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FRICTION AND WEAR PROPERTIES OF CARBON NANOWALLS COATINGS

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In this paper Carbon nanowalls (CNW) coatings deposited by radiofrequency plasma jet are used for tribological investigations in the presence of low sulfur diesel fuel and in conditions of dry lubrication. The tribological behavior was investigated by high frequency reciprocating rig (HFRR) test, while the wear tests were run on a Pin on Disk CSM tribometer. The CNW layers before friction tests were investigated by scanning electron microscopy (SEM), while the wear on the steel balls and disks after friction tests was investigated by SEM and EDX. The study leads to the conclusion that CNW possesses attractive tribological potential and deposition of carbon nanowalls on steel disks results in a decrease in friction and wear rate. It was found that the lubrication environment and the height of the coatings have strong influence of the friction coefficient and wear rates, thicker carbon nanowalls lead to lower friction coefficient and less wear on the friction surface.

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Keywords: carbon nanowalls; nanosheet; anti-wear coatings; dry lubrication

1. Introduction

The supply of the fossil resources is inherently finite and the quality of the crude oil becomes increasingly worse and makes it unsuitable for refining. The average crude oil density declines from 34.0°API (American Petroleum Institute) in 1980 to 30.2° API in 2020 while the sulfur content increases with decreases of the API density [1]. Usually, the sulfur-components from crude oil have been found to be natural lubricating compounds but can generate several problems such as air pollution caused by combustion, corrosion of materials due to acid rains and poisoning of the most petrochemical catalysts, therefore it is compulsory the removal of these compounds [2-6]. Nowadays, environmental regulations limit the sulfur content from diesel fuel to 10 ppm. Unfortunately, ultra low diesel fuel has improper lubrication properties and may rapidly wear out the elements of the engine and of the injection system. Addition of biodiesel in diesel fuel can restore the lubricity of low sulfur diesel fuel [7-9]. An alternative to biodiesel to improve the lubricating properties of low sulfur diesel fuel can be carbon nanomaterials [10-14].

Utilization of carbon nanomaterials coatings to reduce the friction of the counterparts being in sliding motion is a new research topic. It is already proved that carbon nanomaterials such as single wall carbon nanotubes-SWNTs, multiwalled carbon nanotubes-MWNTs or fullerene have interesting tribological properties and are very efficient as additives for fluids lubrication [10-14]. In this paper, we carried out investigations of the friction and wear properties of CNW coatings synthesized by radiofrequency plasma beam deposition on metallic surfaces. In our previous investigation we reported interesting tribological features of CNW and other carbonaceous species and allotropes (i.e. graphite, single wall carbon nanotubes and multiwalled carbon nanotubes) in wet lubricating conditions, the coating being in direct contact with low sulfur diesel fuel during the friction tests [15]. In this paper we studied friction and wear properties of

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CNW coatings grown on AISI-E 52100/535A99 stainless steel disk, under dry lubricating conditions by using a steel ball as a counter surface and we compared the results with that obtained in wet lubricating conditions.

2. Materials and experimental methods

Our previous study [16-17] presents the synthesis process of CNW coatings by radiofrequency plasma jet deposition, as well as the characterization methods such as SEM by using a Hitachi S-3400N scanning electron microscope with SE detector working at 30 kV and maximum resolution of 5 nm coupled with EDX which allows determination of the chemical composition of the surfaces.

In this study, the friction and wear properties of different sizes CNW deposited on steel disks were investigated by HFRR (High Frequency Reciprocating Rig) test and Pin on Disk tribometer and the morphology of the surfaces was investigated by SEM.

2.1. Materials

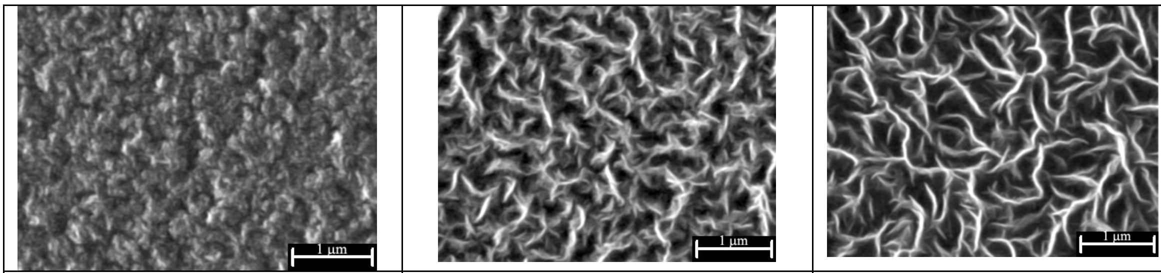
2.1.1. Preparation of CNW coatings by plasma synthesis

For obtaining carbon nanowalls layers, we used an Ar plasma jet fed with H_2/C_2H_2 mixture at 25/1 gas flow ratio. Stainless steel AISI-E 52100/535A99 disks heated at

700^o C were used as support. For comparing the tribological properties of CNW, we have coated the disks with CNW having various dimensions (length and high) and degrees of graphitization. As we demonstrated before the easiest way for changing the CNW dimension (length and graphitization) are the variations of $Ar/H_2/C_2H_2$ gas flow ratio [17]. Here, we changed the Ar flow of 700, 1050 and 1400 sccm in order to obtain a set of samples labeled here as CNW700, CNW1050 and CNW1400. During these samples preparation the other parameters were kept the same (H_2/C_2H_2 at 25/1sccm, 300W, 700 C, 60 minutes deposition time).

2.1.2. The characteristics of CNW coatings

The morphology of CNW layers were investigated by SEM investigations and SEM images are presented in Figure 1.



a) b) c)

Fig.1. Morphology of (a) CNW700, (b) CNW1050 and (c) CNW1400 coated disk samples

The top-view SEM images from figure 1 reveal the morphology of the CNW coatings. From SEM images, it is obvious that the coatings consist of interconnected network of lamellar flakes oriented perpendicular on the substrate. The previous investigations of CNW [16-18] showed that the flakes were assembled from layers of small graphene domains.

The dimensions of CNW were estimating from grey level of SEM images by eyes inspection, followed by sets of more than 10 measurements for each samples, resulting an average and error calculate as standard deviation [18]. By increasing the Ar mass flow rate from 700 sccm to 1400 sccm, the CNW length increased from 0.26 ±0.1 μm to 1.2±0.2 μm in the case of CNW1400. Also, the thicknesses of the layers were increased from 1 μm for CNW700 to about 5 μm in the case of CNW1400, as we found in SEM cross section investigations (not presented here). As concerning the structure, our previous TEM investigations showed the increase of the graphene domain with the flow rate, which was confirmed by the increase of I2D/IG ratio in the Raman spectra [14].

2.1.3. Low sulfur diesel fuel

The friction and wear properties of carbon nanowalls were first investigated in the presence of low sulfur diesel fuel, which was chosen as lubrication fuel because of its poor lubrication properties due to its low sulfur content. The physical characteristics of the low sulfur diesel fuel are presented in table 1.

Table 1. Physical-chemical properties of low sulfur diesel fuel

Properties	Results	Methods
Specific gravity (25°C, kg/m^3)	826.2	ASTM D-1298
Total Sulfur (wt %)	0.0017	ASTM D-2622
Viscosity at 40°C, cSt	4.12	ASTM D-455
Cetane number	49.2	ASTM D-613
Cloud point, °C	-20.0	ASTM D-2500
Distillation °C	-	ASTM D-86
IBP	185.8	
50%	248.2	
EP	365.9	
Hydrocarbon type, % vol	-	ASTM D-1319
Aromatics	28.8	
Olefins	1.9	
Saturates	69.3	
Lubricity WS1.4, μm	636	ASTM-D6079

2.2. Lubricity and wear tests

The lubricity investigations were performed by HFRR test according to ASTM D-6079.

The HFRR test consists in friction of an AISI-E 52100/535A99 steel ball (with a roughness of Ra=0.050 μm and a hardness of RC 58-66) against an AISI-E 52100/535A99 disk (with 10 mm diameter and a roughness of Ra=0.020 μm and a hardness of RC 76-79) in the presence of 2 ± 0.2 ml lubricant at a frequency of 50 ± 1 Hz, 1000 um stroke, 200 ± 1 g load and 60 ± 2°C, cycles 90000 (according to ASTM D-6079). The relative humidity was kept between 40 and 60%, while the ambient temperature was between 24 and 26°C. HFRR results indicate the lubricating ability of the fuel by measuring the diameter of the wear scar imprinted on the steel ball. A high value of the wear scar diameter indicates a poor lubricity efficiency of the fuel. The quoted wear scars are corrected to give the WSD values at a pressure of 1.4 kPa (denoted WS1.4). According to international standards the maximum wear scar diameter allowed for diesel fuel is limited to 460 μm [14]. The high number of cycles achieved during the tests (90 000) was chosen to provide information on the capacity of CNW to preserve their tribological performances in time.

The Pin on Disk tribometer allows determination of the friction coefficient and wear rate on ball and disk under sliding friction torque for class I (ball on plane). The wear test consist in friction of a 100Cr6 steel ball with 6 mm diameter against a 41MoCr4-2 steel disk with 30 mm diameter, in the presence of 20 ± 0.2 ml lubricant at, 4 N load and 0.15 m/s sliding speed.

Steel ball has a roughness of Ra=0.060 μm and a hardness of RC 60-62 while the steel disk had roughness of Ra=0.020 μm and a hardness of RC 25-27.

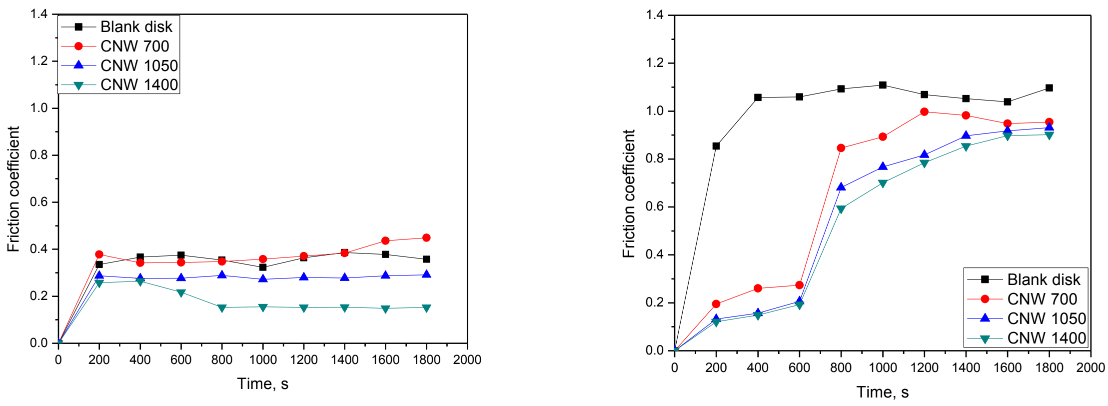
The relative humidity was 30%, while the ambient temperature was between 22-24°C [14].

3. Results and discussion

3.1. Comparison of lubrication parameters of coated surfaces in wet and dry lubricating environment

Dependence of lubrication properties upon lubrication environment

In Fig. 2 is plotted the variation of friction coefficients after ball on disk friction investigation, where disks were coated with various sizes CNW. The tests have been performed in wet environment by using low sulfur diesel fuel such as lubricant (fig. 2a) or in dry sliding conditions (fig. 2b). From graphs it is obvious that the lubricant, even with poor lubrication properties, improve the friction, the friction coefficient almost doubled in dry friction conditions. In the case of wet lubrication environment, from figure 2a it is evident that height of the CNW coatings has a strong influence on friction coefficients thus, the sample with the lowest height CNW700 (about 1 μm) gives the highest value of the friction coefficient, while the thickest layer CNW1400 (about 5 μm) provide the lowest value for the friction coefficient, with about 50% lower than that corresponding to the CNW700.



a) b)

Fig. 2. Friction coefficients after ball on disks coated with various sizes CNW lubricity tests in a) wet environment and b) dry sliding conditions

Interesting findings were observed for friction investigation in the absence of any lubricant, the CNW coatings having the function of a protective layer. Figure 2b shows the friction behavior in dry sliding conditions. In the first 10 minutes, the recorded friction coefficient is much lower than observed in wet lubricating conditions, probably because the graphene layers protect the metallic surface of the disk. After 10 minutes, the graphene layers are destroyed, favoring metal on metal friction, therefore the value of the friction coefficient almost triples. The influence of the height of the CNW coatings is similar to that observed for wet lubricating sliding tests respectively, the highest value of the friction coefficient was achieved for CNW700 while the lowest friction coefficient for CNW1400.

In figure 3 is presented the average friction coefficients after ball on disks coated with various sizes CNW lubricity tests, the results being compared with those observed for friction tests on ball on blank disk uncoated with CNW.

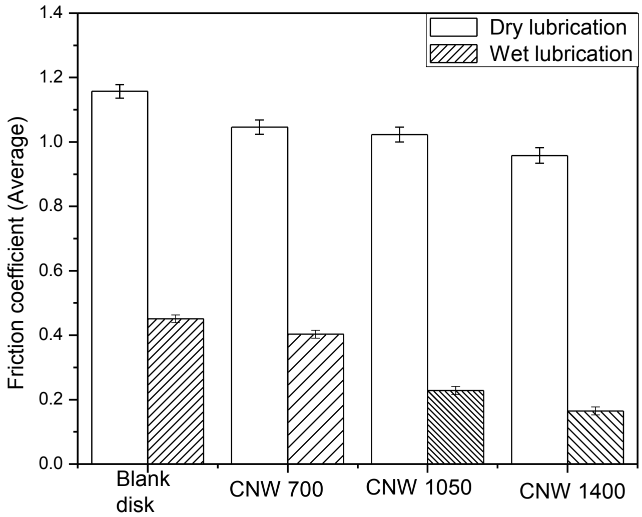


Fig. 3. The average friction coefficients after ball on disks coated with various sizes CNW lubricity tests

These results proved that CNW are very effective in reducing friction with about 20% less than friction coefficient recorded for the uncoated disk. In dry lubrication conditions, the most efficient carbon nanowalls coating was found to be CNW1400 with a friction coefficient lower with about 26 % than that recorded for the blank disk and the less efficient was CNW700 with a friction coefficient lower with about 20 % than that corresponding to the uncoated disk. Actually, the thickness of the carbon nanowalls layers has a strong influence on friction coefficients, the most effective carbon nanowalls coating being that with higher thickness, respectively CNW1400, while the less effective was found CNW700 with lower thickness. Similar tendency was observed for investigations performed in wet lubricating conditions but friction coefficients were found to be much lower than in dry lubricating conditions, the low sulfur diesel fuel being a better lubricant than air.

3.2. Study of the lubrication properties of CNW by HFRR; results on ball

One of the most important characteristic of low sulfur diesel fuel is the lubricating capacity measured as wear scar diameter imprinted on the steel ball after friction tests.

In figure 4 is depicted the variation of the corrected wear scar diameter, quoted WS 1.4, with the thickness of the CNW coatings, in wet and dry lubrication environment.

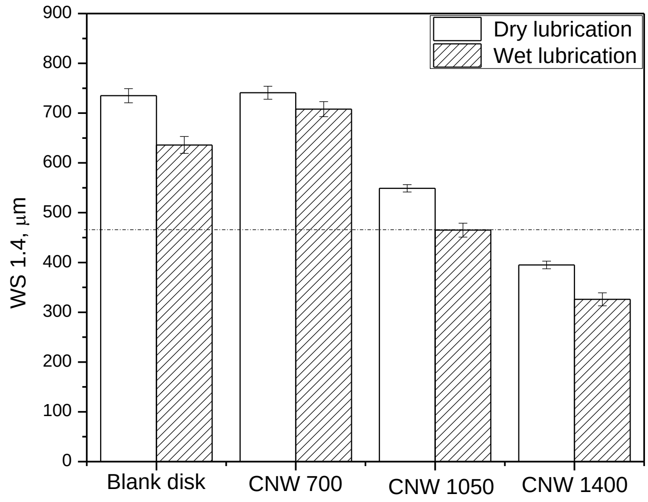


Fig. 4. Wear scar diameters (WS 1.4) of scars imprinted on steel ball after friction on disks coated with various sizes CNW, in the presence or absence of lubricant

In wet lubrication environment, was observed that wear scar diameter is strongly influenced by the height of the carbonaceous coatings, the results for the lowest height coating CNW700 being not promising, the wear scar diameter was superior to the value recorded for the non additivated diesel fuel and much higher than the value imposed by the standards. This result coupled with SEM images from figures 5a and 5b show that during the friction tests, the sample with the smallest value of the thickness is destroyed faster and the friction is taking place in the boundary lubrication domain where a metal-metal friction might occur. However, by coating the surface of the metallic disks with CNW1050 and CNW1400 the wear scar diameters decrease under the value imposes by the standards, respectively 460 μm. The tendency is similar in dry lubrication environment, but only by coating the metal disk with CNW1400 we achieved smaller wear scar diameter than compelled by European regulations.

3.3. Study of the wear track on CNW coated steel disks after friction in dry and wet lubrication environment

The results for the friction coefficients and wear scar diameters are in agreement with the wear rates on ball and disk calculated and depicted in tables 2 and 3. In table 2 are presented the results observed in wet lubrication environment and is easy to observe the same tendency for the wear rate evolution as seen for the friction coefficient and WS 1.4. Minimum wear rate on ball and disk was achieved for the coating with the highest thickness, respectively CNW1400, while the maximum wear rate on ball and disk was recorded for the coating with lowest thickness CNW700.

Table 2. Wear rate on ball and disk in wet lubricating conditions

Sample	Max. Hertzian Pressure [GPa]	Wear rate on ball [mm^3/N/m]	Wear rate on disk [mm^3/N/m]
Blank Disk	1.025	7.350E-007	4.081E-005
CNW 700		5.632E-008	2.219E-006
CNW 1050		4.178E-008	1.835E-006
CNW 1400		3.761E-008	1.465E-006

In table 3 are presented the results observed in dry lubrication environment. In addition to their friction reduction properties, the CNW1400 coating has reduced the wear rate significantly during the tests. The highest value of the wear rate on ball and disk was calculated for CNW700. As expected, the wear rates in dry lubricating environment are much higher than that achieved in wet lubricating conditions.

Table 3. Wear rate on ball and disk in dry lubricating conditions

Sample	Max. Hertzian Pressure [GPa]	Wear rate on ball [mm^3/N/m]	Wear rate on disk [mm^3/N/m]
Blank Disk	1.025	6.670E-005	5.331E-004
CNW 700		4.565E-005	4.704E-004
CNW 1050		4.008E-005	4.151E-004
CNW 1400		3.562E-005	3.802E-004

In addition to the friction coefficients, wear scar diameters and wear rates recorded for different heights of carbon nanowalls coatings, the surface morphologies of the track wear on balls and disks was investigated by SEM. In figure 5 are presented the SEM images of the wear scars of coated disks with different sizes CNW and for uncoated balls used for the friction tests on corresponding coated disks. SEM images are relevant for wear damage mechanism of thick and thin CNW coatings. For thin coating corresponding to CNW700, we can observe from figure 5a that the coating is easily destroyed and carbonaceous particles appear on the metallic surface. As concerning the surface morphology of the ball it is seen from figure 5b that the wear track is noticeable. In order to evaluate the wear resistance of various sizes coating, similar SEM investigation were performed for thicker coatings CNW1050 and CNW1400. The results are presented in figures 5c-d for CNW1050 and 5e-f for CNW1400.

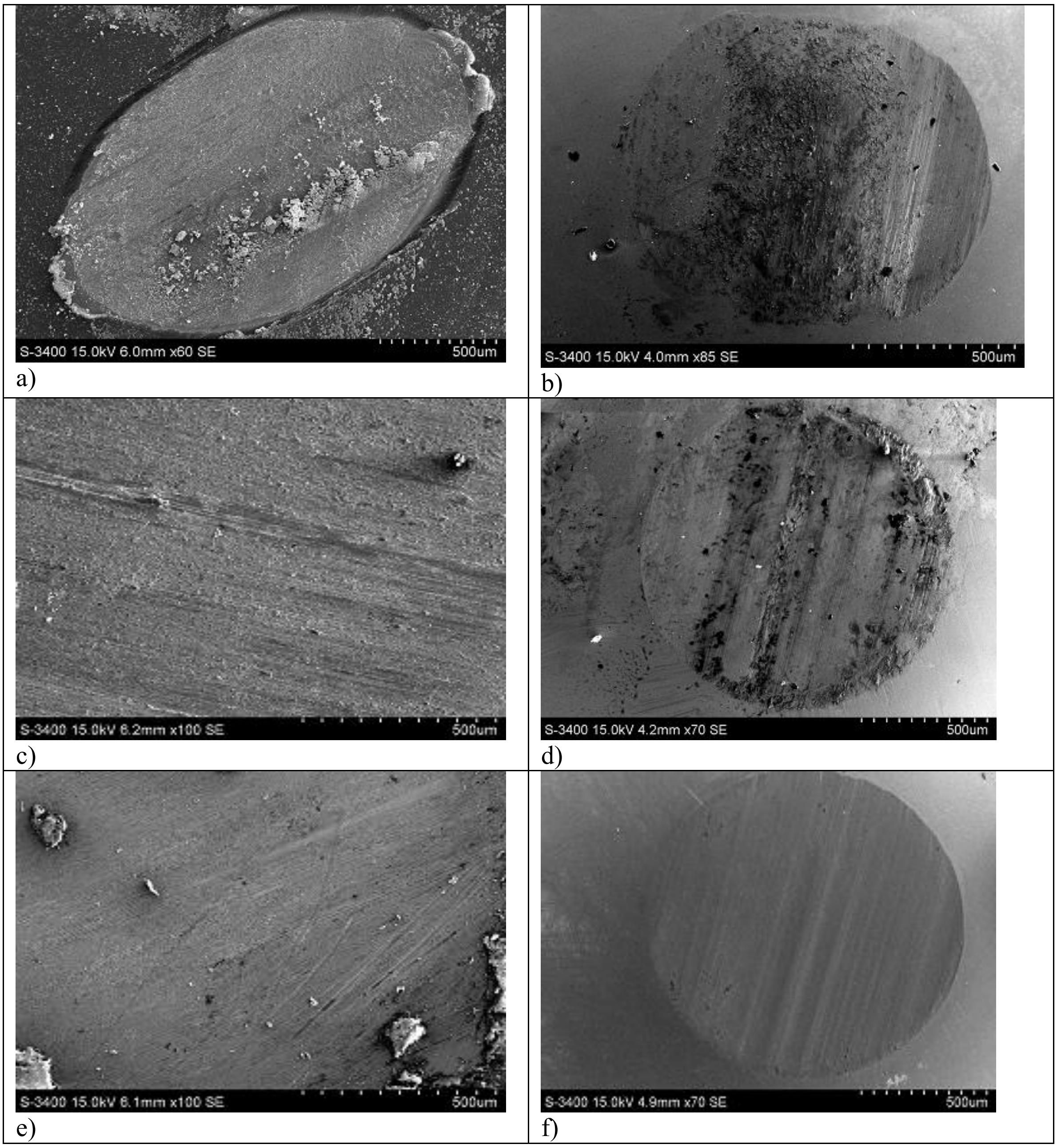


Fig. 5. SEM images of wear scars of coated disks with (a) CNW 700 (c) CNW 1050 (e) CNW 1400 and for uncoated balls use for the friction tests on corresponding coated disks with (b)CNW 700, (d) CNW 1050 and (f) CNW1400

Based on these images, thicker coatings do show better scratch and wear resistance than thinner coatings. This is probably due to better load-carrying capacity of the thick coatings as compared with the thinner ones.

To prove that there is a correlation between the friction coefficient and chemical composition and thickness of the coating, we analyze the chemical composition of the coated surfaces before and after friction tests (figure 6).

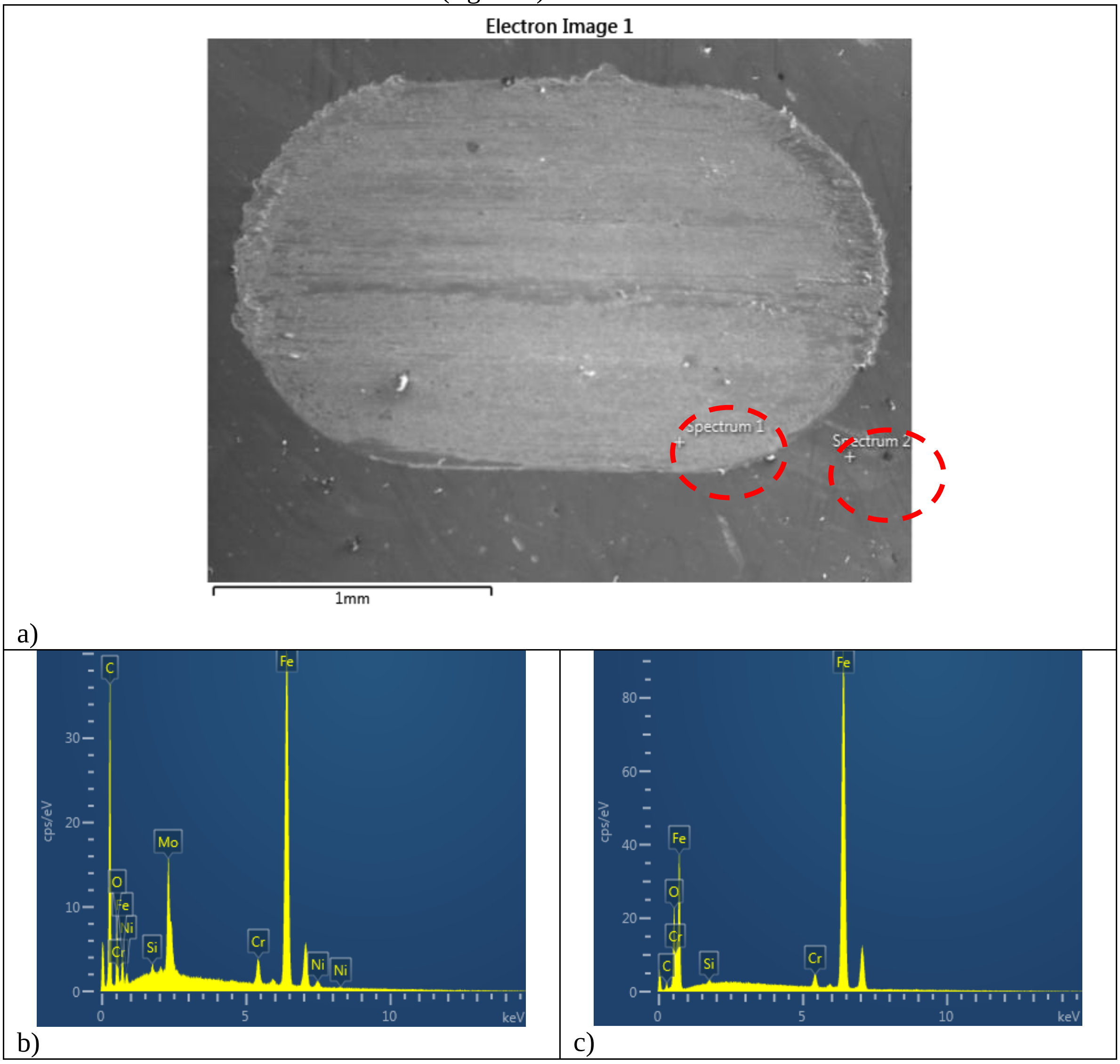


Fig. 6. EDX analyses of CNW700 for b) surface unaffected by friction and c) surface after friction test

In order to confirm that the friction and wear reduction observed were the results of the coating of the metal disks, we analyzed the chemical composition of the uncoated disk (table 4) and of the coated surfaces before friction (table 5) and after friction tests (table 6).

Table 4.Chemical composition of the AISI-E 52100 disk

Component	wt%
C	1.100
Fe	95.850
Cr	2.600
Mn	0.250
P	0.025
Si	0.150
S	0.025
Total	100.0

From table 5 we discovered interesting findings, the carbon content of the coatings increases with the thickness of the carbonaceous material, while the iron content decreases with the height of the carbon nanowalls. These results are not astonishing because for higher heights of the coatings, the X-Ray beam does not reach the metal surface of the disk; therefore the iron and chromium, which belong to the metal disk, decrease with increasing of the coating thickness.

Table 5.Chemical composition of the coated surfaces before friction tests

Component, wt%	CNW700	CNW1050	CNW1400
C	46.5	81.3	83.6
Fe	34.7	9.5	1.2
Cr	1.6	1.4	ND*
Other	17.2	7.8	15.2

*ND not detected

After friction, the carbonaceous coating is destroyed, exposing the metal surface of the disk therefore, the carbon content of the worn surface decreases while the iron and chromium concentrations increase.

Table 6.Chemical composition of the coated surfaces after friction tests

Component, wt%	CNW700	CNW1050	CNW1400
C	3.7	5.5	13.5
Fe	83.3	76.0	74.1
Cr	2.6	1.9	1.4
Other	10.4	16.6	11.0

The EDX and SEM results demonstrate the strong influence of the thickness of the coating on friction coefficient; thicker coatings lead to smaller friction coefficients and diminished wear.

4. Conclusions

Three different sizes CNW coatings synthesized by RF plasma have been chosen to reveal how the heights of the carbon nanowalls together with the lubrication environment have a strong influence on the friction coefficients and wear rate.

CNW, possesses attractive lubrication and tribological properties, being more efficient in the presence of the lubricant, even with poor lubrication properties, rather than in the presence of air. By comparing the results of coated with uncoated disks was proved the efficiency of the carbon nanowalls in tribological investigations, the thicker CNW being more efficient than thinner ones.

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