SELECTED ENGINEERING PROBLEMS
NUMBER6
INSTITUTE OF ENGINEERING PROCESSES AUTOMATION
AND INTEGRATED MANUFACTURING SYSTEMS

Tetiana ROIK[1*], Anatoly GAVRISH[1], Iuliia VITSUK[1]

[1]Reprography Department, Publishing Printing Institute, National Technical University of Ukraine "Kyiv Polytechnic Institute", Kiev, Ukraine,
[*]Corresponding author e-mail address: roik2011@gmail.com

EFFECT OF THE FRICTION FILMS'TRIBOSYNTHESIS MECHANISM ON THE ANTIFRICTION PROPERTIES OF COMPOSITE MATERIALS BASED ON NICKEL

Abstract: In a paper the results of effect the friction films' tribosynthesis mechanism on the antifriction properties of new composite materials based on nickel with solid lubricant CaF2 for high speed printing equipment have been presented. Paper generalizes the formation of antiscoring films, so called secondary structures, on the contact surfaces of the examined materials during friction process. Research of the friction surfaces was carried out using the method of Auger spectrum analysis. It was shown the mechanism of the antifriction films' tribosynthesis depends on operation conditions, material and counterface chemical composition. It has been demonstrated that it is possible to predict and control the anti-friction properties of materials by technological means. To do this, it is necessary to choose a chemical composition of the friction pair, which could ensure the high functional properties, and could open a possibility purposefully to choose the operating conditions of the material in a printing equipment's friction unit.

1. Introduction

In the general problem of improving the quality of machinery and equipment, the service life of which in most cases is determined by the resistance of machine parts various types of contact interaction, the central place belongs to the use of materials of friction pairs, in particular, antifriction materials [1].
To solve this problem, methods of powder metallurgy have no alternatives. Nevertheless, the possibilities of powder technology are insufficient, especially in the creation of antifriction materials.

One of the main obstacles in this way is not sufficiently complete investigation of the processes occurring on the friction surface of material and their effect on the durability of materials, especially at extreme conditions (high rotation speeds, temperatures, loads, aggressive environment).

"Therefore, further progress in the development of new antifriction materials and ensuring optimal conditions of operation depends on the understanding of the mechanisms of friction and wear under the influence of external factors and the accompanying phenomena”.- as noted by the authors [2].

At the friction process in the material’s surface layers the complex mechanical, thermal, physical and chemical processes run, that leads to significant changes in their properties [1-3].

And the durability of materials is determined not so much by their original characteristics as the surface properties of the resulting films.

As established in many studies the regularities of friction process are usually limited and valid only in the narrow confines of a particular experiment, the study of the mentioned phenomena and, above all, the state of the surface layer, which has a decisive influence on the work of the friction pair, is of greatest interest.

It was established [1], the nature and properties of the formed friction films on the contact surfaces (so-called secondary structures) determine operation of antifriction material, and the friction unit as a whole. However, the formed at high-speed friction the secondary structures still remain unexplored, especially when the liquid lubricant is inoperative and the solid lubricant components is added to initial mixture.

A group of authors has developed a number of antifriction materials based on nickel [1-5] to equip the high-speed friction units of printing machines running at speeds up to 5000 rpm, the pressure on the friction pair 5.0-7.0 MPa on air.

As solid lubricant component the chemically and thermally stable powder of calcium fluoride (CaF2) was added in the initial charge [1, 3, 7]. In the conditions of high rotation speeds any liquid lubricant is disabled because of liquid lubricant throwing out from friction zone by centrifugal forces. It is especially important to protect the friction surfaces from the increased wear and frictional seizure. Effect of calcium fluoride on the formation of antifriction layers was researched in [1-5].

However, in these studies the process of friction has not been studied in conditions of both high speeds of rotation and loads. These arguments were a reason for complex researches, which are directed for studying of friction films’ tribosynthesis mechanism at rotation speeds 4000−5000 rpm, loadings (5.0−7.0 MPa) and its influence on the antifriction properties of composite materials based on nickel. Such approach will open the possibility of prognostics and control of materials functional properties in wide range of loadings and speeds of printing machines.

Therefore, the objective of the present paper is to research the friction films (secondary structures) formed on the surface of powder materials based on nickel in the process of friction at high speeds of rotation and loads in combination with the study of anti-seize action of calcium fluoride.

2. Experimental results and discussion

Examination Techniques. Stricture was studied using raster microscopy; calcium fluoride in the matrix was identified using scanning electron microscopy (SEM). Moreover, the SEM images were used for the quantitative description of CaF2 in the composite. The physic mechanical properties of the samples were determined as well. Tribological tests were performed on a VMT-1 friction testing machine (rotation speeds $V = 4000 - 5000$ rpm and pressure $P = 5.0–7.0$ MPa), the counterface is made of EI 961 stainless steel (HRC = 52–54);

shaft–pin friction pair. Friction films (secondary structures) were researched by Auger spectral analysis method.

The objects of the study were new materials [1, 2] based on nickel, the following chemical composition, mas.%:
composition 1: 70Ni+12Mo+12W+6CaF2;
composition 2: 63Ni+13.5Mo+13.5W+10CaF2;
composition 3: 58Ni+15Mo+15W+12CaF2.

The materials were produced by powder metallurgy by mixing, pressing at a pressure of 700-900 MPa and sintering at 1200°C in hydrogen for 2 h. The porosity was 8-10% after sintering.
The material structure (fig. 1) is a γ-solid solution based on nickel alloyed by molybdenum and tungsten, and has a reinforcing phases - intermetallics Ni3Mo, Ni3W, WNi4.

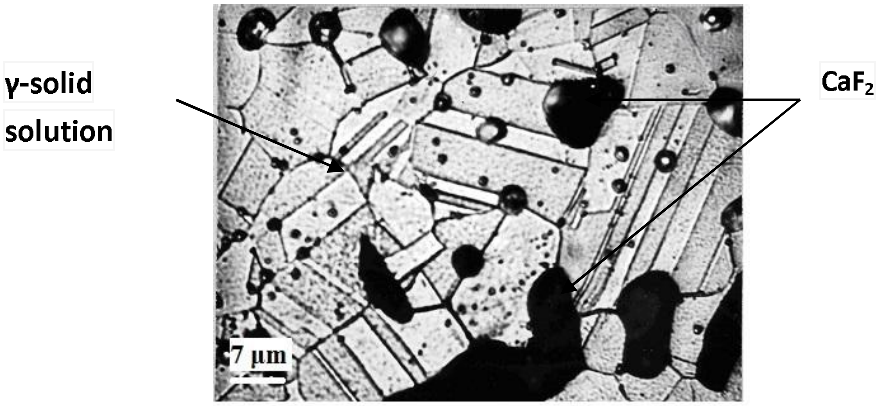


Fig. 1. The structure ofmaterial63Ni + 13.5Mo + 13.5W + 10CaF$_2$

Complex mechanical and tribological tests were carried out in the process of research. The formed heterophase structure of materials ensured providing them the properties listed in tab. 1.

Tab. 1.Physical, mechanical and antifriction properties of materials

№	Composition, mas.%	Resilience KC, J/m^2	Flexural strength, σ_f, MPa	Friction coefficient (f) and Wear (Ì), µ/km, under load, P, MPa						Limit rotation speed, rpm
				5		6		7		
				f	Ì	f	Ì	f	Ì	
1	Ni+12Mo+12W +6CaF$_2$	965	214	0.15	24	0.15	30	0.16	33	4000-5000
2	Ni+13.5Mo+ 13.5W+10CaF$_2$	980	220	0.12	22	0.13	28	0.14	31	4000-5000
3	Ni+15Mo+15W +12CaF$_2$	970	227	0.14	23	0.14	32	0.15	34	4000-5000
4	Ni+(24-30)Mo + (6-12) +CaF$_2$ [1]	800-900	167-185	0.15-0.18	26-32	0.24-0.26	78-94	0.28-0.32	156-188	1200-1400

The friction films (secondary structures) were formed both on the surface of materials and on the surface of counterface from EI 961 stainless steel. Friction films were examined by Auger spectral analysis method and electron microscopy.

The distribution of the main elements in the secondary structures was evaluated using an Auger spectrometer of system "Varian" whose accuracy in the absolute value of 0.5 eV, the layer depth - to 100 nm. The distribution of elements represent the corresponding energy spectra of Auger electrons that are excited by primary electrons with an energy of 5 keV. The specimen surface was sprayed with argon ions (Ar +) with energy Ei (Ar +) = 600 eV and a current density i = 5μA /cm2. It ensured that the etching rate of the friction films ≈ 0.5 nm/min. The results of the Auger analysis are shown in fig. 2.

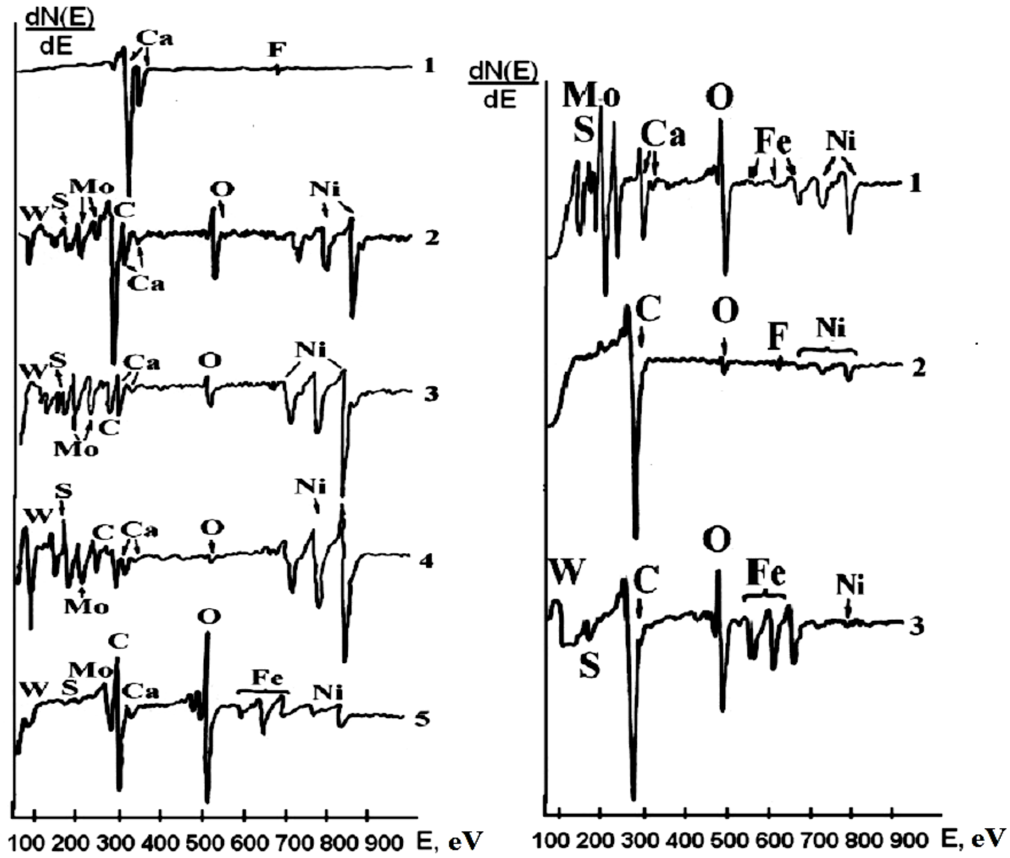
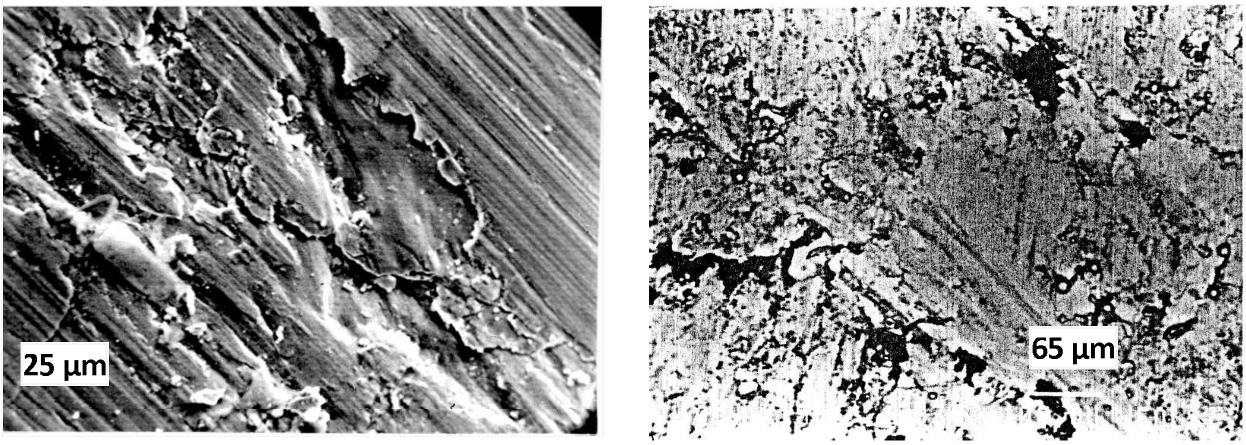


Fig.2. Augerspectrum of the surface layer after the tribological tests ata pressure of 5MPa:a- the material(Ni-Mo-W) +10% CaF2(1 - white portions2,3 –smooth surface areas, 4.5 -wear products) b – counter face ofsteelEI961(1 –smooth light area, 2-smoothdark zone, 3-wear products).

Typical spectra of Auger electrons from the surface of material (Ni–Mo–W)+10%CaF2, and counterface are presented in fig. 2 (a, b). It can be seen that the smooth areas (bright area) (fig. 2b, curve 1) contains intense lines of Auger electrons Mo, W, Ca, O, and Ni. A significant amount of carbon is contained in the dark areas (fig. 2b, curve 2). Carbon has a shielding effect and probably determines a reduced content of other elements in the Auger spectra. Wear products mostly contain C, O, Fe with variations in content of S, W, Mo and Ni.

In studying the topography of the materials' friction films after tribological tests with loads of 5-8 MPa, it was found the friction films (formed secondary structures) have a smooth microtopography, they are characterized by the absence of significant areas with splittings, deep cuts-away and fatigue failures. One of the distinctive features of the surface relief is a high degree of fluoride inclusions dispersion (≤0,5 μm) (fig. 3a). It allows to suggest the formation of the fine structure of the active layer and the maximum localization of the surface deformation therein at a friction. In the Auger spectra of wear (fig. 2) the elements such as C, W, Ca, S, Mo, N, O, Ni and the main component of counterface - iron have been fixed. There are only their different ratios. Carbon is in a free state in all cases.



a b

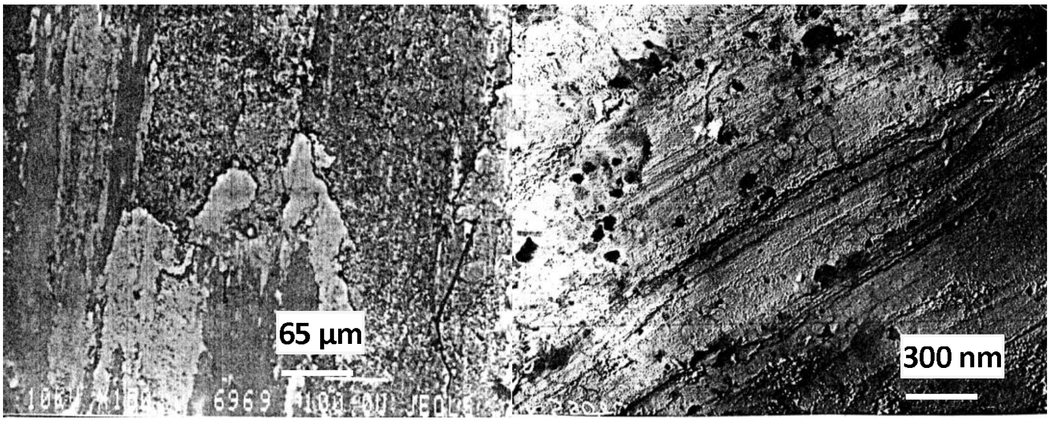
Fig.3.The material(Ni-Mo-W) +10% CaF2 friction surface's fragments after tribologicaltests at7MPa:a-secondary structures' topographic relief; b -image in the Auger electrons

Image of friction track fragments in Auger electrons (fig. 3b) shows that the intensity and size of Ca, O, W, and Mo areas are greater than Ni. Nickel was distributed in the form of individual circular sections with the clusters' size the tenths of a micrometer. Areas of Ca, O, W, and Mo are spread over the surface and occupy almost half of the area. The observed a significant oxygen saturation of a friction zone (fig. 2a) shows that in terms of friction an oxidative wear occurred. Periodic force action facilitates its running under friction. Oxygen permeates to the deformed volumes, increases the fluidity and mobility of these volumes, and increases of shear deformation degree.

It was detected thick layer of Ca and F in the Auger spectra from the white zones (fig. 2, curve 1). This layer shielded of all other elements. Probably, this layer has a thickness greater than 1 nm. It doesn't allow the Auger electrons of other elements to achieve the vacuum level and be registered by the Auger electrons detector. Thus, we can assume the identified "white" areas are the places of fluoride particles' localization in a structure of the friction film. The embrittlement of layer is formed in places fluoride particles.

There is a presence of such elements as S, Mo, W, C, Ca, O, and Ni in the Auger spectra of the secondary structures' smooth areas (fig. 2b, curve 2). It is possible that visible very bright areas are the artifacts of the surface's geometry such as ridges in places of embrittlement in the friction film.

Thus, the study showed that the technology of manufacturing the material Ni–Mo–W–CaF2 ensures the fine structure formation of the active layer on the surface during friction process. Intermittent load and speed effect facilitates the sorption effects under friction. Structure refinement of the active layer increases the role of its plastic deformation [1, 5]. Plastic deformation causes the smoothing effect of relief and microgeometry of the secondary structures (friction films) and reduces its abrading ability in the conditions of brittle calcium fluoride destruction with increasing its dispersibility during friction process. Calcium fluoride dispersion reduces the time of burnishing for the conjuncted parts. Formation of the friction film's smoothed microgeometry of the relief stabilizes the friction pair operation. It facilitates sliding and prevents a grasp of the two contact surfaces due to high thermal and chemical stability of calcium fluoride [1, 6, 7]. State of the surface layer's microtopography in the friction zone of counterface (EI 961 stainless steel) after friction is evidence of this fact. (fig. 4a).



a b

Fig. 4. Friction area of the counter face from steel EI961SH: a - in the mode of composite contrast; b - replica

We can see that the real physical relief of counterface has a favorable smoothed microtopography. Even damaged areas do not contain traces of gross failures. This is studied by the electron microscopic research of the counterface's friction zone microtopography with using replicas. (fig. 4b).

The wear products have a high degree of dispersibility in the friction zone.

The light rounded CaF2 inclusions have been revealed at the transmission electron microscopic study of friction film (fig. 5). They have dispersion from tenths to hundredths of a micrometer with clearly defined borders' contours. These particles are easily deformed and flattened to oval form without destruction under the action of shear loads during friction process. It indicates such layer has superplasticity.

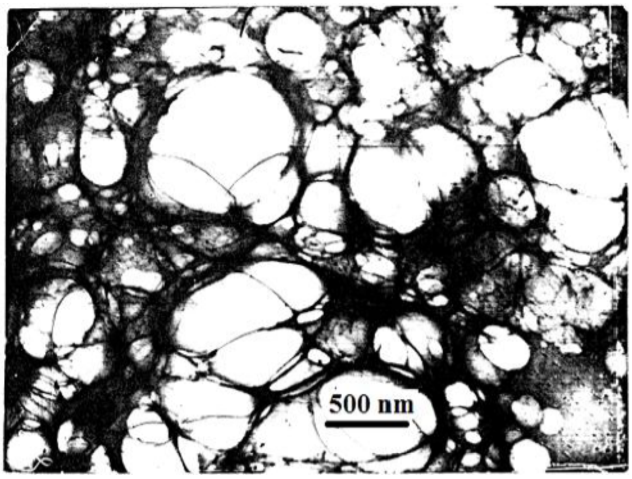


Fig. 5. Inclusions in the friction film of second arystructures

The high strength of particles with a sufficient reserve of plasticity is caused due to the irultra-dispersion. It's known [7, 8] that since the grain size less than 100 micrometers, its further decrease leads to increase strength while maintaining ductility.

It was identified extremely small size of the spherical particles in the secondary structures film on materials with calcium fluoride(10-40nm). It determines their zero-defects and increases the forces of cohesion and adhesion inside of layer and between the layers of secondary structures, even only due to physical forces of interaction.

Ultra fine particles are formed from the film components brittle fracture, especiallyCaF2. It is easily cleaved along(111) planes due to insufficient mechanical strength. Calcium fluoride is crushed by friction, especially in the presence of oxygen and moisture.

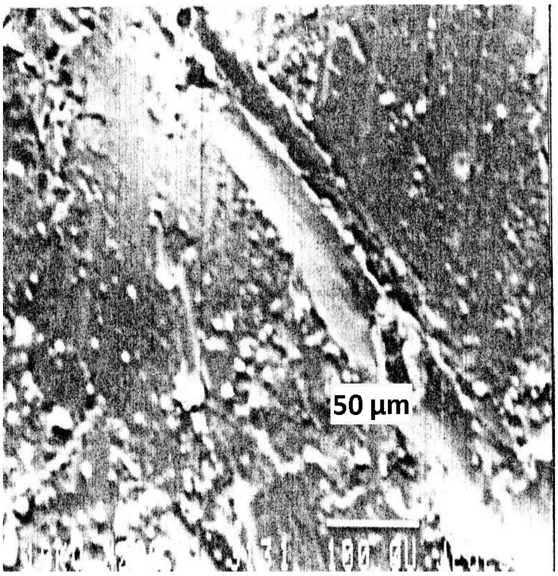
At the same time the surfaces of splitting have the point defects in the form of fluoride positions that determine the penetration of atmospheric oxygen into the fluoride inclusion.

The obtained data indicate about a fine structure of the active layer and maximum localization of the deformation in the surface during friction process. Thislayer'smicroplasticdeformationoccursasaresultofgravityandmovementofthe micro volumes. An opportunity of the multiple redistribution of layer's lattice micro distortions and residual stresses of the second kind determines the high resource of elastic deformation in the friction film due to the occurrence of the elemental shift areas large number in micro volumes. This phenomena determines the friction film's wear-resistance.

Additional shift formation is ensured by internal adsorption of oxygen in the deformable volume to depth of 50 n min the active layer(Fig.4). Oxygen is adsorbed in the micro cracks, micro voids, at grain boundaries and in the other defect sites. Oxygen, along with the chemical interaction can sign ificantly reduce the strength of the surface layer and facilitate wear products' dispersion during friction process. Discrete loads and speeds of friction facilitates orption effects. Shredding of the secondary structures' phases increases the role of plastic deformation in layer. In turn, the increased role of the plastic deformation causes a smoothing effect of the secondary structures' relief and suppression of the abrasive effects in the film.

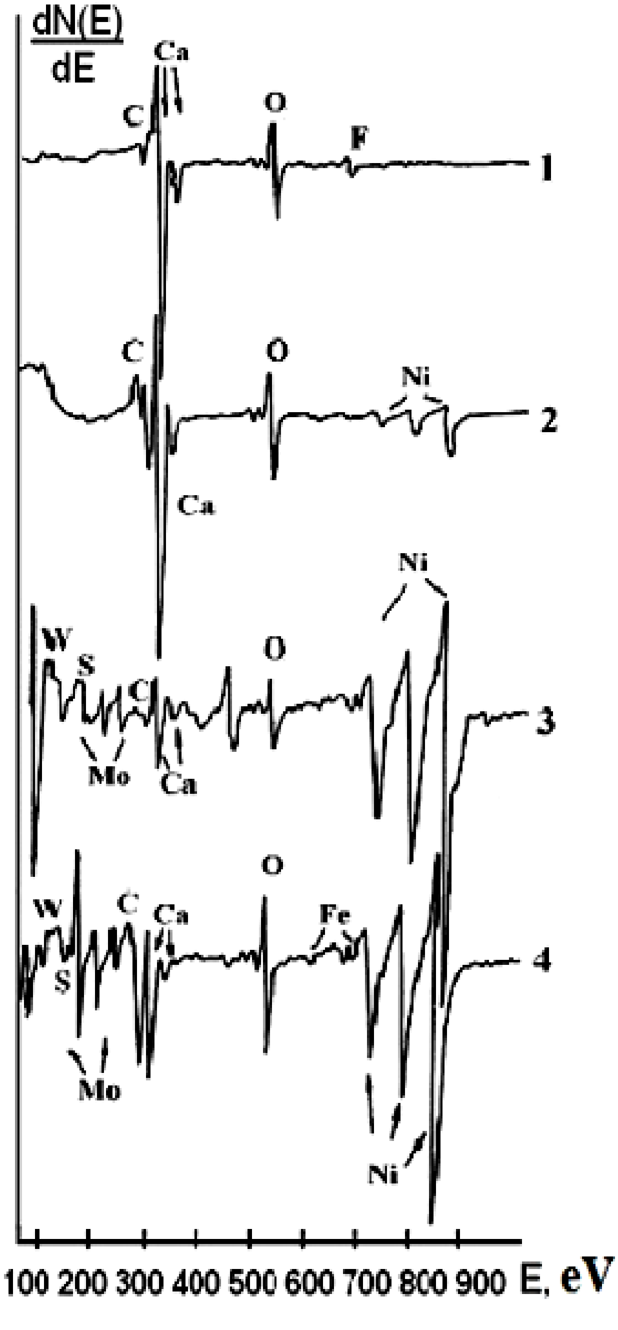
There is a sharp increase of the friction coefficient and wear after tribological test of material(Ni-Mo-W) +10%CaF2at a load 9 MPa (tab. 1). In this connection the study of a thin surface layer showed the following. The friction surface of the material(Ni-Mo-W)

+10%CaF2revealsa complex geometric pattern. The fragments with traces of plowing and brittle cleavages are identified(fig. 6a).



a

b



c

Fig. 6. The friction surface of the material(Ni-Mo-W) +10%CaF2after tribological testing at9MPa:a-drippingtraces and brittle cleavages;b -friction track in a mode of composite contrast; c-Augerspectra(1 -dark field, 2, 3 -brightfields,4 -wear products)

The surface includes a plurality of nano-dispersed wear products. A wear of material occurs by the mechanism of embrittlement layer and peeling of friction surface's individual layers. Survey in composite contrast mode shows the localization of light elements (Ca, O, F) in the friction film (black areas in fig. 6b). This is evidenced by the Auger spectrum (fig. 6c) obtained from a dark field, whose main components are calcium (high intensity), oxygen and fluorine. At the same time the light field of friction track is also enriched by nickel. The friction film is characterized by discontinuities and microheterogeneity of composition, so-called "a structure of coarse phase conglomerate". In this case, the "island" structure of the secondary structures (friction films) is represented in the discrete and random distribution of its equilibrium and non-equilibrium phases. Their structural components are mostly highly oxidized and alloyed by nickel, molybdenum, tungsten and iron formations. It evidences about predominantly oxidative wear of material.

Studies have shown that in this case, the main reason for the large wear is high intensity of material's film formation. Highly oxidized formations grow and flake off faster than the wear occurs. Not having sufficient cohesive and adhesive strength, such film of secondary structures is easily embrittled during friction. A lack of the antifriction layer leads to a sharp increase of the friction coefficient and wear rate, and ultimately - to seizing of the contact surfaces.

3. Conclusions

Thus we can scientifically choose the operation modes of materials basing on the results of studies on the analysis of the friction films formation mechanism (so called secondary structures) for antifriction composite materials based on (Ni-Mo-W)+10% CaF2 that were formed under different loads (5-9 MPa) on friction pair.

Further studies will be aimed to determining the phase composition and quantitative ratio of the phases in the friction film. It opens an opportunity to not a priori, but from the standpoint of the deep analysis of the secondary structures to forecast and control the functional properties of antifriction composite materials based on nickel by selecting alloying elements and their amounts in the starting mixture.

References

1. Kyrychok P.O., Roik T.A., A. Gavrish P., A. Shevchuk V., Vitsuk Iu. "New Composite Materials of the friction parts for printing machines: Monograph, [in Ukrainian], NTUU „KPI", Kyiv (2015), 428 p.;
2. Roik T. A., Shevchuk Yu. F. "Development of predictable secondary structures in materials for high-temperature bearings" Powder Metallurgy and Metal Ceramics Springer/New York: Volume 45, Issue 11, 531-539, (2006);
3. Roik T. A., Gavrish A. P., Kyrychok P.O., et al., Composite Bearing Material [in Ukrainian], Ukrainian Patent No. 60521, IPC (2009), C22C9/02, Bulletin No. 12, Publ. June 25 (2011);
4. Roik T., Gavrish A., Kyrychok P., Vitsuk Y.: "Effect of making technology on the antifriction properties of new bearings for printing machines"//Selected engineering problems, Silesian University of Technology, Faculty of Mechanical Engineering, Glivice, Poland, №4, 147-152, (2013);
5. Roik T., Gavrish A., Kyrychok P., Vitsuk Iu., Askerov M. "Phisical Mechanical And Tribotechnical Properties Of New Composite Bearings For Printing Equipment"//Journal

of Science of the Gen. TadeuszKościuszko Military Academy of Land Forces, Wroclaw, Poland.-№2(172), 141-149, (2014);

6. Konopka K., Roik T. A., Gavrish A. P., et al., Effect of CaF_2 surface layers on the friction behavior of copper-based composite//Powder Metallurgy and Metal Ceramics.-Springer/New York: Volume 51, Number 5-6, 363-367, (2012);
7. Jianxin D. and Tongkun C., “Self-lubricant mechanisms via the in situ formed tribofilm of sintered ceramics with CaF_2 additions when sliding against hardened steel,”//J. Refract. Met. Hard Mater., **25**, No. 2, 189–197 (2007).
8. Phillips W. L., Handlon G. E.:“Oxygen penetration into single crystals of calcium fluoride”//J. Amer. Soc. 46, № 9, 447–450, (1983).