Digest Journal of Nanomaterials and Biostructures Vol. 14, No. 4, October-December 2019, p. 907-915

IMPROVEMENT OF ANTIWEAR PROPERTIES BY COATING THE STEEL SURFACES AND BY LUBRICANT ADDITIVATION

D. L. CURSARU[a], N. GIAGKAS[a,*], S. VIZIREANU[b], S. MIHAI[a], D. MATEI[a], B. BIȚĂ[b], C. STANCU[b], A. M. MANTA[a], I. RAMADAN[a]
[a]*Petroleum-Gas University of Ploieşti, Romania*
[b]*National Institute for Laser, Plasma and Radiation Physics, Romania*

The antiwear properties of metal surfaces have been improved by applying surface coatings, and the results have been compared with those obtained by additivation of the lubricant with a classic antiwear additive. In order to enhance the antiwear properties, carbon nanowalls (CNWs) and copper coatings were applied to AISI-E 52100/535A99 steel substrate. The second phase of the experimental part was focused on the improvement of the antiwear properties of the lubricant by using an antiwear additive such as zinc-dialkyldithiophosphate (ZnDTP). Different concentrations of additive (1%, 3%, 5% and 10 wt. %) of ZnDTP were used in order to decrease the friction coefficient. It was observed that the optimum concentration of additive was found to be 5 wt. %. Carbon nanowalls (CNWs) layers obtained by PECVD and copper coatings obtained by magnetron sputtering were evaluated from friction and wear point of view by High Frequency Reciprocating Rig (HFRR) and Pin on Disk C.S.M tribometer. Composition, thickness of the layers and morphology of the surfaces were investigated by energy dispersive X-Ray spectroscopy and scanning electron microscopy (SEM). It was established that the thickness of the coatings influences the wear scar diameter imprinted on the steel ball.

(Received February 18, 2019; Accepted October 15, 2019)

Keywords: Carbon nanowalls, Copper, coatings, Friction, Wear, Antiwear additive

1. Introduction

Due to the impact of friction, approximately 23% of the world’s total energy consumption is originated from tribological contacts. Of that, 20% is used to overcome friction and 3% is used to remanufacture worn parts and spare equipment due to wear and wear-related failures [1]. This is the reason why many researches and surface engineering in general, are axed on the new surfaces, materials, and lubrication technologies for friction reduction and wear protection in vehicles, machinery and other equipments. Surface engineering involves the enhancement of certain properties of the surface of a component independently from those of the underlying substrate material. The enhancements may be in areas as diverse as visual appearance, tactile properties, optical properties, wettability, corrosion resistance or tribological behavior. There are two common objectives in the use of surface engineering for tribological applications: to increase the wear resistance or damage resistance of the component, and to modify its frictional behavior. There are many processes that a component can be surface engineered but this study was focused on the process which applies a material to the surface, referred as coating processes [2].

More studies have been done in order to reduce the mechanical friction between two metal surfaces. So far, most of the tests were based on properties of the lubricant but recent studies were focused on improving the metal surfaces [3-7]. Nowadays, an increased interest is directed toward to improve the hardness, the chemical stability, the protection against corrosion and wear. This study was focused on the modification of the surface by deposition of diverse types of coatings such as Carbon Nanowalls (CNWs) and copper coating with different thickness. Carbon Nanowalls (CNWs) are wall-like carbon structures, perpendicular to the substrate surface and are

[*] Corresponding author: giagkasnikos@ymail.com

composed by graphene sheets stacked together [8], while the copper coating is a solid, metallic copper thin film deposited on the surface of the item. Both coatings were synthesized by radiofrequency plasma beam deposition, using as substrate an uncoated AISI-E 52100/535A99 steel disk [9].

In order to investigate the antiwear properties of coatings, different friction experiments (ball on disk) were performed in the presence of a mineral base oil used as lubrication environment. Prior to investigations, the disks were coated with CNWs or copper and the results were compared to establish which coating has superior properties. These investigations were also compared with similar tests performed for the same tribosystem but for the uncoated disk, by using the same mineral oil as lubricating medium but additivated with a specific antiwear additive.

2. Materials and experimental methods

Our previous studies provide details about synthesis and characterization of CNWs, therefore this work is focused on synthesis and characterization of copper coatings and by a comparison between tribological properties of both coatings. The tribological investigations consists of HFRR and Pin on Disk C.S.M tribometer procedures of various sizes of CNWs deposited on steel disks.

2.1. Materials

2.1.1. Synthesis and characterization of CNWs coatings

Synthesis procedure of CNWs by low pressure RF plasma jet in $Ar/H_2/C_2H_2$ gas mixture, was detailed in our previous papers [9-13]. In order to obtain coatings with different thicknesses, morphology and graphitization degree, the Ar flows were modified (200, 500, 700, 1050, 1400 and 1600 sccm) while all other parameters were kept constant (H_2/C_2H_2 ratio was 25/1 sccm, RF power 300 W, substrates temperature 700^{o}C, 30 minutes deposition time) [14]. Therefore, the samples were labeled depending on the Ar flow used with names: CNW200, CNW500, CNW700, CNW1050, CNW1400 and CNW1600, respectively. This synthesis method allows to cover the substrate with uniform CNWs coatings, the Ar flow influences the surface density of the nanowalls and the thickness of the layers.

The morphology of CNWs layers was investigated by SEM (FEI S Inspect working at 20 kV and the images are depicted in figure 1. SEM investigations revealed similar tendency of morphology variation with the Ar flow rate for all CNWs samples [13]. By increasing the Ar flow rate it was possible to increase the size and thickness of CNWs, while the number of individual CNWs on substrate decreases. Our previous investigations have shown that thickness of CNW200 ~0.2 μm, CNW500 ~ 0.5 μm, CNW700 ~1 μm, CNW1050 ~4 μm, CNW1400 has almost 5 μm and CNW1600 ~7 μm [15].

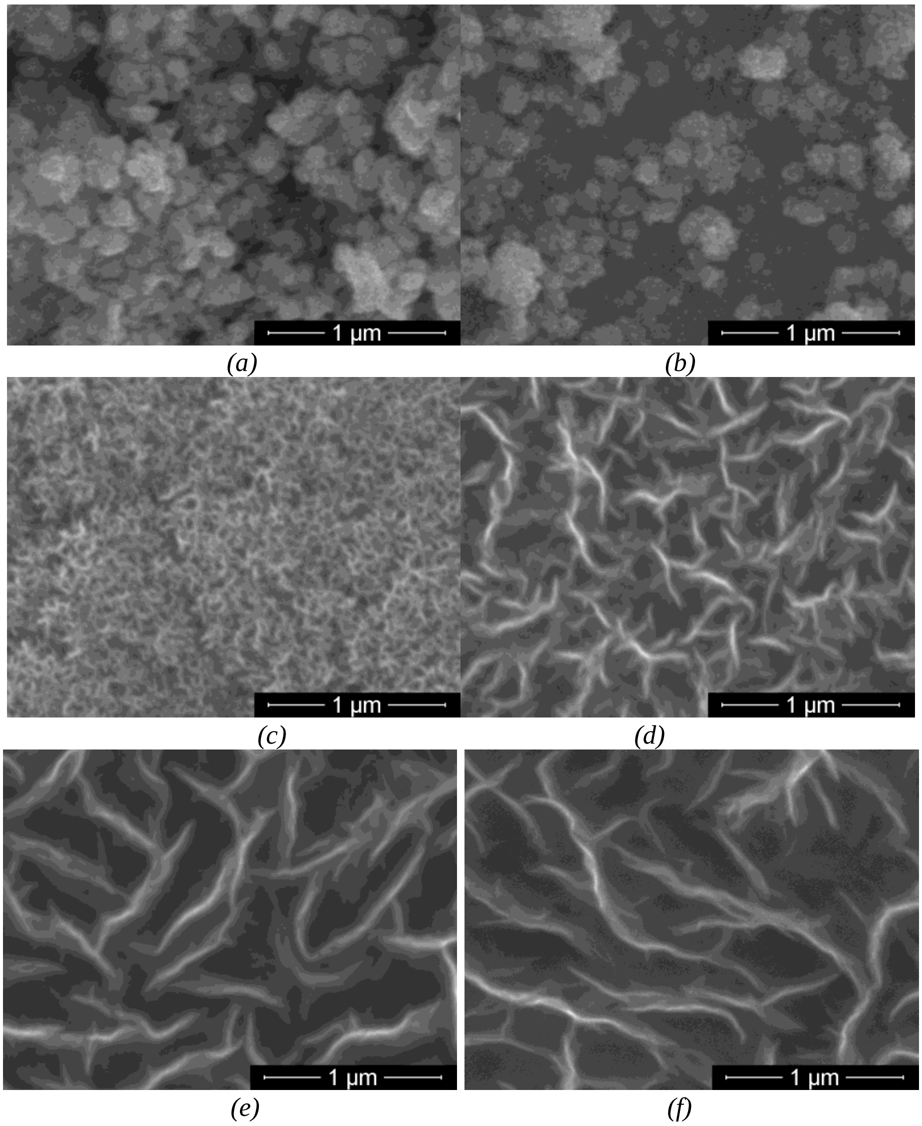

Fig. 1. Morphology of (a) CNW200, (b) CNW500 and (c) CNW700 (d) CNW1050 and (e) CNW1400 and (f) CNW1600 coated disk samples.

2.1.2. Synthesis and characterization of copper coatings

Copper coating was obtained by magnetron sputtering technique. The target was copper (99.99% purity) and steel disks of AISI-E 52100/535A99 (with 10 mm diameter, roughness of Ra=0.020 µm and a hardness of RC 76-79) were used as substrate for deposition of coatings. The magnetron sputtering was performed at low pressure RF plasma jet in Ar flow of 50 sccm/min, at RF power 100 W, and work pressure 4E-3 torr. By varying the deposition time, it was possible to modify the thickness of the coatings. By profilometry (not shown here) it was possible to depict the evolution of the copper coating thickness with deposition time (figure 2).

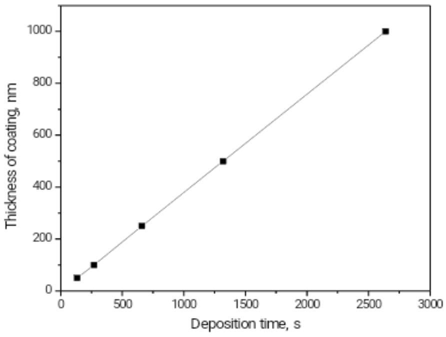

Fig. 2. Influences of the deposition time on thickness of the copper coating.

2.1.3. Base oil

In order to study one of the possibilities which decrease the friction between two surfaces, a base oil (SAE 20) was selected as lubrication fluid. The physical characteristics of base oil are described in table 1. The selected basic mineral oil has inferior antiwear properties. To improve those properties (in order to further protect the metal surfaces in the case of partial of total destruction of the film, especially under critical conditions that can occur with the progression of the tribosystem), the introduction of antiwear additives is required. For the experimental investigation zinc-dialkyldithiophosphate (ZnDTP) was selected, which is a classic extreme pressure and antiwear additive suitable for mineral base oils [17]. This additive was provided by Lubrizol.

Table 1. Physical-chemical properties of mineral base oil (SAE 20).

Properties	**SAE 20**	**Methods**
Density (20°C, kg/m^3)	880	ASTM D-1298
Kinematic viscosity (40°C, cSt)	31.80	ASTM D-445
Kinematic viscosity (100°C, cSt)	5.9	ASTM D-445
Viscosity index	130	ASTM D-2270
Flash point (°C)	>210	ASTM D-92
Pour point, (°C)	-15	ASTM D-97
Copper corrosion (at 100°C)	1a	ASTM D-130
Acid value (mgKOH/g)	0.12	ASTM D-974

2.2. Tribological investigations

High Frequency Reciprocating Rig (HFRR) equipment was used to investigate the evolution of the wear scar diameter imprinted on the steel ball affected by the thickness of the coating, while a Pin on Disk tribometer was used for determining the wear rate on ball and disk resulting after friction studies.

The HFRR investigations were performed according to ASTM D-6079 standard. Conventionally, this technique is diesel-specific, but can successfully be used for base oils or even lubricants. The equipment it is a tribosystem included in class 1, which contains triboelements such as ball and disk being in sliding motion. The test consists in friction of a steel ball AISI-E 52100/535A99 (with a roughness of Ra=0.050µm and a hardness of RC 58-66) against a steel disk AISI-E 52100/535A99 (with 10 mm diameter and a roughness of Ra=0.020µm 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 (according to ASTM D-6079). The relative humidity was sustained between 40 and 60%, while the ambient temperature was between 24 and 26°C. With this investigation it is possible to assess the effect of wear quantified as wear scar diameter imprinted on the steel ball, the friction coefficient and the mean thickness of the lubricant film during tests. A high value of the friction coefficient and of wear scar diameter indicate poor efficiency of the lubricant or the coating [9].

The Pin on Disk test consists in friction of a 100Cr6 steel ball against a 41MoCr4-2 steel disk in the presence of 10±0.2 ml lubricant at, 4 N load and 0.15 m/s sliding speed.

Steel ball with 6 mm diameter, roughness of Ra=0.060 µm and hardness of RC 60-62 were used. The disks with 30 mm diameter used for all experiments had roughness of Ra=0.020µm and a hardness of RC 25-27. The relative humidity was 33%, while the ambient temperature was between 20-23°C [16].

3. Results and discussion

3.1. Comparison of lubrication parameters of the coated surfaces

3.1.1. Study of the wear track on CNWs coated steel disks

The results of HFRR investigations were somehow surprising because by increasing the thickness of the coatings, no decrease in wear was achieved, but on the contrary, there was an increase of the wear scar diameter imprinted on the steel ball (figure 3). In order to explain this behavior, the coated disks were evaluated by SEM. In the SEM images from Figure 4, we can observe the wear scars imprinted on coated disks, after ball sliding on their surface. It seems that during tribological investigations, the CNWs coating is destroyed, probably because are soft materials, and the broken carbon walls contributes to increasing of the wear debris. Therefore, by increasing of the thickness of the coating it is expected to have more carbon debris into lubricant, which contributes overall to increasing of the wear and of the friction coefficient.

All these results are in accordance with those obtained by Pin on Disk Tribometer. The evolution of the wear scar diameter is similar to the evolution of the wear rate on ball and disk calculated and depicted in table 2. Minimum wear rate on ball and disk was achieved for the uncoated disk and the maximum was observed for CNW1600. Utilization of CNWs as coating leads to increasing of the wear rate on ball and disk.

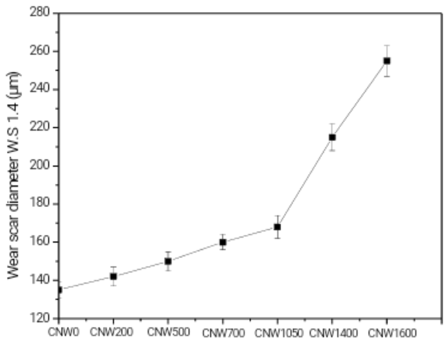

Fig. 3. Wear scar diameters for tribological investigation of CNWs coated steel disks in the presence of SAE 20 base oil as lubrication medium.

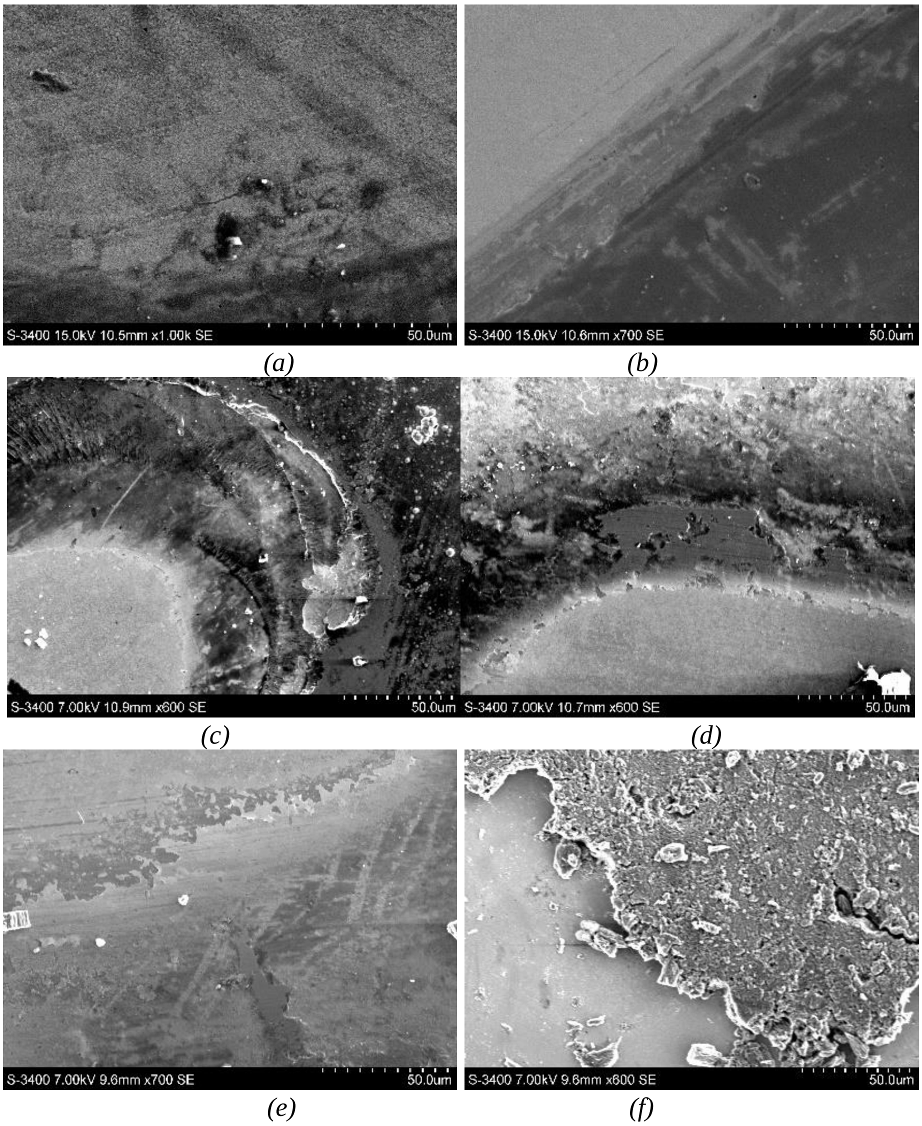

Fig.4. Morphology of (a) CNW200, (b) CNW500 and (c) CNW700 (d) CNW1050 and (e) CNW1400 and (f) CNW1600 coated disk samples after tribological investigations.

Table 2..Wear rate on uncoated balls and coated disks with CNWs.

Sample	Max. Hertzian Pressure [GPa]	Wear rate on ball [mm^3/N/m]	Wear rate on disk [mm^3/N/m]
SAE 20	1.03	6.21E-009	3.03E-006
CNWs 200 (0.2µm)		6.67E-009	3.26E-006
CNWs 500 (0.5µm)		6.90E-009	3.37E-006
CNWs 700 (1 µm)		7.36E-009	3.60E-006
CNWs 1050 (3µm)		7.73E-009	3.78E-006
CNWs 1400 (5µm)		9.20 E-009	4.50E-006
CNWs 1600 (7µm)		11.73E-009	5.74E-006

3.1.2. Study of the wear track on Cu coated steel disks

Tribological investigations on the copper coating disks reveal interesting results. By increasing the deposition time during RF synthesis, the thickness of coating increases. The HFRR investigations performed for coated disks show that wear scar diameters decrease with increasing of the thickness of the coating (figure 5). The worse result was observed for the uncoated disk, while the best result was obtained for the copper coating with highest thickness (1 µm). Although copper is a malleable metal, by coating the surface of the metallic disks, notable antiwear results are achieved; the wear scar diameters decrease with increasing of the thickness of the coating, probably because copper has an inherent flexibility that keeps the adhesion on the surface, even the substrate is subject of manipulation post depositing the coating.

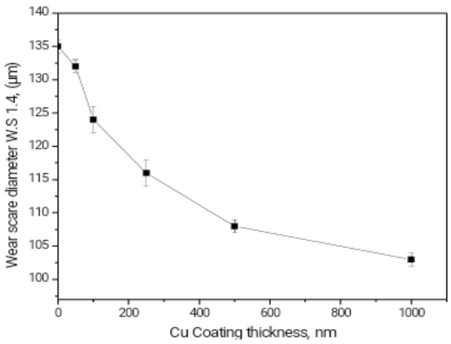

Fig. 5. Wear scar diameters for tribological investigation of Cu coated steel disks in the presence of SAE 20 base oil as lubrication medium.

The variation of the wear scar diameter with thickness of the coating is similar to the wear rate on ball and disk observed after Pin on Disks investigations, which are calculated and depicted in table 3. Minimum wear rate on ball and disk was achieved for copper coating with 1µm thickness and the maximum wear rate was calculated for the friction when the disk was uncoated.

Table 3. Wear rate on uncoated balls and coated disks with copper.

Sample	**Max. Hertzian Pressure [GPa]**	**Wear rate on ball [mm^3/N/m]**	**Wear rate on disk [mm^3/N/m]**
SAE 20	1.03	6.21E-009	3.03E-006
Cu (0.05µm)		6.07E-009	2.96E-006
Cu (0.1µm)		5.82E-009	2.78E-006
Cu (0.25µm)		5.45E-009	2.64E-006
Cu (0.50µm)		5.08E-009	2.46E-006
Cu (1µm)		4.85E-009	2.37E-006

3.1.3. Study of the wear track on uncoated steel disks in the presence of SAE 20 base oil additivated with AW additive, as lubrication medium

Conventionally, antiwear protection of surfaces has been achieved for decades by utilization of special lubricants or by utilization of lubricants with specific antiwear additives. One of the most famous antiwear additive is Zinc-dialkyldithiophosphate (ZnDTP). To compare its efficiency cu that of the coatings, 4 concentrations of additives have been used (1, 3, 5 and 10 wt.%). From Fig. 6 we can observe that the wear scar diameter had the highest value for the pure base oil and by raising the additive concentration up to 5 wt. %, the wear scar diameter decrease monotonically.

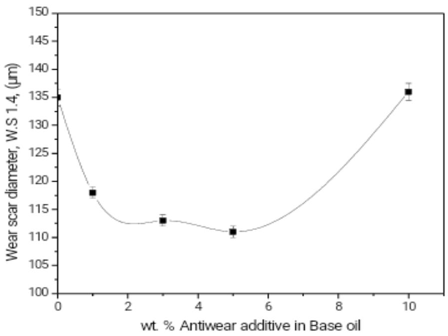

Fig. 6. Wear scar diameters for tribological investigation of uncoated steel disks in the presence of SAE 20 base oil additivated with AW additive, as lubrication medium.

Utilization of higher additive concentration (>5 wt.%) did not result in a reduction effect of the wear scar diameter, probably because the additive has been already physically or chemically adsorbed on the surface and the excess lead to an increase of the wear scar diameter and of the wear rate (table 4), even higher than the value recorded for the non additivated base oil.

Table 4. Wear rate on uncoated balls and disks.

Sample	Max. Hertzian Pressure [GPa]	Wear rate on ball [mm^3/N/m]	Wear rate on disk [mm^3/N/m]
SAE 20	1.03	6.21E-009	3.03E-006
SAE 20+1 wt.% AW		5.42E-009	2.64E-006
SAE 20+3 wt.% AW		5.34E-009	2.60E-006
SAE 20+5 wt.% AW		5.11E-009	2.49E-006
SAE 20+10 wt.% AW		6.23E-009	3.07E-006

It was observed that the optimum concentration of antiwear additive was found to be 5 wt. %. The results achieved for this concentration are comparable to that obtained in the case of utilization of copper coated disk with 0.50µm thickness.

4. Conclusions

This paper reports useful information about tribological properties of two type of coatings, one based on carbonaceous structured materials and the other, copper based. The results were compared to that obtained by modification of the antiwear properties of lubricant by adding different concentrations of a classic antiwear additive ZnDTP. From the antiwear properties perspective, it was observed that during tribological investigations, the carbonaceous coating is very fast destroyed, leading to increasing of the wear scar diameter and of wear rate. Promising results were obtained for copper coating. By increasing the thickness of the copper coating it was possible to decrease the wear scar diameter and the wear rate. When compared, the wear scar diameters achieved during HFRR investigations for CNWs coating and copper coating with the same thickness (1 µm), it is obviously that in the case of carbonaceous coating, the wear scar diameter is with 60% higher than for the copper coating. Also, the results obtained for copper coatings with thickness in the range of 0.25µm and 1µm are comparable to that observed for base oil additivated with 1-5 wt.% ZnDTP.

However, by coating the surface of the metallic disks could be an alternative to the conventional antiwear additives. A reasonable reason for choosing the more expensive coating procedure instead of additivation, could be the fact that classic additives for mineral base oils are no longer suitable for vegetable base oil and applying coating on the metallic surfaces could replace the presence of the additives. Moreover, by applying the coating it is possible to increase the corrosion resistance.

In conclusion, copper coatings obtained by RF plasma prove their utilization in tribological applications, their potential being superior to CNWs coatings, probably because the adhesion of copper to the surface is superior to that of the carbonaceous coating.

Acknowledgements

This work was supported by a grant of the Romanian Ministry of Research and Innovation, CCCDI - UEFISCDI, in the frame of Nucleus Programme INFLPR/2019 and project number PN-III-P1-1.2-PCCDI-2017-0387 /80 PCCDI EMERG2Ind, within PNCDI III

References

[1] K. Holmberg, A. Erdemir, Costs and Emissions Friction **5**(3), 263 (2017).
[2] I. Hutchings, P. Shipway, Tribology Friction and Wear of Engineering Materials, 2nd Ed, (2017).
[3] W. D. Sproul, Surface and Coatings,Technology **81** (1996)
[4] W. Tillmann, M. Dildrop, Surface & Coatings Tehnology **321**, 448 (2017).
[5] W. Ming'e, M. Guojia, L. Xing, D. Chuang, Rare Metal Materials and Engineering **45**(12), 3080 (2016).
[6] K. Bobzin, N. Bagcivan, N. Goebbels, K. Yilmaz, B.-R. Hoehn, K. Michaelis, M. Hochmann, Surface & Coatings Technology **204,** 1097 (2009).
[7] K. V. Pool, C. K. H. Dharan, I. Finnie, Wear **107**, 1 (1986).
[8] A. Malesevic, S. Vizireanu et.al, Carbon **45**, 2932 (2007).
[9] D. L. Cursaru, D. S. Vizireanu, S. Mihai, D. Ghiţă, D. S. Stoica, Gh. Dinescu, Digest Journal of Nanomaterials and Biostructures **9**(3), 1105 (2014).
[10] S. Vizireanu, A. Lazea Stoyanova, M. Filipescu, D.-L. Cursaru, Gh. Dinescu, Digest Journal of Nanomaterials and Biostructures **8**(3), 1145 (2013).
[11] S. Vizireanu, L. Nistor, M. Haupt, V. Katzenmaier, C. Oehr, G. Dinescu, Plasma Processes and Polymers **5**, 263 (2008).
[12] S. Vizireanu, S. D. Stoica, C. Luculescu, L. C. Nistor, B. Mitu, G. Dinescu, Plasma Sources Science and Technology **19**, 034016 (2010).
[13] S. Vizireanu, B. Mitu, C. R. Luculescu, L. C. Nistor, G. Dinescu, Surface and Coatings Technology, doi:10.1016/j.surfcoat.2011.07.09 (2011).
[14] S. Vizireanu, M. D. Ioniţă, R. E. Ioniţă, S. D. Stoica, C. M. Teodorescu, M. A. Husanu, N. G. Apostol, M. Baibarac, D. Panaitescu, G. Dinescu, Plasma Processes and Polumers **14**(11), e1700023 (2017).
[15] Z. Gonzalez, S. Vizireanu, G. Dinescu, C. Blanco, R. Santamaria, Nanoenergy **1**(6), 833 (2012).
[16] D. L. Cursaru, D. I. Ramadan, C. Tănăsescu, R. Rîpeanu, Digest Journal of Nanomaterials and Biostructures **8**(2), 805 (2013).
[17] T. Mang, W. Dresel, Lubricants and lubrication, Wiley-VCH, 2nd Ed. (2007).