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Mechanical and Tribological Properties of TiN Coatings Produced by PIII&D Technique

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The structure, mechanical and tribological properties TiN coatings produced with PIII&D by using rectilinear filtered vacuum arc plasma system are present. The results of scratch testing and wear reciprocating testing clearly revealed the positive effect of pulse bias (0.5÷2.5 kV) application on tribological behavior of the TiN coatings in comparison the coatings deposited with DC bias (150 V). Application of pulsed bias potential leads to a significant reduction in the friction coefficient and increasing of coatings wear resistance due to a change in their structure. The orientation of crystal planes parallel to the surface changes from (111) to (220) with the application of pulse bias, which is accompanied by a transition from fibrous grains structure to denser columnar grains.

Keywords: Nitride coatings, Filtered vacuum arc deposition, Pulsed substrate bias, Residual stress, Mechanical and tribological properties.

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1. INTRODUCTION

Vacuum-arc deposition is an established technology to obtain hard and wear resistant coatings on various substrates. One of the most important parameters is the average energy per incoming particle. Changes in the surface morphology, texture and internal stresses are observed with higher energies. Plasma immersion ion implantation and deposition (PIII&D) is ideally suited for a regime where energy deposition is decoupled from the layer growth as the ion bombardment occurs only during the intermittent high voltage pulses [1].

The role of pulse voltage magnitude and frequency during PIII&D has been investigated in detail for TiN and TiAlN coatings [1-5], however there are very limited studies in the literature considering the mechanical and tribological properties of these coatings.

The aim of this study is to investigate the tribological properties of PIII&D TiN coatings produced by using different magnitudes of pulse bias voltages and correlate them with the structural and intrinsic stress changes induced by the application of high pulse bias voltages

2. MATERIALS AND METHODS

Polished high speed steel samples are used as substrates for deposition of TiN coatings. The coating process is conducted in rectilinear filtered arc system [6] using DC (– 150 V) and pulse voltages (0, – 0.5, – 1.0, – 1.5, 2.5 kV). In the intervals between pulses the substrate was under a self-consistent "floating" potential -(3÷20) V. In all the experiments conducted under pulse bias, the frequency and duration of high voltage period of pulse bias is kept constant as 24 kHz and 5 µsec respectively. During the deposition process 100 A cathode current and a mixture of nitrogen and argon with partial pressures 0.1 and 0.01 Pa is used. Although high bias voltages are used during the process, the sample temperature did not increase above 200 °C.

Structural investigations of the samples are conducted by using XRD measurements. Cu-Kα radiation is used in all investigations. Intrinsic stress in the coatings were measured by the X-ray tensometry technique using $\sin^2\psi$ method modified for textured samples.

Samples are fractured after keeping in liquid nitrogen for the investigation of their growth morphology. A FEG-SEM (Jeol 7100F) scanning electron microscope is used in these investigations.

Hardness of the samples are determined by using a nanoindenter (G200) model in CSM (continuous stiffness measurement) mode.

The scratch resistance of the coatings are determined with a scratch tester using an Rc indentor. A loading rate 10 N/mm and a maximum load of 100 N are used. The scratch tracks are then investigated under optical and scanning electron microscopy.

For the determination of the wear properties of the coatings a reciprocating wear testing system was used with testing parameters listed below: normal load – 5 N; counterbody – 10 mm alumina ball; rate – 1 cm/s; total distance – 100 m. After the tests the wear tracks are observed under 3D profilometer for determination of the wear depths and widths

3. RESULTS AND DISCUSSION

3.1 Thickness of Coatings and Hardness Measurements

Hardness values of the coatings and their thicknesses are presented in Table 1. The thicknesses of the coatings were 9-10 µm, thus deposition rate were all close to 20 µm/h verifying the high efficiency of the filter system.

The hardness of the reference coating produced by the application of DC bias was measured as 28 GPa. For coatings produced with 0.5 kV pulse bias coating hardness increased to 36 GPa and than gradually decreased to 32 GPa by further increase of pulse bias magnitude.

3.2 Structure of Coatings

According to X-ray diffraction data the single crystal phase in the coatings is the cubic nitride with the structure of titanium nitride (structural type NaCl). When substrate bias potential is floating (no bias), the crystallites of nitride are preferred orientated with (111) plane parallel to the surface of the coating. The TiN coatings produced by using DC bias 150 V exhibited a strong (111)-oriented structure as expected. By the application of 0.5 kV pulse bias the (220) oriented planes started to be the dominant planes parallel to the surface. With the increase of bias voltage this effect became more pronounced; (220) planes showed themselves as the major planes oriented parallel to the surface. These results are in accordance to the studies of [3, 5, 7]. The calculation result of grain (coherent scattering zone) size for the nitride coatings synthesized under different pulse bias potentials were listed in Table 1. The TiN coatings deposited with using the pulse bias have much less grain size in comparison with DC bias potential.

The magnitude of pulse bias exhibited a pronounced effect on the internal stress of the coatings. The internal stress in coatings produced with "floating" potential and with a DC bias voltage of 150 V was measured as (4.2-4.5) GPa. By the use of 0.5 kV pulse bias the internal stress in the coatings reached to a very high level, namely 9.7 GPa. By further increase of the bias voltage internal stress decreased gradually reaching to 5.7 GPa for samples produced with 1.5 kV pulse bias (Table 1). These results are again in accordance to the results of previous studies conducted in a similar manner [3, 5].

The fracture cross section of the sample produced under 150 V DC bias, with a strong (111) orientation, consists of sub micron sized fine columns similar to zone *T* structure exhibiting staircase like fracture edges following the same direction (Fig. 1a) [8]. By the application of 0.5 kV pulse bias, (220) oriented planes starts to become as one of the dominant orientation planes parallel to the surface. This change results in increased column size and random orientation of the staircase like fracture patterns. The fracture cross section of this coating resembles the transition between zone *T* and zone 2 [8]. For the coatings produced with the application of 1 kV and 1.5 kV pulse bias, the reflections from planes other than (220) are barely distinguishable indicating highly (220) oriented coatings. In these coatings very well defined columnar structures are clearly observable with very limited number of staircase like fracture within the coating (Fig. 1b). The column widths showed a distinct increase with the increase of pulse bias voltage, exhibiting a denser structure. All of these structures are similar to the ones defined as zone 2 [8]. The fracture cross section of the coating produced under 2.5 kV bias (with a strong (220) orientation similar to 1 kV and 1.5 kV coatings) was similar to the one produced with 1.5 kV bias, with a slight refinement of the columnar structure.

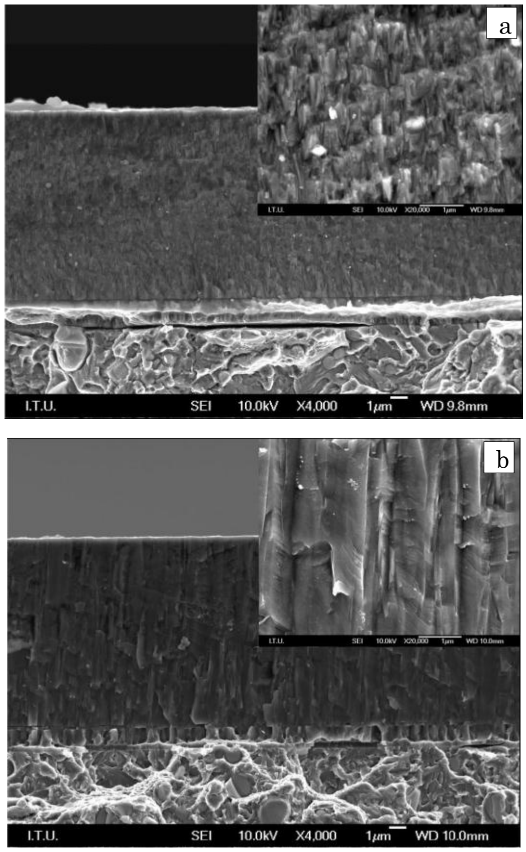

Fig. 1 – SEM cross-section image of TiN vacuum-arc coatings deposited from the filtered plasma at different substrate bias: a – DC bias – 150 V; b – pulse bias – 1.5 kV

Table 1 – Thickness, hardness, and structure characteristics of TiN coatings deposited at various substrate bias potential

Sample		Thickness, μm	Hardness, GPa	Preferred orientated	Grain size, nm	Internal stress, GPa
no bias		7.1	36	not strongly (111)	23	5
Pulsebias	0.5 kV	9.0	36	not strongly (220)	12	9.7
	1.0 kV	8.5	34	(220)	12	7.9
	1.5 kV	10.5	32	(220)	13	5.7
	2.5 kV	9.0	32	(220)	17	5.4
DC 150 V		9.2	28	(111)	39	4.2

3.3 Scratch Tests

Scratch testing behavior of the coatings was determined by SEM observations of the scratch tracks, depending on the normal load applied onto the coating. Other than SEM observations, F_n-F_r-AE graphs obtained from scratch tests were also used to complement the findings. Scratch test behavior of the 150 V DC sample was taken as a reference for the evaluations.

On the sample coated under 150 V of constant DC bias, lateral cracks start to appear at an F_n of 20 N. Spallation of the coatings starts to take place at a normal load of 50 N, parallel to the initiation of conformal cracks in the coating. The L_{c1} and L_{c2} values are determined as 35 N and 49 N respectively. This behavior is typical for hard coatings deposited on hardened substrates.

The sample prepared by using 0.5 kV pulse bias exhibited a different behavior, compared to the one prepared under constant 150 V DC bias. In this coating, the cracking initiated as lateral cracks. A region of very well defined conformal cracks was observed within the normal load range of 55 N to 80 N. With increasing normal load, arc-tensile cracks start to appear which are then followed by spallation of the coating. The L_{c1} and L_{c2} values are determined as 60 N and 81 N respectively. With respect to L_{c1} and L_{c2} values, this coating with the highest hardness and compressive stress content among all the samples, exhibited a better scratch behavior compared to the other coatings. Exposure of substrate material did not occur within the range of 0-100 N of normal load. Due to the higher compressive stress content of this coating, the dominating failure mode is cohesive as revealed by the acoustic emission data obtained during the scratch testing (Fig. 2). The acoustic emission levels of this coating are extremely low compared to those of the other four coatings despite the clearly observable crack pattern within the scratch track. This is indicative of cracks being contained within the coating structure rather than reaching the coating-substrate interface.

The scratch test behavior of samples produced under 1 kV and 1.5 kV pulsed bias exhibited a behavior similar to each other. Cracks on the coatings initiated as lateral cracks followed by the initiation of conformal cracks. Spallation of the coatings took place following the appearance of cracks of tensile nature. The L_{c1} and L_{c2} values are determined as 60 N and 70 N respectively for the 1 kV sample, 70 N and 80 N for the 1.5 kV sample.

On the 2.5 kV pulsed bias sample, lateral cracks start at 22 N F_n. Scratch behavior of this sample is similar to the sample coated under constant bias of 150 V DC, however the L_{c1} and L_{c2} values are 45 N and 62 N respectively.

It is possible to explain the scratch behaviour of the coatings depending on their structure and mechanical properties. Coating produced under DC bias posses a zone T structure exhibiting a staircase fracture pattern on its cross section. In this case the initial cracking is expected to be cohesive. Chipping and spallation follows the cohesive cracking of the coating by the increase of the normal load.

The sample produced under 0.5 kV pulse bias exhibited the best scratch test behaviour. This coating has a structure that can be defined as a transitionary state between zone *T* and zone 2. It has the highest hardness and compressive stress among all the coatings. The combined effects of these properties resulted in a very good scratch behaviour. Although the coating starts to crack at about 20-30 N normal load (as determined from SEM images of the scratch track) these cracks did not propagate to the substrate coating interface even at the maximum load. The very low intensity of AE signals is another indication of very low propagation rate of cracks. The random orientation of crystal planes parallel to the surface may have also contributed to this behaviour by creating longer paths for cracks to propagate to the coating substrate interface.

All of the other coatings produced by using 1-2.5 kV exhibit similar behaviours. These coatings posses a distinct zone 2 structures with a preferred orientation of (220). Their cross sections do not exhibit a staircase like fracture pattern. In these coatings, the crack starts to initiate by breaking of the bonds between the columns. The dense structure and high elasticity modulus of the (220) oriented planes [5, 8] retards the formation of intercolumnar cracks as indicated by the high critical load (L_{c1}). However once cracking starts it rapidly propagates to the coating substrate interface due to the columnar growth.

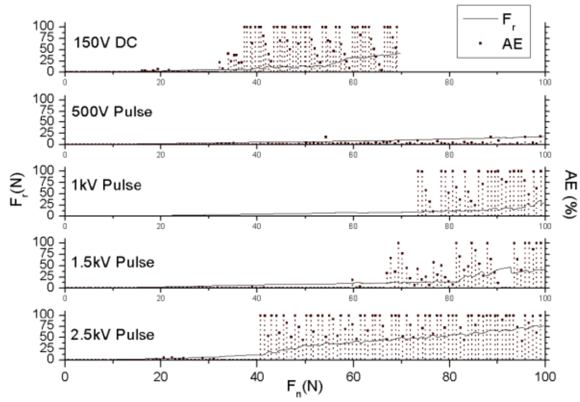

Fig. 2 – Normal load (F_n) vs lateral load (F_n) graphs acquired by scratch testing. Right hand side shows acoustic emission (%) values

3.4 Reciprocating Wear Tests

Wear testing carried out in the reciprocating mode revealed significant decrease in wear rates and coefficient of friction (CoF) values of the pulse bias coated samples compared to the sample coated by DC bias. The highest steady state CoF (0.76) was observed for the sample produced with 150 V DC bias. The CoF of this coating was low at the beginning but increase rapidly within 10 m of sliding distance and reaches to a steady state in 20 m (Fig. 3). This behavior is similar to the wear behavior of TiN coatings produced with CAPVD utilizing DC bias [9, 10]. The CoF for the other samples produced with pulse bias are in the range of 0.1-0.15 and did not show an appreciable difference depending on the sliding distance.

The depth and width of the wear track after 100 m of total sliding on the sample coated with the application of 150 V DC bias, is 3.7 μm and 400 μm respectively. With the application of 0.5 kV pulsed bias, the wear track resulting from the same sliding parameters is less than a micron deep and only 70 μm wide. The depth and width of the wear tracks for the samples produced with pulse bias did not show an appreciable difference.

Most of the existing wear data for CAPVD produced TiN coatings are for (111) oriented films since the coatings produced with DC bias this is the general growth direction. There are very limited studies on orientation dependent wear behavior of TiN coatings [11, 12]. In these studies mostly (111) and (200) oriented films are compared to each other without any definitive indication on the role of orientation on wear behavior. There are no studies on the wear behavior of highly (220) oriented TiN films in the literature

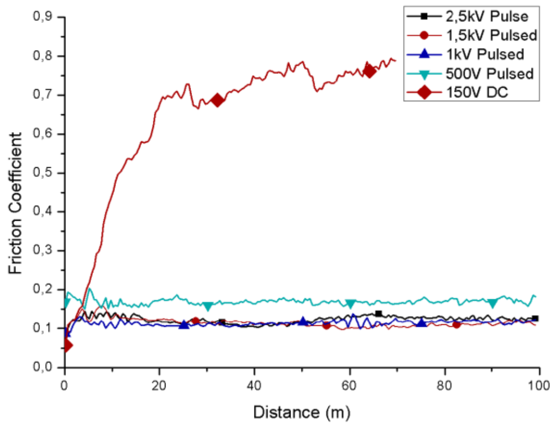

Fig. 3 – Coefficient of friction – sliding distance relation for reciprocating wear tests

The results of wear testing clearly revealed the positive effect of pulse bias application on tribological behavior of the TiN coatings. Thus the drastic decrease in the wear rate and the coefficient friction should be a result of structural changes occurred on coating with the application of pulse bias. The major differences between the coating produced with DC and pulse bias are the orientation of the planes parallel to the surface and the growth structure and columnar structure that becomes denser with thicker columns. The orientation of crystal planes parallel to the surface changes from (111) to (220) with the application of pulse bias, which is accompanied by a transition from zone T to zone 2 type structure.

CoF of the coating produced at 150 V was low in the initial 10 m of sliding distance. It is believed that the debris produced at this stage showed a pronounced role on the further wear behavior. This coating chipped easily under loading as indicated by the scratch tests. The chipping action may have resulted in the production of abrasive debris in the wear track that accelerated the wear rate of this coating. On the SEM and 3D optical profile images of this wear track, deep grooves resulting from the action of chipped coating particles are clearly visible. For the coatings produced under pulse bias such a gradual increase in the CoF with the sliding distance is not observed. These coatings as indicated by the scratch tests did not exhibit any chipping till reaching high normal loads. Thus for these coatings the debris only result from wear action between the coating and the counterbody. This type of debris is expected to be finer than and not as abrasive as the larger chipped particles. On the SEM and 3D optical profile image of sample produced under 1.5 kV pulse bias, instead of deep grooves only narrow and shallow abrasive wear marks are observed, which is in agreement with this expectation.

The positive influence of pulse bias application on wear behavior can mainly be attributed to the denser columnar structure, which reduces the formation of abrasive debris during sliding. The changing of preferred growth orientation from (111) to (220) may also have contributed to the improvement of wear resistance, since the elastic moduli of (220) planes are higher than (111) oriented planes [5, 8].

4. CONCLUSIONS

In this work have been studied the structure, mechanical and tribological properties TiN coatings produced with plasma immersion ion implantation deposition (PIII&D) by using rectilinear filtered vacuum arc plasma system. The results of scratch testing and wear reciprocating testing clearly revealed the positive effect of pulse bias application (0.5÷2.5 kV) on tribological behavior of the TiN coatings in comparison the coatings deposited with DC bias (150 V). Application of pulsed bias potential leads to a significant reduction in the friction coefficient and increasing of coatings wear resistance due to a change in their structure. With the pulse bias application, preferred orientation of crystal planes parallel to the surface changes from (111) to (220) accompanied by a transition from fibrous grains structure to denser columnar grains. An increase at 0.5 kV and then a decrease of compressive internal stress is observed with increasing pulse bias potential from 0 to 2.5 kV.

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