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INVESTIGATION OF MICRO AND NANO TRIBOLOGICAL PHENOMENON BY EDX

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Abstract: *In this paper, limited results of research of tribological phenomena at fretting test of TiN hard coating, deposited at surfaces with different roughnesses are shown. Wear zone was investigated by different EDX beam energies in order to compare obtained results and to realize how much valuable data can be obtained for wear and friction phenomena clarification. Additional useful information in our case can be obtained by EDX linear scanning. Combination of EDX analysis with AFM measurements can provide complete data necessary for micro and nano tribological phenomena research. EDX results can be very useful for the qualitative research of worn surfaces on thin layers.*

Keywords: *EDX, Surface roughness, Friction coefficient, TiN, AFM, Nanotribology*

1. INTRODUCTION

Energy dispersive X-ray analysis is very useful for investigation the wear processes, particularly for qualitative studies inside wear tracks [1]. It is convenient to combine SEM for morphologies of wear track, with EDX for composition analyses of wear debris after sliding test [2]. In some case EDX results could sagest that tribofilm and wear debris are mainly generated from the wear of the coating [3]. Analyzing Scopus data base it becomes obvious that very small number of paper related to application of EDX in investigation hard coatings TiN or TiAlN [4,5,6].

The long mean free path of X-ray causes a relatively large excitation volume, but if apply low kV electron beam, poor ionization for the elements and significant spectral overlap appear. Low kV EDX is extremely sensitive to surface contamination, particularly in case when sample surface have longer period of exposition to electron beam [7]. Beam energy 10 keV can excite the Ti*K* peak (4.509 keV). Higher keV incident beam results in higher count rate and reveals additional non-overlapping peaks. These benefits come at count of deeper and more complex beam to sample interaction. Very important is that in the case of low EDX count rates are to be expected from a low energy incident e-beam, both the instrument and operational methodologies must be appropriately modified.

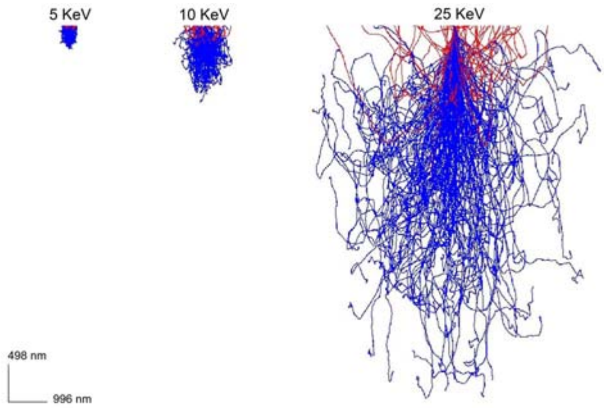


Figure 1. Comparative interaction beam-sample for different beam energy.

Table 1. Suitable acceleration voltages for EDX [7].

Operation range	Application
2 -3 kV	Surface detection
5 – 7 kV	General detection at nanoscale
10 – 25 kV	Broad elemental detection

The aim of this paper is to present some of our results connected with our investigation the tribology phenomenon at surface of TiN hard coating deposited by IBAD.

2. MATERIALS AND EXPERIMENT

TiN coatings were deposited in an Ion Beam Assisted Deposition (IBAD) chamber with a base pressure of $1.5x10^{-6}$ mbar. The used apparatus consists of a 5 cm Kaufman ion source, 5 kW e-beam evaporator, residual gas analyzer, thickness monitor, and mechanical and cryopumps. Carburizing steel (0.165%C, 0.2%Si, 1.2%Mn and 1%Cr) disks were used as substrate material. Cemented steel was used due to its high load bearing capacity. Three types of substrates with different surface pretreatment were used. : sample 1 - TiN film on grounded substrate; sample 2 - TiN film on fine-grounded substrate; sample 3 - TiN film on polished substrate. Prior to deposition substrates were sputter-cleaned by argon ion beam. In order to improve adhesion between TiN layer and base material an interface was made by ion beam mixing atoms of base material and atoms of titanium (Ti) sublayer. The Ti sublayer was deposited keeping operating pressure around $5.6•10^{-5}$ mbar. TiN deposition was performed in a mixed Ar and N_2 atmosphere with a partial nitrogen pressure between 1.1 and $1.2•10^{-5}$ mbar. Total operating pressure was around $7•10^{-5}$ mbar. Growing film was bombarded by argon ion beam. Ion energy was 1 KeV, ion current density 53 $\mu A/cm^2$ and ion incidence angle between 52º and 53º. Titanium was evaporated using power of 720 W, producing condensation rate of 0.2 nm/s. During deposition of both, the Ti sublayer and the TiN coating temperature did not exceed 58 °C.

Friction coefficient measuring was realized by ball-on-block tests without lubrication. The tests were conducted at CSM Nanotribometer with following parameters: counter material – 2 mm Al_2O_3 ball with hardness of 2700 HV, movement type - linear reciprocating movement.

Coating hardness was measured using CSM nanohardness tester. Surface roughness and morphology were evaluated by atomic force microscope VEECO di CP II with tip type Reflective contact mode Etched Silicin Probe Symetric typ MPP-31123-10. All images were required in contact mode by etched silicon probe symmetric typ. Scanning electron microscopy (SEM JEOL JSM 6460 LV with an embedded Oxford Instrument EDX analyzer) was employed to investigate wear zone morphology.

Sample with dimension ∅25 x 5 mm was prepared by grinding (sample 1) or by polishing (sample 2). Roughness results were presented in table 1.

Table 2. Sample roughness

sample	Ra nm	R pv
1	53,028	816,3
2	3,544	72,177

Coating hardness was measured using CSM nanohardness tester. Surface roughness and morphology were evaluated by VEECO di CP II atomic force microscope. All images were required in contact mode by etched silicon probe symmetric tip. Scanning electron microscopy (SEM) was employed to investigate wear zone morphology.

3. RESULTS AND DISCUSSION

Hardness of TiN coating was between 2601 and 2867 HV, while elastic modulus varied between 444 and 467 GPa. SEM image of fretting surface at sample 1 – grinded quality surface is presented in figure 1. This figure shows place where EDX analysis was done with 2 different energy levels 10 and 25 kV.

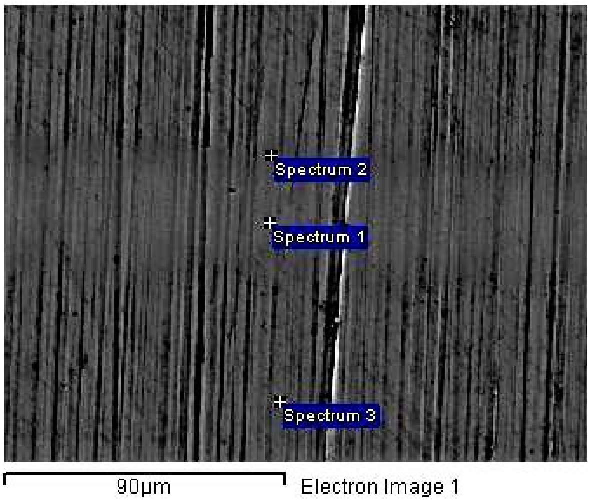


Figure 2. SEM image of fretting surface at sample 1

Table 3. Results with EDX 25kV

spectrum	Ti%	N%	Fe%	Cr%
1	11.82	9,21	75.52	1.20
2	16.84	13.07	67.12	0.99
3	17.41	17.57	57.42	0.85

EDX energy 25 kV obvious affected base materials of substrate so we have great amount of iron and chromium. Chromium percentage is proportional to content in carburizing steel used in our experiment. The rest to 100% in upper table related to content of C, Si and Mn are also present in base material.

EDX with lower energy 10 kV shows great difference in composition results as it is obvious from next table 3. relating to significant decreasing of beam impact energy we have more information about composition the surface TiN layer with thickness approximately 900-1000 nm (after deposition). At the place with lower thickness on worn surface (spectrum 1 and 4) we got some trace of Fe, but typical composition for TiN at the spectrum 3 (untouched surface). Significant information from this EDX analysis is presence of oxide at the worn surface. That fact could explain relatively low friction coefficient, but EDX analyse couldn't get answer what is the source of oxide generation. It is possible that some oxide from is generate like nano wear debris from counter material (ball Al_2O_3). Another possible reason could be increased local temperature at tribo contact surface connected with oxidation of titanium. These assumptions support the fact that we couldn't get any EDX signal of Al presence at worn surface.

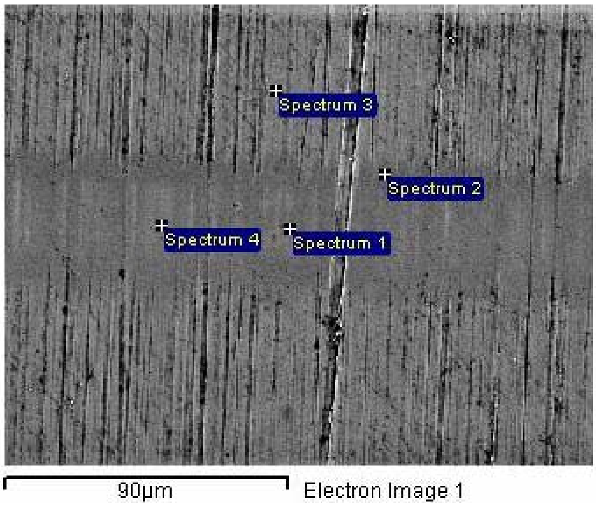


Figure 3. SEM image of fretting surface at sample 1

Table 4. Results with EDX 10kV

spectrum	Ti%	N%	Fe%	O%
1	62.05	19.56	3.42	5,23
2	65.59	20.56	0.00	3,12
3	77.24	21.89	0.00	
4	55.26	14.85	7.01	9.07

Interesting result of EDX analysis can be obtained when wear zone on grinded surface by line scanning (figure 4).

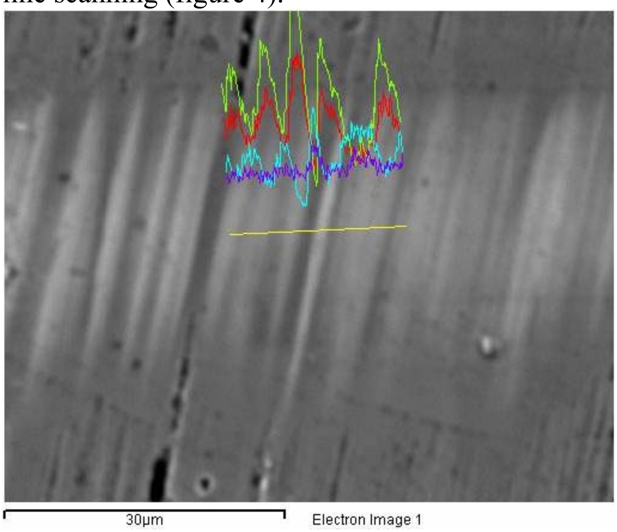


Figure 4. EDX image of worn zone with beam energy 10kV

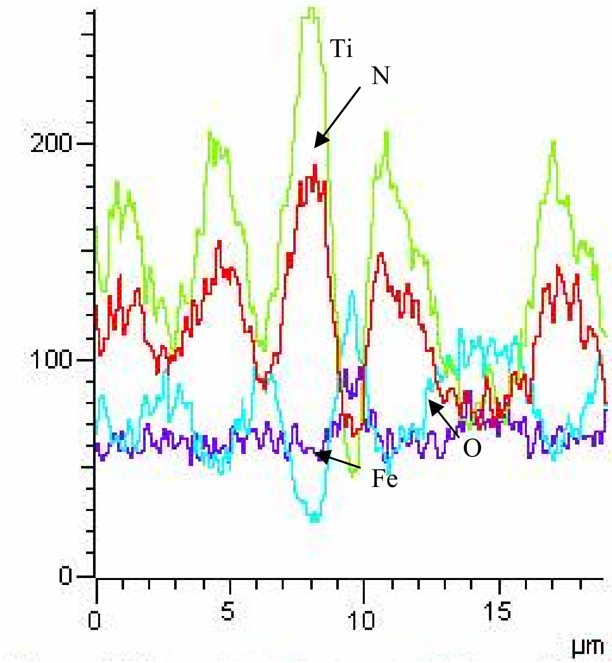


Figure 5. EDX linear spectrum with 10 kV

From figure 4 and 5 is obvious that during linear scanning content of Ti and N simultaneously changed depending of beam position. Contrary, the content of Fe decreasing in every point where Ti and N increased. It could be explained by the fact that the thickness of analyzed TiN surface layer has different thickness due to fretting wear. Original surface at that place has asperities due to grinding and counter ball partially flattening those asperities, but particularly at the top of asperities. So, the level of Ti could serve as indication how deep worn the surface layer after fretting. Interesting fact could be noticed at figure 5 that level of O didn't changed during the line scanning, so this fact confirms that presence of O was generated due to friction processes.

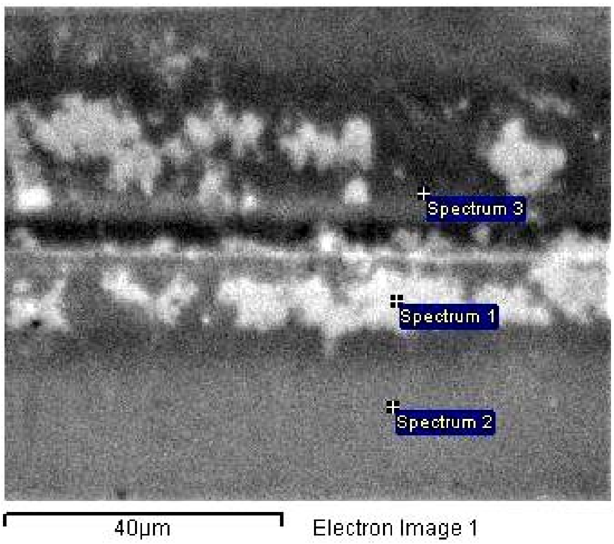


Figure 6. EDX spectrum on sample 2 worn surface with 10 kV

Table 5. Results connected with figure 6

	Ti	N	O	Fe
Spectrum 1	73.47	14.98	11.54	-
Spectrum 2	78.71	16.72	4.56	-
Spectrum 3	68.05	12.53	10.81	8.6

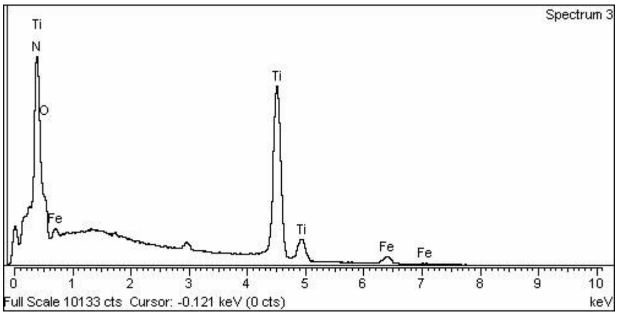


Figure 7. EDX spectrum 3 – connected with figure 6

From figure 6 and table 5 it can be concluded that white spots at worn zone contained increasing content of O (spectrum 1). Spectrum 3 shows presence of Fe what only cold be explain by decreased dimension of TiN at worn surface at measured point.

To prove it we measured nanomorphology at this zone at same sample by AFM (figure 7). This image clearly shows that white spots visible in figure 6 are not significantly thick wear debris. To prove it, we analyzed place with image software at AFM (figure 8).

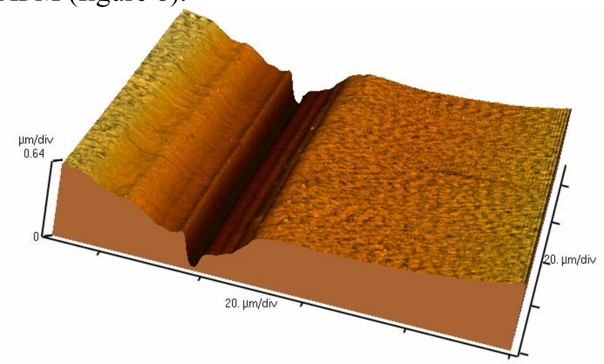
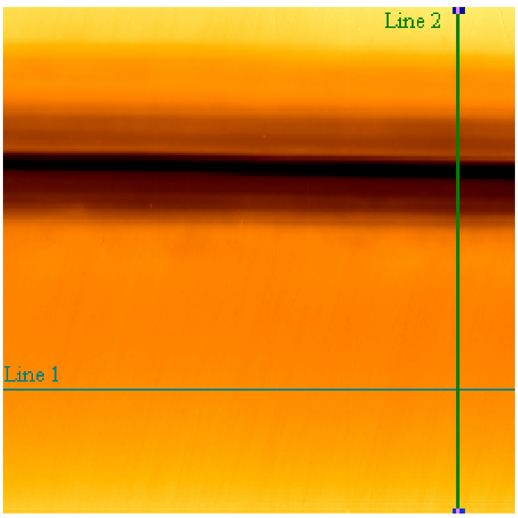


Figure 8. AFM 3D image of worn surface at sample 2



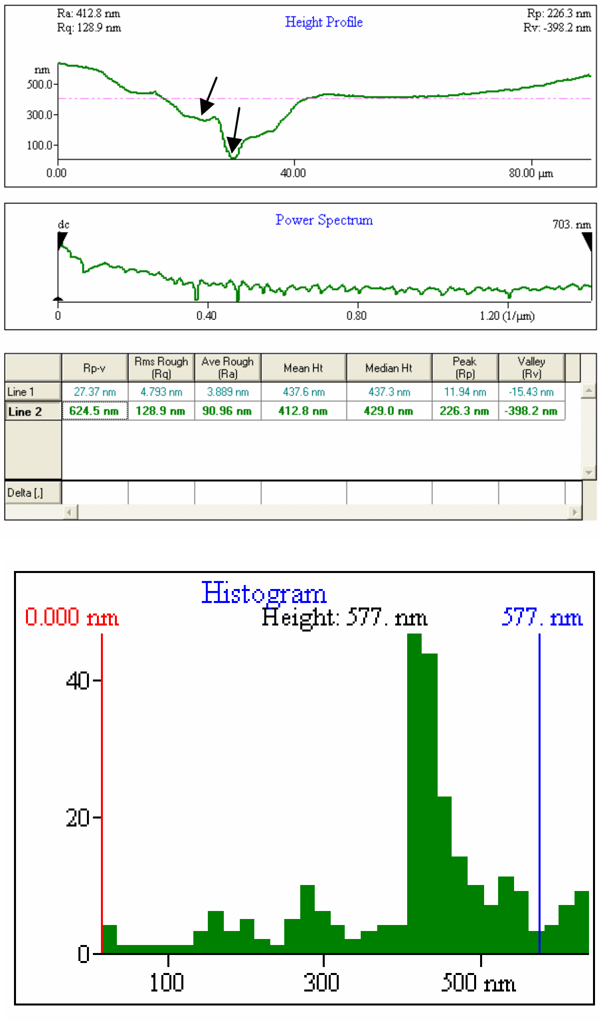


Figure 9. Result of detailed line analyze at worn surface presented in figure 7

The depth of worn channel is relatively regular but has two parallel traces what is visible on cross-section. Similar double channel wear zone we have exactly at all tested samples with polished surface. It could be attributed to constructing problem of fretting testing machine but not like characteristic behavior of samples. Characteristic depths are signed with arrows 397 and 175 nm respectively. These results confirm why the spectrum 3 from table 5 shows presence of Fe.

4. CONCLUSION

Energy dispersive X-ray analysis could be very useful for investigation the wear processes, particularly for qualitative studies inside wear tracks even for TiN surface layer. It is very important to pay attention to beam energy in accordance with thickness of surface layer after tribo testing.

It is convenient to combine SEM for morphologies of wear track, with EDX for composition analyses of wear debris after sliding.

Linear EDX spectrum could give interesting results on worn grinded surface covered with TiN.

Wear debris after sliding have to be analyzed by lower beam energies as possible because it could appear overlapping of signals as it is shown on figure 7. In contrary, application of too high energy could result with losing information about composition of worn surface.

Simultaneous application of SEM, EDX and AFM analysis with complete nano measurement of surface geometry can serve for complete conclusion about wear and friction process of TiN hard coating.

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