

# Tribological properties of ternary nanolayers, obtained from simple/compound materials

V Jinga<sup>1\*</sup>, D Cristea<sup>1</sup>, C Samoilă<sup>1</sup>, D Ursuțiu<sup>2</sup>, A O Mateescu<sup>3</sup>, G Mateescu<sup>3</sup>,  
D Munteanu<sup>1</sup>

<sup>1</sup> Department of Material Science, Transilvania University of Braşov, 1 Colina  
Universităţii street, Braşov, Romania

<sup>2</sup> Department of Electronics and Computers, Transilvania University of Braşov, 1  
Politehnicii street, Braşov, Romania

<sup>3</sup> Horia Hulubei National Institute of Physics and Nuclear Engineering, Reactorului  
street, Bucharest, Romania

E-mail: jingavlad@yahoo.com

**Abstract.** Numerous recently investigations are oriented towards the development of new classes of thin films, having dry-lubrication properties. These efforts were determined by the enormous energy losses generated by friction, and due to technical complications determined by the systems used for classic lubrication. This paper presents our results concerning a new class of nanomaterials, with ternary composition deposited from simple/compound materials ( $\text{Ti}/\text{Ti}_x\text{N}_y$ ,  $\text{TiB}_2/\text{Ti}_x\text{Bi}_y\text{N}_z$ ,  $\text{WC}/\text{W}_x\text{C}_y\text{N}_z$ ). The films were deposited by magnetron sputtering, with varying sputtering parameters (sputtering power, reactive gas) on stainless steel substrates - ultrasonically and glow discharge cleaned before the deposition process. The influence of the deposition parameters on the mechanical and wear properties was assessed by nanoindentation, scratch resistance (to quantify the adhesion of the films to the steel substrate) and by pin-on-disk wear tests. The general conclusion was that the sample deposited at  $550^\circ\text{C}$ , with  $\text{N}_2$  as reactive gas and 0.5 kV for substrate polarization, has the best mechanical characteristics (hardness and elastic modulus) and lubricant properties (represented by  $\mu_{\text{average}}$ ), when compared to the remaining samples.

## 1. Introduction

In recent times friction increased its influence and importance from both technical and economical point of view. Friction generates energy losses causing energy waste, increased costs for production and has a significantly negative environmental impact.

According to the studies done in the industrialized countries, friction is the main cause for energy losses summing a total more than 5% of the country's Gross Domestic Product [1] – a considerable value that should be minimized as much as possible.

Friction must be avoided if possible, or at least reduced. Generally, if the friction is reduced due to external lubrication, one has to consider the negative environmental impact caused by the production and waste disposal of these lubricants. A new approach is taken into consideration for this matter: the development of coatings with dry lubrication properties, meaning a reduced friction coefficient, and consequently, better wear performance.

\* 11 Cîbinului street, Braşov – Romania, e-mail: jingavlad@yahoo.com



This subject was already of interest for other researchers in material science. Hall – Petch and Frank – Read theories regarding surface's tribological behaviour are slightly less significant if the thickness is lower than the critical value. When layer's thickness decreases [2] additional layer's coherence can be totally absorbed by the layers. If the thickness increases, the energy of surfaces being in contact is generating dislocations that don't fit. The border separating these two trends is called critical thickness [3]. Misra, Hirth and Hoogland [4] explained the increase effect of multilayers systems: for layers having thickness larger than 100 nm, variation of increasing tensions is defined by Hall – Petch relation, meaning that tension increasing in the deposited layer is proportionally reversed with the layer's thickness square root,  $\sigma = 1/\sqrt{h}$  where  $\sigma$  is the yield stress in the film and  $h$  the layer thickness. The decreasing of the layer thickness less than tens of nanometers was noticed that Hall – Petch relation break down and the equation is transformed in logarithm dependence  $\sigma = \ln(h/b_B)/h$  where  $b_B$  is the Burgers vector of metal law dislocation line energy.

Tambe and Busham [5] established that there is an essential connection between material's Young modulus, friction coefficient and adherence. The rule is that a lower Young modulus implies a higher friction coefficient and a higher Young modulus results in a lower friction coefficient.

Bowden and Tabor's model [6] from microtribology considers generation of pinning surfaces due to cold welding junctions appearance, but at nanometric scale it is stated that stick-slip is a result of overcoming energy barriers necessary for surpassing leaps over atom's concentrations on probe's surface.

The authors will thoroughly describe the manner in which depositions were made, the tests that were done (not only scratch tests, but also friction coefficient determinations, elastic modulus and hardness testing) and will comment on obtained results from the tests, concluding with influence of deposition parameters regarding the coating's properties.

These contributions describe a new approach in designing tribological coatings based on mono-layered structures made of Ti/TiB<sub>2</sub>/WC in presence of N<sub>2</sub> as a reactive gas or not. Their properties and perspectives for application are taken into account based on author's contributions in several patents [7].

## 2. Experimental procedures

### 2.1. Materials and process parameters

Stainless steel plates were used as substrates, and before each deposition were ultrasonic and glow discharge cleaned. During the deposition process, substrates were in a rotation movement (20 rpm), to increase the coating homogeneity. The substrates were heated at 300°C or 550°C and the bias voltage was set at 0.5 kV during the reactive deposition processes.

For the film deposition was used a multifunctional vacuum thin film deposition system. The chamber is equipped with three DC sputtering magnetrons (guns, all with maximum power of 600 W). Ar was used as a bombardment gas and N<sub>2</sub> as a reactive gas. The distance between the substrate holder and the sputtering target was set at approximately 12 cm.

The working process parameters for the DC magnetron sputtering deposition method used to obtain the samples described in this paper are presented in Table 1. One can notice from Table 1 that all the films were deposited by simultaneously sputtering with three targets, resulting in a quasi-composite film, each component having its distinctive role: Ti for having great adherence to stainless steel and an increased hardness, TiB<sub>2</sub> and WC for their hardness and for dry-lubrication.

### 2.2. Characterization methods

The mechanical and tribological properties of the coated samples described above were investigated by the following methods: Scratch Test Methods, Hardness Test Method and Pin-on-disk Tribometer.

Mechanical and tribological parameters: analyses were done using CSM Table Top Platform which includes the standard Micro/Nanoindentation head (NHT2) and the standard Micro scratch tester head (MST) into a small and simple-to-use instrument.

**Table 1.** Working process parameters for deposition of samples no. 1, 2, 3 and 4.

Sample No.	Materials	Working gases		Power injected in the gun's plasma [%P <sub>max</sub> ]	Deposition time [min]	Working pressure [mbar]	Temperature [°C]	Bias Voltage [kV]
	Deposited layers	Ar [sccm]	N <sub>2</sub> [sccm]					
1	1x(Ti +TiB <sub>2</sub> +WC+N <sub>2</sub> )	100	40	9 for Ti 50 for TiB <sub>2</sub> 22 for WC	13	2.7 x10 <sup>-3</sup>	300	0.5
2	1x(Ti +TiB <sub>2</sub> +WC)	100	0	5 - 3 for Ti 30 for TiB <sub>2</sub> 25 for WC	10	2.9 x10 <sup>-3</sup>	300	-
3	1x(Ti +TiB <sub>2</sub> +WC+N <sub>2</sub> )	150	40	15 for Ti 30 for TiB <sub>2</sub> 30 for WC	30	3.5 x10 <sup>-3</sup>	550	0.5
4	1x(Ti +TiB <sub>2</sub> +WC)	150	0	15 for Ti 30 for TiB <sub>2</sub> 30 for WC	30	3.4 x10 <sup>-3</sup>	550	-

Scratching method: the micro scratch tester head (MST) has a Rockwell type indenter. The Micro Scratch Tester (0 – 30 N) is suited for analyzing thin hard or soft coatings. It contains a full software package for data acquisition and analyses of mechanical properties. The Nanoindentation Tester (0 – 500 mN) provides low loads with depth measurement in the nanometric scale. The system can be used to characterize organic, inorganic, hard and soft materials.

Tests were done with the Rockwell indenter (100 Cr6 material) having a 100 µm range. The linear scratch was progressive, having the begin load 0.03 N and the end load 10 N for all samples, the loading rate constant at 5 N/min for samples no. 2 to 4 and 8 N/min for sample no. 1. AESensitivity was 9 and the scratch length was 5 mm for samples no. 1 and 2, 2mm for sample no. 3 and 4 mm for sample no. 4. Speed varied from 4 mm/min for sample no. 1 to 2.5 mm/min for sample no. 2, 2mm/min for sample no. 3, sample no. 4 having a speed of 4 mm/min.

For samples no. 2 to 4, three scratch tests were done using the same settings for each measurement, sample no. 1 having only two scratch tests performed on. After carrying out the tests, critical loads could be established: Lc<sub>1</sub> – load observed for first crack occurrence, Lc<sub>2</sub> – load necessary for first delamination (first section of film removed from the substrate), Lc<sub>3</sub> – load necessary for removal of more than 50% of film from the scratch track.

Nanoindentation technique: a diamond tip –NHT2 – the standard Nanoindentation head, mounted on a stainless steel cantilever is used in order to obtain good statistics. Nanoindentation measurements were performed with a diamond tip Berkovich indenter, penetration depth being constant (no greater than 20% of coating thickness in order to minimize the effect of the substrate on the results). Thickness measurements were done using Rutherford Backscattering Spectrometry method and it was established that the film thickness is ~220nm.

Several measurements were performed on each sample, to increase the statistical relevance of the results, with the following protocol: loading/unloading speeds of 200 nm/min with a pause of 10 s between loading and unloading stages for samples no. 1 and 2 and loading/unloading speeds of 100 nm/min with a pause of 2 s between loading and unloading stages for samples no. 3 and 4.

Tribometer method: a sphere, a pin or a flat section is loaded onto the test sample with a precisely known force. The probe is mounted on a stiff lever, designed as a frictionless force transducer. The friction coefficient is determined during the test by measuring deflection of the elastic arm.

On each sample tests were performed using 6 mm 100 Cr 6 steel balls as counterparts, in rotation mode, normal load being 1 N. Atmospheric conditions were constant during all tests, 24°C temperature, and 32% humidity. Variable parameters were the Radius [mm], the Linear Speed [cm/s] and the Stop Condition [m] meaning the length of the wear track. No lubricating solutions were used.

### 3. Results and discussions

#### 3.1. Adherence: scratch tests

For sample no. 1,  $L_{c1}$  values varied from 0.458 N to 0.5 N, mean value being calculated at  $0.479 \text{ N} \pm 4.5\%$  measurement error.  $L_{c2}$  was determined at 1.198 N and  $L_{c3}$  at 2.906 N.

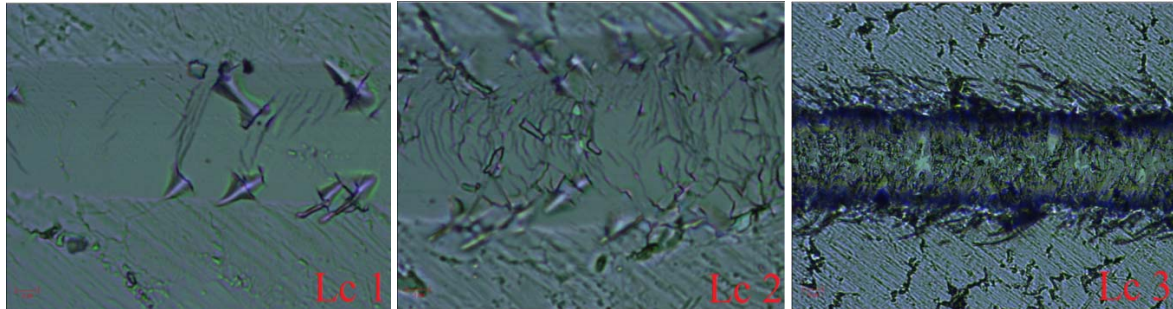


Figure 1. Critical loads for sample no. 1 ( $L_{c1}$ ,  $L_{c2}$ ,  $L_{c3}$ ).

For sample no. 2,  $L_{c1}$  values varied between 0.266 N and 0.404 N, having a mean value of  $0.3186 \pm 27\%$ ,  $L_{c2}$  values varied from 0.474 N to 0.892 N, mean value being  $0.715 \pm 30\%$  determined measurement error and  $L_{c3}$  had a value of 0.933 N.

For sample no. 3,  $L_{c1}$  had a variation from 0.44 N up to 0.74 N, mean value being calculated at  $0.616 \pm 29\%$ .  $L_{c2}$  varied between 1.69 N and 2.46, with a mean value of  $1.986 \text{ N} \pm 24\%$ .  $L_{c3}$  varied from 8.02 N up to 8.29 N, mean value being calculated at  $8.163 \text{ N} \pm 2\%$ .

For sample no. 4,  $L_{c1}$  values varied from 0.26 N to 0.35 N, mean value being calculated at  $0.313 \text{ N} \pm 17\%$  measurement error.  $L_{c2}$  variation started at 0.73 N up to 0.89 N, mean value being  $0.826 \pm 12\%$  and  $L_{c3}$  from 5.39 N up to 6.45 N, with a mean value of  $5.973 \text{ N} \pm 10\%$  error.

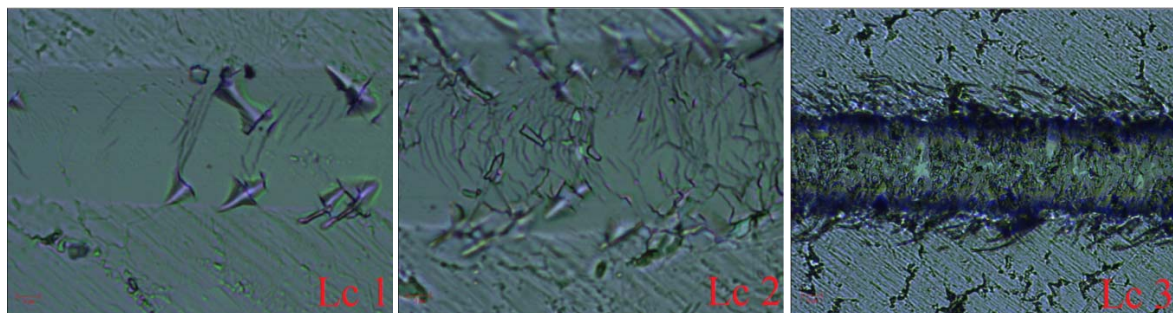


Figure 2. Critical loads for sample no. 2 ( $L_{c1}$ ,  $L_{c2}$ ,  $L_{c3}$ ).

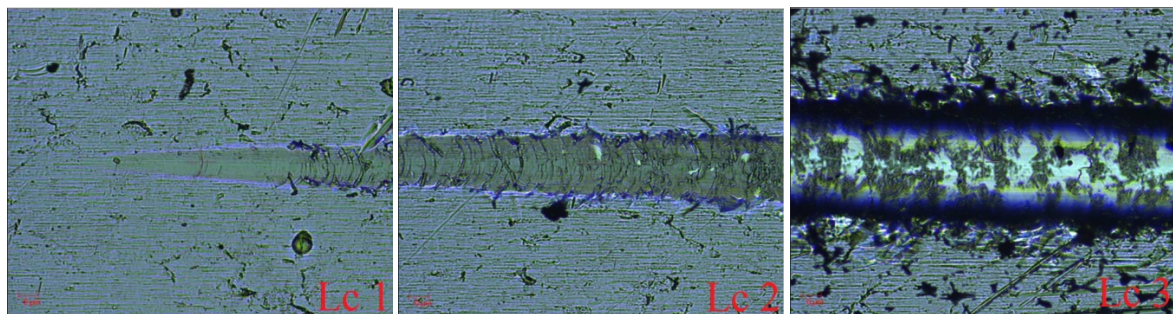


Figure 3. Critical loads for sample no. 3 ( $L_{c1}$ ,  $L_{c2}$ ,  $L_{c3}$ ).



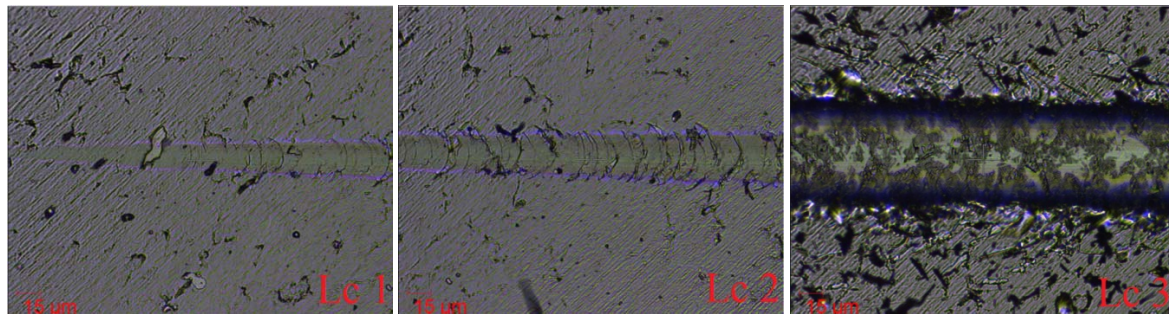


Figure 4. Critical loads for sample no. 4 (Lc<sub>1</sub>, Lc<sub>2</sub>, Lc<sub>3</sub>).

### 3.2. Hardness indentation and elastic modulus

Five indentations were performed on sample no. 1. Hardness values varied from 1703.2 MPa to 2274.1 MPa, mean value being  $1938.44 \text{ MPa} \pm 17\%$  error. Elastic modulus had values starting at 163.47 GPa up to 212.67 GPa, its mean value being calculated at  $185.692 \text{ GPa} \pm 14.5\%$ .

For sample no. 2, seven indentations were done. Hardness varied from 1842 MPa to 2525.1 MPa, having a mean value of  $2196.329 \text{ MPa} \pm 16\%$ . Values for elastic modulus started at 115.55 GPa and ended at 200.2 GPa, mean value being  $167.0471 \text{ GPa} \pm 30\%$  error.

Seven indentations were performed for sample no. 3 also. Hardness variation was between 12095 MPa and 16841 MPa, mean value being  $14627.14 \text{ MPa} \pm 17\%$ . Elastic modulus values varied from 184.14 GPa up to 270.36 GPa, mean value being calculated at  $217.7143 \text{ GPa} \pm 25\%$  error.

For sample no. 4, seven indentations were performed. Hardness started to vary from 8308 MPa up to 10328 MPa, having a mean value of  $8996.8 \text{ MPa} \pm 8\%$ . Values for elastic modulus started at 128.46 GPa and ended at 187.93 GPa, mean value being  $148.3 \text{ GPa} \pm 14\%$  error.

### 3.3. Friction coefficient: wear tests

On sample no. 1 three wear tests were performed.  $\mu_{\min}$  coefficient had values between 0.07 and 0.245, its mean value being  $0.1746 \pm 60\%$  error.  $\mu_{\max}$  coefficient varied between 0.787 and 0.829, having a mean value of  $0.815 \pm 3.5\%$ .  $\mu_{\text{average}}$  coefficient started at 0.526 up to 0.555, its mean value being calculated at  $0.54 \pm 3\%$ .

Three wear tests were done for sample no. 2 also.  $\mu_{\min}$  coefficient values varied from 0.206 to 0.248, its mean value being  $0.2213 \pm 12\%$ .  $\mu_{\max}$  coefficient varied between 0.682 and 0.752, mean value being  $0.712 \pm 10\%$  error.  $\mu_{\text{average}}$  coefficient had values starting at 0.397 up to 0.474, its mean value being calculated at  $0.445 \pm 10\%$ .

On sample no. 3 was performed only one wear test.  $\mu_{\min}$  coefficient had a value of 0.262,  $\mu_{\max}$  coefficient's value was 0.399 and 0.317 for  $\mu_{\text{average}}$  coefficient.

Four wear tests were done for sample no. 4.  $\mu_{\min}$  coefficient values varied between 0.209 and 0.231, its mean value being calculated at  $0.219 \pm 5\%$ .  $\mu_{\max}$  coefficient varied from 0.789 to 0.867, mean value being  $0.825 \pm 5\%$  error.  $\mu_{\text{average}}$  coefficient had values starting at 0.572 up to 0.675, its mean value being calculated at  $0.622 \pm 8.5\%$ .

## 4. Comparative discussions

Analyzing the critical loads Lc<sub>1</sub>, Lc<sub>2</sub> and Lc<sub>3</sub> for all sample (figure 5) it can be stated that the best adhesion (that means the highest value for Lc<sub>1</sub>/ Lc<sub>2</sub>/ Lc<sub>3</sub>) was obtained for sample no. 3 (obtained at high temperature and by using of N<sub>2</sub> as reactive gas and bias voltage at 0.5 kV) and the lowest adhesion was obtained for sample no. 2 (achieved at low temperature and without bias voltage and reactive gas).

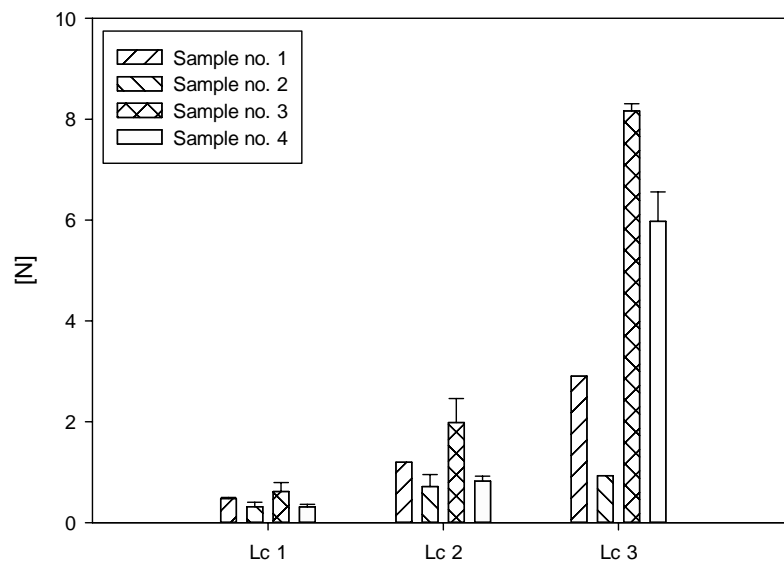


Figure 5. Scratch test's comparative results.

The highest value of the hardness was obtained for sample no. 3 (obtained at high temperature and by using of  $N_2$  as reactive gas and bias voltage at 0.5 kV) and the worst hardness value was obtained for sample no. 2 (achieved at low temperature and without bias voltage and reactive gas).

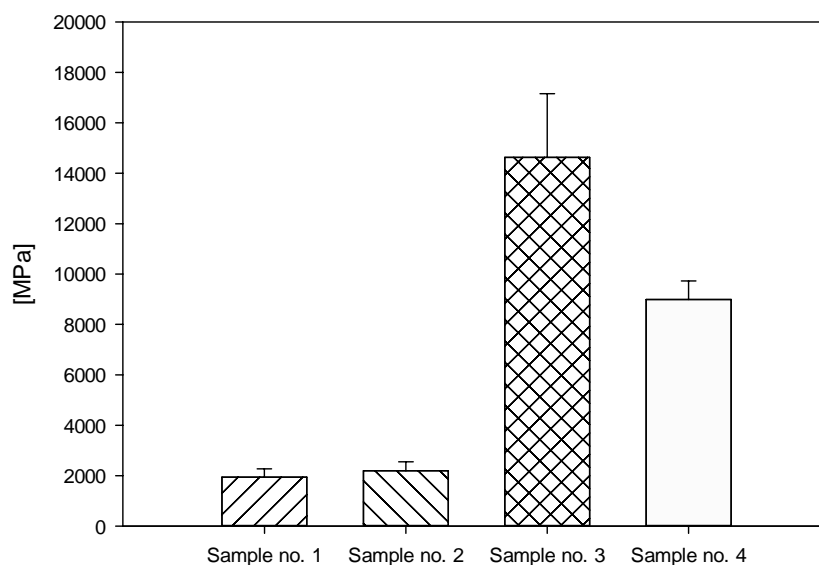


Figure 6. Hardness test's comparative results.

Also, the highest value of the elastic modulus was obtained for the same sample no. 3 (obtained at high temperature and by using of  $N_2$  as reactive gas and bias voltage at 0.5 kV) and the worst elastic modulus value was obtained for sample no. 2 (achieved at low temperature and without bias voltage and reactive gas) and for sample no. 4 (obtained without bias voltage for substrate and reactive gas).

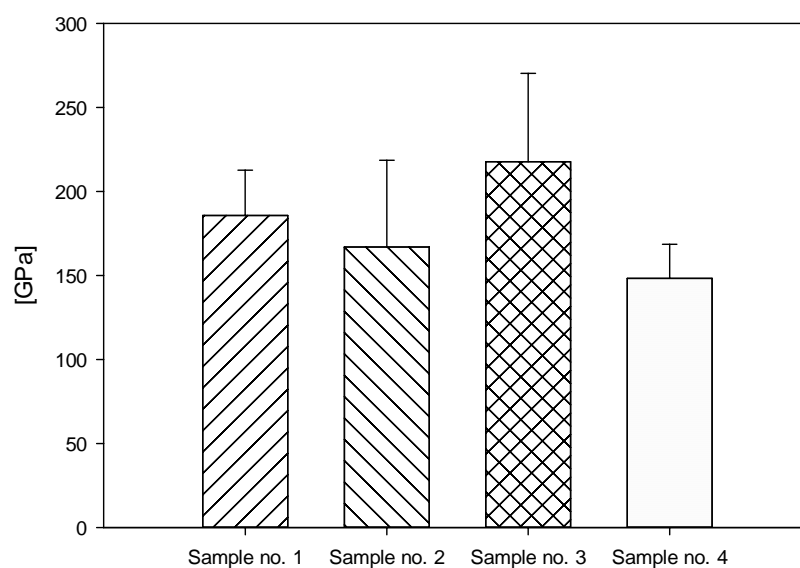


Figure 7. Elastic modulus comparative results.

All the samples have average friction coefficients with almost the same values (close to 0.4). The lowest friction coefficient ( $\mu_{\text{average}}$ ) was obtained for sample no. 3 that was achieved with  $\text{N}_2$  as reactive gas and 0.5 kV as bias voltage.

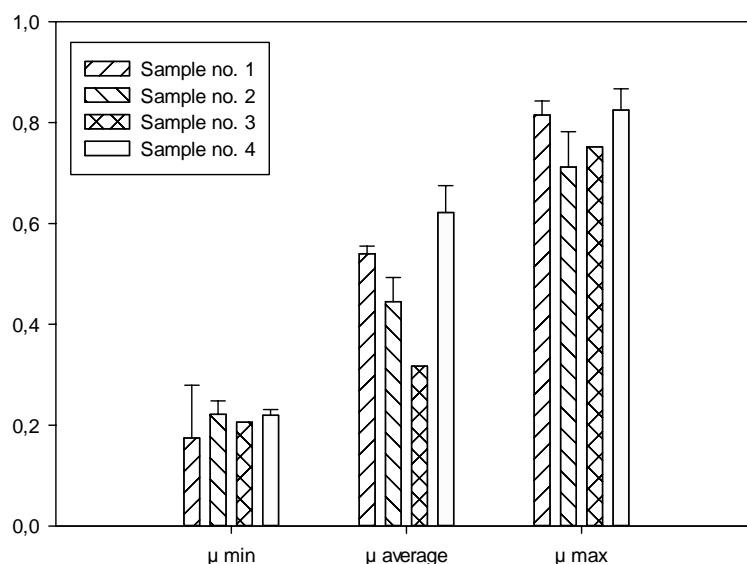


Figure 8. Friction coefficients comparative results.

## 5. Conclusions

Sample no. 3, deposited at 550 °C, with  $\text{N}_2$  as reactive gas and 0.5 kV for substrate polarization, has the best mechanical characteristics (hardness and elastic modulus) and also lubricant properties (represented by  $\mu_{\text{average}}$ ).

In theory using  $N_2$  as a reactive gas during the deposition process would mean that  $N_2$  gas atoms deposit on the surface and create hard particles that don't help in achieving dry lubrication. But if the used gas concentration is not so large, the  $N_2$  deposited particles can create on the sample a wear resistant layer without degrading the dry lubrication properties of the surface (just like in case of sample no. 3), resulting as a plus for the deposited sample (the film is not so easily destroyed in case of wear tests).

Hardness and elastic modulus values are varying quite much for each sample from one test to another, meaning that the used technique for deposition is not perfect and should be improved for the deposited thin films to be more homogeneous along all the sample's surface. For this reason, the deposition time should be considerably increased, having in mind though not to increase a lot the thickness of the thin films.

By increasing the deposition time and the thickness of the deposited layer, the film should become also more wear resistant (gaining cumulative properties for industrial usage), so this hypothesis should be put to test as soon as possible for finding the best recipe.

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