# PHYSICS AND CHEMISTRY OF SOLID STATE

V. 22, No. 2 (2021) pp. 233-241

Section: Technology

DOI: 10.15330/pcss.22.2.233-241

Vasyl Stefanyk Precarpathian National University

ФІЗИКА І ХІМІЯ ТВЕРДОГО ТІЛА Т. 22, № 2 (2021) С. 233-241

Технічні науки

PACS: 72.20.Dp

ISSN 1729-4428

## V.I. Kyrychenko<sup>1</sup>, V.S. Ribun<sup>2</sup>, V.P. Nezdorovin<sup>1</sup>, M.B. Skladaniuk<sup>3</sup>

# Monitoring of Friction Node Surfaces in the Context of their Physico-Chemical Interactions with Lubricating Media of Different Surface Activity

<sup>1</sup>Khmelnytsky National University, Khmelnytskyi, Ukraine, <u>vikirich@ukr.net</u> <sup>2</sup>Chemical - Analytical laboratory of the PJSC Ukrnafta, Kyiv, Ukraine, <u>ribun.vika@gmail.com</u> <sup>3</sup>Vasyl Stefanyk Precarpathian National University, Ivano-Frankivsk, Ukraine, <u>skladanyuk16@gmail.com</u>

The article deals with tribochemical influence of the surface activity of biosynthetic oils on the operational efficiency and reliability of lubricated friction nodes under the critical conditions. It is proved that the oil surface activity is caused by the structure and properties of their molecules and interactions with steel surfaces. Evaluating criteria of oil tribochemical activity influence on the steel surface modification has been studied. The significant influence of biooils on the steel surface nanolayer phase transformations, friction and steel wearing is claimed. It has been established that the effect of the steel crystal structure deformation and strengthening its surface depends on activity of composition of lubricant. It is proved that biooils lead to improved friction and wear indicators of lubricated samples. X-structural analysis of the steel surfaces showed that during friction the austenite is destroyed and ferrite is formed. Penetration in the lubricated steel nanolayers shows increasing the ferrite and decreasing the austenite content, that cases reducing the deformation degree of metal crystals, which leads to the strengthening of its surface under the plasticized layer and to decreasing the level of friction and wear due to the formed intersurface servitotribopolymer film, which is stable under critical friction.

Key words: tribochemistry, steel, friction unit, biooils, surface deformation, surface activity, austenite, ferrite.

Received 23 March 2021; Accepted 10 April 2021.

### Introduction

Friction nodes as important parts of all equipments and a set of interrelated functional factors, including their design, type of materials, lubricants and mode of operation are called tribosystems. Among the whole set of factors that determine the efficiency of tribosystems, a special place is occupied by the factor of tribological quality of such elements of these systems as lubricants, in particular base oils and lubricating compositions based on them (b.ol-l.comp.). When the tribological quality of b.ol.–l.comp is talking about, it usually means such their integrated property as surface activity of friction pairs. Moreover, it is important to take into account the level of such activity, which is estimated by physicochemical properties. Therefore, as the practice of friction node operation shows, base oils are one of the important factors in controlling the process of formation of frictionresistant lubricating films, which reduce the intensity of friction and wear. Constantly growing importance of tribological quality b.ol-l.comp. over the past 25 - 30 years, caused forming a new promising and relevant branch of tribological science – tribochemistry.

In the context of development of theoretical and applied aspects of tribochemistry of lubricants, it is important to investigate the influence of structure and properties of new biosynthetic materials obtained from technical oils on tribotechnical quality of nanofilms formed between lubricated metal surfaces of friction nodes [1-4].

### I. Problem analysis

The first scientific studies of the influence of physicochemical processes that take place in friction nodes greased with lubricants and their properties, the establishment of optimal conditions for their efficient and reliable operation date back to the 60-80s of last century. The results of contemporary studies of processes, which make bases of a new and important branch of tribological science - tribochemistry, are considered in the scientific monograph "System analysis in tribonics" (H. Chihos, Translated from English -Moscow: Mir, 1982. - 352 p.) Further intensive development of scientific and technological principles of tribochemistry as an important component of tribological science, as well as analysis of the achievements of its applied part - tribotechnics, are presented in two monographs [5, 6].

Stages of tribology development in the context of systematic analysis of physicochemical processes occurring in the friction nodes under the critical conditions are considered in [5]. The paper of the authors [6] is devoted to the achievements in solving scientific and technical problems of tribology of lubricants, primarily base oils, additives, and in particular in the formation of the foundations of their tribochemistry. Scientific and technical monograph of Ukrainian scientists is devoted to the analysis of the current state and prospects of the lubricant industry development of traditional samples and biosynthetic, as well as tribochemical aspects of their use [1]. Tribotechnical features of operation of friction nodes lubricated with both traditional and biosynthetic lubricants are considered.

The whole complex of scientific and technical problems of modern tribology and tribotechnics is set out in a fundamental paper called "Tribologi-Handbuch" [7]. The paper is based on a systematic analysis of energy issues and mechanisms of diverse phenomena and processes that occur in lubricated tribosystems, as well as optimization of the conditions of their effective operating, taking into account the factor of tribomaterials and methods of tribometry.

Innovative trends in modern tribology are reflected in a monograph on such important and interrelated parts of tribology as tribocatalysis, tribochemistry and tribocorrosion [8]. The mechanism of the corresponding triboprocesses in the lubricated friction nodes operating under the critical conditions is considered in the context of the phenomenon of electron triboemission from the activated surfaces of friction pairs. "Triboelectrons" cause plastic deformation of surface nanolayers and promote the formation of energy-resistant lubricating films, and thus ensure efficient, reliable operation of friction nodes. For the first time, due attention is paid to the tribocatalysis, which has a decisive influence on the energy of chemisorption processes and tribochemical reactions in friction nodes, reducing their activation energy [9].

Of particular importance is the coverage of the results of the study of the influence of surface activity (SA) of lubricants, in particular the values of dipole moments of base oil molecules, their polarity and polarizability on the processes of their hemisorption and tribochemical reactions [10]. It is shown that the level of polarity and ability to polarize base oils significantly affects a number of surface phenomena in nanolayers of friction metals, primarily the density of dislocations and plastic deformation of surfaces, as well as their deformation hardening and as a consequence on energy and material friction criteria. [9, 11, 12].

Due attention is also paid to highlighting the shortcomings of methods for studying the surfaces of materials in general, and the surfaces of functioning friction nodes in particular, taking into account the mechanisms of friction and wear. Analysis of the essence of methods and features of their use are considered in the context of dynamics and mechanisms of physicochemical processes occuring on the surface nanolayers of lubricated friction nodes, and the efficiency of their work [1, 7, 13]. Thus, the surface activity of oils is the initiating factor of a complex of tribochemical and tribocatalytic processes that take place between the elements of the lubricating nodes of friction and, therefore, significantly affect the efficiency of their work [8, 9, 11, 12].

# **II.** Experimental

Studying the processes and phenomena that occur in lubricated with oils (lubricants in general) friction joints, the main attention was paid to the critical mode of their taking into account its functional operation, characteristics, namely: a) high energy intensity of the surface layers of friction bodies in their contact area; b) the graphical dependence of the friction coefficient (f) and the thickness of the superficial oil film (h) on the complex parameter " $\eta \cdot \upsilon \cdot F_N^{-1}$ " (where  $\eta$  - viscosity,  $\upsilon$  speed, F<sub>N</sub> - normal load), known as " Stribeck curve "; c) conditional parameter " $\lambda$ " according to the formula  $\lambda$  = h/R (where R is the root mean square value of surface roughness), and under critical friction  $\lambda \le 0.4$  [3, 4, 5].

Chemical processing of technical oils has been proposed to create alternative base oils with high SA that would meet the optimal requirements of "price - high quality - environmental safety". Taking into account these requirements, methods and technologies for obtaining a new type of biosynthetic oils, in particular bio-oils, bio-additives, technical bioliquids, biocomponents of plastic oils using oils of industry basic products [2, 3]. The specific chemical structure of molecules of such biosynthetic products (primarily basic biooils), high content in their structure of unsaturated chemical bonds and highly polar functional groups cause high levels of SA and favorable physicochemical activity in tribochemical processes of their lubricated friction nodes. Of particular practical importance was the comparison of the influence of base oils of different surface activity, namely: mineral and biooils on tribochemical interactions in the lubricated interfacial layers of friction nodes, which decrease the processes of friction and wear and, as a result, increase efficiency and reliability [1, 2].

Taking account the tribological quality of basic

#### Table 1

Values of dipole moment and polarization ability of the main chemical bonds

	$\mu$ , D $\alpha$ , cm <sup>3</sup>	Bond	μ, D α, cm <sup>3</sup>	
H-C	0.3 1.7	C=C	— 4.2	
H-O	1.5 31.9	C-O	0.36 1.5	
C-C	— 1.3	C=O	2.7 3.3	

Table 2

Force field parameters of some functional groups

	Fuctional groups			
Force field parameters				
	-OH	-C(O)-OR(-C=O)	-CH=CH-CH(OH)	
$\Delta G_{o}' / S' \cdot 10^2$ , Дж/м <sup>2</sup>	4,15	3,30	1,84	
S', м <sup>2</sup> /кмоль	1,50	2,20	0,68	

biooils (lubricating compositions based on them) as a surface activity, it is important to analyze the value of their quantitative characteristics, namely: a) polarity and polarization ability (e. g. dielectric constant) of oil molecules; b) free energy of functional groups. Both characteristics relatively reflect the peculiarities of the structure of oil molecules, and hence the energy level of their force fields. On the one hand, there is an effect on the surface activity of oils of dipole moment values ( $\mu$ , D) and the polarization ability ( $\alpha$ , cm<sup>3</sup>) of the main chemical bonds according to Table 1.

On the one hand the highest surface activity is found in those oils whose molecules contain the bonds H-O, C = C and C = O (Tab. 1). On the other hand, the surface activity of oils is affecyed by the free energy of highly polar functional groups, in particular, -OH, -C (O) -OR; -CH = CH — CH (OH) etc., according to the presented two characteristics: a) specific free energy of certain groups  $\Delta G_0' / S'$ , J/m<sup>2</sup>, b) surfaces of certain groups S', m<sup>2</sup>/kmol, which energy  $\Delta G_0'$ , kmol is distributed.

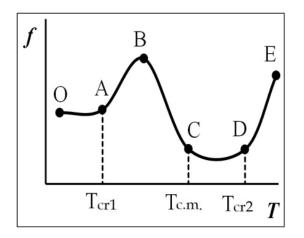
The largest values of force fields and surfaces have such groups as hydroxyl -OH and ester (carbonyl) -C (O) -OR (-C = O) (Tab. 2) [4, 6, 7].

These estimates of the level of surface activity of biooils are fully confirmed by the analysis of the proposed mathematical equations, which functionally relate the specific friction force, as well as the coefficient of friction with two types of leading performance characteristics of oil-lubricated tribosystems:

a) indicators of surface activity of oils, in particular: dipole moments, polarizability, dielectric constant;

b) energy indicators of plastic deformation of surfaces and formation of lubricating film, in particular: specific friction force, surface tension, density of surface dislocations of metal nanostructures, heat of adsorption, film thickness, etc. Analysis of mathematical dependences showed that the specific friction force decreases with increasing values of both dislocation density and activity indicators of oils ( $\mu$ ,  $\alpha$ ,  $\varepsilon$ ), as well as with decreasing film thickness (h) [11].

The tribochemical process energy of lubricated surfaces of tribosystems is characterized by the value of activation energy (Ea, kJ/mol) basing on the dependence of the friction coefficient (f) on temperature (T). The graph of the dependence is characterized by three



**Fig. 1.** Generalized dependence of the friction coefficient (f) on the temperature (T) in the tribological contact of the friction unit lubricated with tribochemically active oil [12].

transient temperature regimes: two regimes are critical with maximum values of T<sub>cr.1</sub> and T<sub>cr.2</sub>, as well as the temperature of chemical modification - T<sub>c.m.</sub> (Fig. 1). It is established that when the value of T<sub>cr.1</sub> is reached the destruction of the energetically weak adsorption boundary layer occurs, whereas under the T<sub>cr.2</sub> condition there is a destruction of the energetically stronger modified layer formed because of hemisorption influence. When process temperature reaches T<sub>ch.m.</sub>, friction node effective operation with optimization such its leading functions as antifriction, anti-wear and antiemergency due to the formed interfacial lubricating nanofilm, which has the structure of a specific quasisolid composite with low shear resistance, resistant to under extreme conditions, is provided. failure Temperatures T<sub>cr.1</sub>, T<sub>cr.2</sub> and T<sub>c..m</sub> depend primarily on the content of functionally high quality biooils (oils in general) in the lubricating film structure (composite), in particular on the level of their surface activity (polarity), as well as on the optimization of the leading operating parameters of the friction node [1, 12].

In accordance with the objectives of the study, three lubricating compositions, surface activity of which is increasing, were prepared. All the compositions are plastic lubricants formed on the basic lubricant - "Tsiatim-201" (GOST 6267-74), which is a mineral oil of medium viscosity, thickened with lithium stearate  $C_{17}H_{35}COOLi$ . This ink is intended to lubricate the friction nodes, which are operated at low loading and under the temperature within – 60 °C and 90 °C [1, 2]. Compositions 1, 2 and 3 were prepared by adding into base oil (composition-1) 25 % wt. of new biooils obtained as a result of chemical modification of technical oils. a) bio-ol-1 oil (from rapeseed oil) is added to the

base oil to obtain composition-2. b) bio-ol-2-gl oil, which is made from a mixture of rapeseed and castor (20 %) oils, is added to the base oil to obtain composition-3, which is characterized by the highest values of  $\mu$ ,  $\alpha$  and  $\Delta G_o'/S'$ , and therefore the largest surface activity (Tab. 3) [2, 3].

Tribological tests of steel samples, lubricated with the proposed prepared compositions using standardized friction machines (tribometers) to determine the main functional properties of the compositions were an important stage of the study (Tab. 4).

Table 3

Characteristics of lubricating compositions used to lubricate steel-45 surfaces during	g tribotechnical tests
of samples [2, 3]	

	of sample	5 [2, 5]	
Lubricating compositions and their triboactivity	Composition	M <sub>av.</sub> ; η, Pa∙s	Functional groups and their physical and chemical activity
Composition 1 with low triboactivity Composition 2 with medium triboactivity	Tsiatim-201 – plastic lubricant based on naphthenic oils which is thickened with lithium stearate $C_{17}H_{35}$ -C(O)-O-Li. a) Tsiatim-201 — 75% wt. b) Rest — "bio-ol-1" [R <sub>HFA</sub> -C(O)-OCH <sub>2</sub> ] <sub>2</sub> , M = 650, v <sub>100</sub> 1012 mm <sup>2</sup> /s, R <sub>HFA</sub> -C(O) – groups of rapeseed oil HFA; where R - C <sub>17:1</sub> H <sub>33</sub> -, C <sub>17:2</sub> H <sub>31</sub> -, C <sub>17:0</sub> H <sub>35</sub> -; -C-CH <sub>2</sub> -CH <sub>2</sub> -O ethylene glycol dioxyl residue [11].	~350; 1800 Pa·s (0°C, 10 <sup>-1</sup> sm) ~430, 1500 Pa·s (0°C, 10 <sup>-1</sup> sm)	C <sub>17:0</sub> H <sub>35</sub> C(O)O <sup>-</sup> has medium surface activity determining by physical adsorbtion and Wan der Waals forces. -C(O)-O-; [-C(O)-O-CH <sub>2</sub> ] <sub>2</sub> ; -CH=CH- ; [-CH=CH <sub>2</sub> ] <sub>2</sub> -CH <sub>2</sub> ; have medium surface activity determining by; adsorbtion and particly by plastic deformation effect of complexation.
Composition 3 with high triboactivity	a) Tsiatim-201 — 75% wt. b)Rest — "bio-ol-2 consisting of: $[R_{HFA}-(OH)-C(O)-OCH_2]_2$ and $R_{HFA}-(OH)-C(O)-OCH_2-$ -CH <sub>2</sub> -OH, $M_{cep}.493$ , $v_{100}$ 8 - 10 mm <sup>2</sup> /s, where $R_{HFA}$ – rapeseed oil residues; $R_{HFA}$ (OH) – residues of OH-containing ricinoleic acid C <sub>17:1</sub> H <sub>31</sub> (OH)- [11].	~410, ~1400 Pa·s (0°C, 10 <sup>-1</sup> sm)	-OH, CH=CH-CH(OH)-, [-C(O)-O-CH <sub>2</sub> ] <sub>2</sub> , -CH=CH-, [-CH=CH <sub>2</sub> ] <sub>2</sub> -CH <sub>2</sub> groups with high surface activity caused by tribochemical reactions and expressed plastic deformation effect.

Notes: M,  $M_{av}$  – molecular and average molecular weight;  $\eta$ ,  $v_{100}$  - viscosity, respectively, dynamic, kinematic at 100oC, HFA - high fatty acids

#### Table 4

Basic functional operations and characteristics of tribotechnical tests of experimental samples of steels on

			tribometers	[9]			
Regulatory documents	Friction couple of tribometer, types of steel	Test temperature, t °C	Rotation frequency W <sup>-1</sup> , Hz	Typical loading, H	Tribological indicators	Friction tsting mashine	
	types of steel	.,	ng of antifricti	on properties		masinine	
ASTM D 6425-99	Mashine CHЦ-2 of SRV, Planes of reciprocating motion, Steel-45	50	110-300	4MPa	Coefficient of friction (during 2 hours)	Optimol; CMЦ-2; SRV; BПС-1	
	Measuring of antifriction properties						
ASTM D 4172-94	Four balls, Steel IIIX-15	75	1200	147 (15); 392 (40)	Diameter of wear spots, d <sub>ws</sub> , mm	Falex; ЧКМ-К1М	
	Measuring of anti scuffing properties						
GOST 9490-75 ASTM D 2783-88	Four balls, Steel IIIX-15	20	1460	Step (10s) magnification from 196 (20) to 9800 (1000)	Load, H: a) critical P <sub>cr</sub> ; б) welding P <sub>w</sub> ; в)індекс задиру Із.	ЧКМ-К; ЧКМ-1М; Falex; Extrem Pressure (ЕР)	

Tribotechnical tests of lubricated with prepared compositions (Tab. 3) steel 45 (HB 193) samples were carried using SMTs-2 modified tribometer configured to implement reciprocating mutual movement of friction surfaces which were studied using X-ray structural analysis. The average speed of relative movement of the samples is 0.4 m/s; contact pressure - 4 MPa, oscillation frequency —110 min<sup>-1</sup>. The results of tribological tests of lubricated with prepared compositions Steel 45 and Steel SHH-15 samples on SMTs-2 modified tribometer are given in Table 5.

Investigation of the surfaces of Steel 45 both in the initial state and after testing on a tribometer in order to estimate the effect of each lubricating composition (1, 2, 3) (Tab. 5) on the structure and properties of steel thin surface layers was carried basing on the modern method of X-ray structural analysis, namely the method of a sliding beam of X-rays (X-) [3, 4]. The thickness of the studied steel layers is determined by the inclination angle of the X-rays to the sample surface. This method allows to analyze the layers deepened from the surface by  $10^{-8}$ ...  $10^{-6}$  m, which are not available for traditional methods of X-ray studies. A set of equipment was used for X-ray

structural examinations, namely: URS-1.0 apparatus; BSV-2 tube; LCD camera. The time of exposure to X-rays was 6 hours. The angle of inclination of the samples was chosen equal to  $1^{\circ}$ ;  $2^{\circ}$ ;  $4^{\circ}$ ;  $6^{\circ}$ ;  $10^{\circ}$ ;  $20^{\circ}$ .

Structural changes in the thin surface layers of steel-45, which occurred during friction in the lubricating compositions 1, 2 and 3, were evaluated by determination of the phase composition of the steel surface at the depths of 0.5... 7  $\mu$ m. The physical expansion of interference lines on bar diagramms was also evaluated, since the width of X-ray lines is determined by the presence of coherent scattering (blocks) in the crystals and micro-deformation of the crystal lattice. It is known that the density of dislocations at a given surface depth of the metal can be estimated by the values of the width of the interference lines [7, 9, 11].

X-structural analysis of the steel-45 surface showed that its structure consists of  $\alpha$ - and  $\gamma$ -phases. On the radiograph there is a decrease in the integral intensity of interference lines as in  $\alpha$ -phase and  $\gamma$ -phase of the metal at large Bragg-Wulf angles, both on lines (220) for  $\alpha$ -Fe and on lines (222) for  $\gamma$ -Fe (Fig. 2). The drop in the intensity of the lines indicates a static curvature of the

#### Table 5

with prepared compositions (tab. 1) on adapted tribometers (ta4)					
Lubricating compositions and their triboactivity	Steel 45 (HB 193)		Steel.SHH-15		
	f at	t <sub>cont</sub> ,	d <sub>зн</sub> ,	Ркр,	Рзв,
	200 H	°C	MM	H	Н
Composition 1 with low					
triboactivity	0,16	60	0,68	620	1470
Composition 2 with					
medium triboactivity	0,11	53	0,62	670	1850
Composition 3 with high					
triboactivity	0,08	48	0,45	820	2020

Tribotechnical indicators determined during the tests of steel samples (Steel 45, Steel SHH-15) lubricated with prepared compositions (tab. 1) on adapted tribometers (ta4)

Notes: f - coefficient of friction;  $t_{cont}$  - the temperature of the contact zone (measured with a thermocouple at a distance of 0.7 - 0.8 mm from the friction surface);  $d_{ws}$  - the diameter of the wear spot of the balls after testing on the tribometer; Rcr., Rw. - critical and welding load.

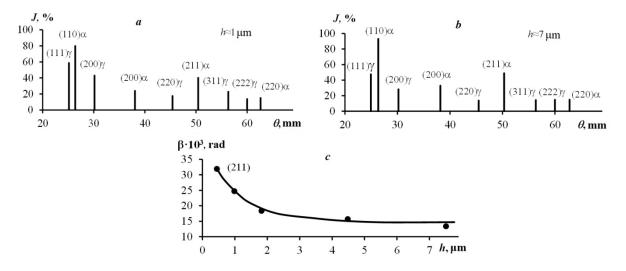


Fig. 2. The results of X-structural analysis of the surface of steel 45 before the tests, where J is the intensity of the reflected radiation;  $\theta$  - is the distance of the lines from the reference point; 2a, b - bar diagrams of decoded X-spectra taken from the friction surface a) at a depth of h $\approx$ 1 µm; b) at a depth of h $\approx$ 7 µm. 2c - change of physical width of interference lines depending on depth of a surface layer of steel.

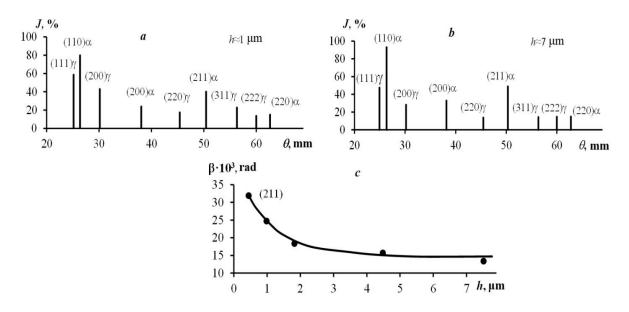


Fig. 3. The results of X-structural analysis of the surface of steel 45 after testing with a tribometer (Tab. 3) in the environment of the lubricating composition-1; 3a, b - bar diagrams of decoded X-spectra taken from the friction surface a) at a depth of  $h \approx 1 \mu m$ ; b) at a depth of  $h \approx 7 \mu m$ ; 3c - change of physical width of interference lines depending on depth of a surface layer of steel.

crystal lattice of the solid solution, which is formed as a result of the penetration of carbon and nitrogen atoms into the steel lattice. The number of  $\alpha$ - and  $\gamma$ -phases varies depending on the depth of the surface layer. At a depth of  $\approx 1 \ \mu m$ , the number of  $\alpha$ - and  $\gamma$ -phases is approximately the same.  $\gamma$ -Fe phase on metal surface is rather stable because of presence of small amounts Mn, Ni and some other metals in steel composition. So they can cause prevention of austenite decomposition. Whereas at a depth of  $\approx$  7 µm, the number of  $\alpha$ -phases increases, as evidenced by the changes in the ratio of the intensities of the interference lines in the diagram shown in Fig. 2 a, b. The changes in the physical width of interference lines (211) indicates that in the surface layers at a depth of  $\approx$  0.5  $\mu m$  there is a maximum curvature of the crystal lattice as a result of the penetration of other atoms during casehardening of steel with nitrogen. In the deeper layers ( $\geq 2 \mu m$ ) the physical width of the interference lines is stabilized (Fig. 2 c).

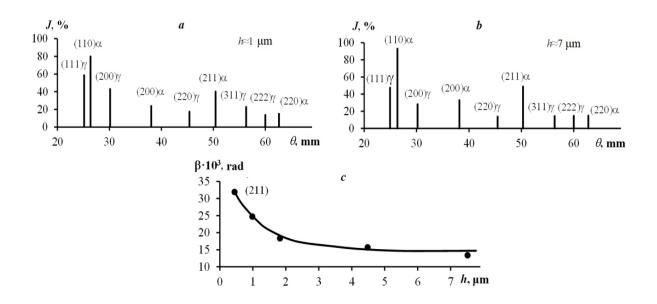
X-structural analysis of the Steel 45 surface after friction and wear testing of the samples in the environment of the base lubricating composition-1 (Tab. 1), which is characterized by low tribochemical activity, showed some changes in structure, namely: a) there is an increase in ferrite influence as a result of austenite decomposition; b) deepening into the surface of the sample causes the increase in the amount of ferrite, and decrease the content of austenite (Fig. 3 a, b). There is a tribo-modification of phase of steel surfaces with the transformation of the austenitic phase into ferritic. Moreover, ferrite, as a solid solution of carbon in  $\alpha$ -iron, is characterized by low strength and hardness, but high ductility and toughness.

Whereas austenite as a solid solution of carbon in  $\gamma$ iron (exists at a temperature of  $\geq 1400$  °C) is characterized by high rates of solubility of carbon in  $\gamma$ iron (with a solubility limit  $\approx 2.01$  %) and strength and hardness, but low ductility. During the steel test in the same medium (composition-1), it has been determined the interference line physical width  $\beta$  (211), which is slightly larger in the surface layer compared to the same lines in the initial state of steel. At a depth of  $\approx 7 \mu m$ , the values of  $\beta$  (211) become lower in comparison with the initial state of the steel surface (Fig. 3 c). The decrease in the values of  $\beta$  (211) with deepening into the sample surface is probably due to the decomposition of the austenite structure and the release of the  $\alpha$ -phase. That means that under such friction, the crystal lattice of steel becomes less distorted (less deformed).

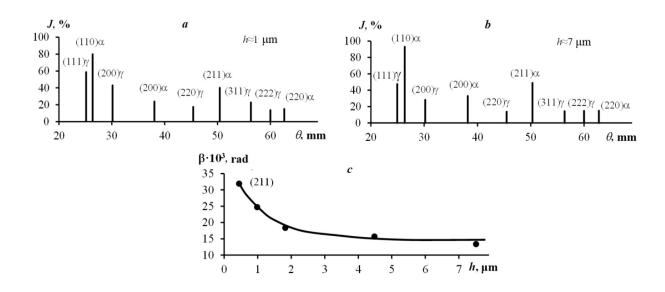
The study of the surface structure of steel-45 (in composition and phase state) during the subsequent test for friction and wear in the environment of the lubricating composition-2 (Table 1), which was characterized by higher tribochemical activity at the level of hemisorption of polar groups of oils, proved that in such an environment there is an intensification of the process of decomposition of austenite in comparison with the friction in the inert medium of the composition-1 (Fig. 4 a, b). At a depth of  $\approx$  7 µm, the presence of mainly  $\alpha$ -phase (ferrite) is recorded. At the same time the physical width of the interference lines decreases (Fig. 4 c).

The results of X-structural analysis of the surface of steel samples tested with the tribometer for friction and wear (Table 3) in the environment of the tribochemically most active composition-3 (Tab. 1), which activity is due to surface chemical reactions, convincingly prove the further growth of the ferrite content in the nano-layer and in particular with deepening into the surface (Fig. 5 a, b). This process is most clearly observed at a depth of  $\approx 7 \ \mu m$ . In addition, the analysis revealed a tendency to reduce the width of the interference lines  $\beta$  (211) in the subsurface layers (Fig. 5 c).

All that indicates that during test there was an even more active process of plastic deformation of the steel surface and the formation of stable lubricating film of the



**Fig. 4.** The results of X-structural analysis of the surface of steel 45 after testing with a tribometer (table 3) in the environment of the lubricating composition-2 (table 1); 4a, b - bar diagrams of decoded X-spectra taken from the friction surface a) at a depth of  $h\approx 1 \mu m$ ; b) at a depth of  $h\approx 7 \mu m$ ; 4c - change of physical width of interference lines depending on depth of a surface layer of steel.



**Fig. 5.** The results of X-structural analysis of the surface of steel 45 after testing with a tribometer (tab. 3) in the environment of the lubricating composition-3 (tab. 1); 5a, b - bar diagrams of decoded X-spectra taken from the friction surface a) at a depth of  $h\approx 1 \mu m$ ; b) at a depth of  $h\approx 7 \mu m$ ; 5c - change of physical width of interference lines depending on depth of a surface layer of steel.

quasi-solid composite type under the conditions of the critical mode.

### Conclusions

The main points of the plastic deformation effect of the friction pairs of tribosystems (Rebinder effect) and its importance as a criterion for the tribochemical effect of lubricating media on tribosystem efficiency. It is shown that the thickness of the plasticized nanolayer of metal of the friction node depends on the indicators of chemical and physicochemical activity of new biooils and their influence on the intensity of tribochemical interactions between metal surfaces and oils.

It is proved that the tribochemical activity of biooils in nodes is higher in comparison with the activity of mineral oil. The direction and method of achieving of desired tribochemical activity level of oils are established.

X-structural analysis of the friction surfaces of steel samples both in the initial state and after tests in the media of compositions 1, 2, 3 showed that during friction there is destruction of the austenite structure with the release of  $\alpha$ -phase. Hhe intensity of austenite decomposition progressively increases in samples tested sequentially in compositions  $1 \rightarrow 2 \rightarrow 3$ . It was found that with the penetration into the surface layers of the metal after the tests, the amount of ferrite increases and the content of austenite decreases.

This process is accompanied by a decrease in the deformation ability of the metal crystals and the

strengthening of the metal surface under its plasticized layer. There is no reasonable relationship between the physical width of the interference lines and the wear intensity of the steel in the various lubricating compositions.

*Kirichenko V.I.* – professor, Dr of Sc; *Ribun V.S.* – laboratory assistant of Chemical – analytical laboratory; *Nezdorovin V.P.* – assistant professor PhD; *Skladaniuk M.B.* – PhD, assistant professor of ChemistryDepartment.

- [1] G.O. Sirenko, V.I. Kirichenko, I.V. Sulima, Physico-chemistry of fuels and lubricants (Privat Publisher, Ivano-Frankivsk, 2017).
- [2] V.I. Kirichenko, G.O. Sirenko, V.V. Kirichenko, Modern fuels and lubricants: state and progress of development (Private Publishers, Ivano-Frankivsk, 2017).
- [3] V.I. Kirichenko, V.V. Kirichenko, V.P Nezdorovin, Energy technology and resource conservation 4, 33 (2019).
- [4] L.S. Shlapak, T. Shihab, P.M. Prysyazhnyuk, I.P. Yaremii, Metallophysical latest technologies 38(7), 968 (2016) (<u>http://doi:10.15407/mfint.38.07.0969</u>).
- [5] I.A. Buyanovsky, I.G. Fuchs, T.I. Shabalina, Boundary lubrication: stages of tribology development (Oil and gas, Moskow, 2002).
- [6] Yu.S. Zaslavsky, Tribology of lubricants (Chemistry, Moscow 1991).
- [7] H. Czichos, K-H. Habid, Tribologie-Handbuch: Tribometrie, Tribomaterialien, Tribotechnik (Springer Vieweg, 2015).
- [8] Kajdas Czesław, Hiratsuka Ken'ichi, Tribocatalysis, Tribochemistry, Tribocorrosion (Jenni Stanford Pablishing, 2018).
- [9] P.G. Alekseev, A.V. Shcheglova, Friction and wear 4(2), 189 (1983).
- [10] V.I. Kyrychenko, V.V. Kyrychenko, V.S. Ribun, M.B. Skladaniuk, Physics and chemistry of solid state 21(3), 552 (2020) (<u>http://doi:10.15330/pcss.21..3.552-559</u>).
- [11] A.I. Bereznyakov, Friction and wear 22(5), 513 (2001).
- [12] I.A. Buyanovsky, Friction and lubrication in machines and mechanisms12, 22 (2006).
- [13] L.I. Kuksenova, I.G. Lapteva, L.G. Komakov, L.N. Rybakova, Friction and wear test methods (Internet-ring, Moscow, 2001).

В.І. Кириченко<sup>1</sup>, В.С. Рібун<sup>2</sup>, В.П. Нездоровін<sup>1</sup>, М.Б. Складанюк<sup>3</sup>

# Контроль стану поверхонь вузлів тертя у контексті фізико - хімічних взаємодій їх із змащувальними середовищами різної поверхневої активності

<sup>1</sup>Хмельницький національний університет, Хмельницький, Україна, <u>vikirich@ukr.net</u> <sup>2</sup>Хіміко-аналітична лабораторія ПАТ «Укрнафта», Київ, Україна, <u>ribun.vika@gmail.com</u> <sup>3</sup>Прикарпатський національний університет імені Василя Стефаника, Івано-Франківськ, Україна, <u>skladanyuk16@gmail.com</u>

Розглянуто трибохімічний вплив поверхневої активності біосинтетичних олив нового типу на ефективність і надійність роботи змащених ними за умов межового режиму вузлів тертя. Доведено, що поверхнева активність олив зумовлена особливостями будови і властивостей їх молекул, енергетичні поля яких спричиняють трибохімічні взаємодії із трибоактивованими наноповерхнями сталей вузла тертя. Сформовані критерії оцінювання впливу трибохімічної активності олив на процес модифікування стальних поверхонь функціонуючих вузлів тертя. Рентгенографічно досліджено вплив змащувальних середовищ на поверхню сталі методом ковзаючого пучка Х-променів. Виявлений ефект суттєвого впливу біоолив на фазові перетворення поверхневого наношару сталі під час трибовипробувань зразків на тертя і зношування. Встановлено, що ефект деформування кристалічної структури сталі із зміцненням поверхні під деформованим шаром залежать від трибохімічної активності запропонованих мастильних композицій. Доведено, що біооливи призводять до покращення показників тертя і зношування змащених ними зразків. Х-структурний аналіз поверхонь зразків сталі показав, що в процесах тертя руйнується структура аустеніту та утворюється ферит. Виявлено, що із заглибленням у поверхневі шари сталі (від 0,5 до 7 мкм), змащених біооливами, кількість фериту в шарах зростає, а вміст аустеніту зменшується. При цьому зменшується ступінь деформації кристалів металу, що призводить до зміцнення його поверхні під пластифікованим шаром та до зниження рівня тертя і зношування за рахунок сформованої міжповерхневої сервовітно-трибополімерної плівки, стійкої за умов межового режиму тертя.

Ключові слова: трибохімія, сталь, вузол тертя, біооливи, деформація поверхні, поверхнева активність, аустеніт, ферит.