it is 70 nm. Becouse of low deposition temperature, it is possible that another planes also have small width of columns.

The stress determination follows the conventional $\sin^2\psi$ method. Stress determination was performed using a PHILIPS XPert diffractometer. The (422) diffraction peak was recorded in a 2θ interval between 118^o and 130^o, 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 compact film, with residual stresses σ = -4.28Gpa, has TiN(PVD).

4. DISCUSION

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 three times thinner (900 nm TiN-IBAD).

The individual values of E are the different for all measurements. 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.

The topography of TiN coatings was investigated SEM (Figure 7).

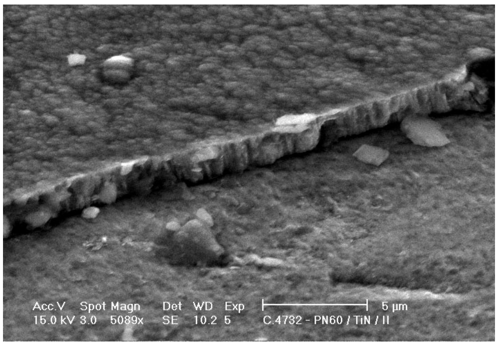

Figure 7. Surface morphology of coating with ion implantation.

The PVD coating process did not significantly change roughness. 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 formation of TiN by IBAD has its origin in a kinetically controlled growth. The nitrogen atoms occupy the octahedric sites in varying number 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 coating morphology was evaluated using the well-known structure zone model of Thornton. All observed morphologies, Figure 8, are believed to be from region of zone I (PVD) and from the border of region zone T (IBAD).

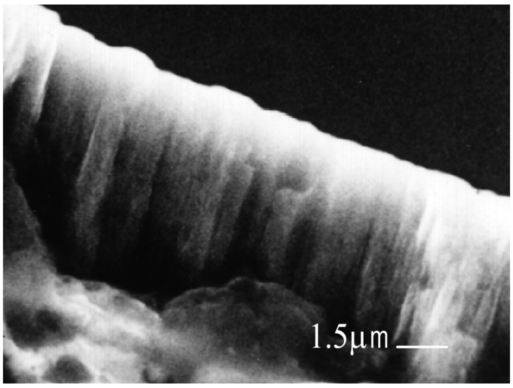

Figure 8. SEM of coating cross-section TiN(PVD).

It has been suggested [7], 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 hardness, 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 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 micro cracks when subjected to loads or stresses.

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

The present coating method can produce dance structures, high hardness and the high critical load values can be achieved. Tribological tests confirm that these composite coatings are wear resistant and provide very low friction coefficient

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