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SELF-ORGANIZATION OF FRICTION SURFACE OF Fe-Mn-C-B COATING WITH INCREASED RESISTANCE TO ABRASION

SAMOORGANIZACJA POWIERZCHNI TARCIA POWŁOKI Fe-Mn-C-B O ZWIĘKSZONEJ ODPORNOŚCI NA ZUŻYCIE ŚCIERNE

The paper concerns the research on self-organization of the surface of coating of hypoeutectic alloy Fe-Mn-C-B modified Si, Ni, Cr, Cu with friction with C45 steel. The coatings were obtained by arc welding using a flux-cored wire. Tests of resistance to wear were carried out for hypoeutectic coatings with use of the friction pair pin-on-disc in the conditions of sliding friction, in model lubricating environments. The surface-active (glycerol oil) and inactive (Vaseline grease) lubricant was used. Tribological tests carried out showed that cooperation of hypoeutectic alloy coating with counterbody of C45 steel with lubrication with surface-active lubricant results in a significant improvement in tribological properties than in case of the lubrication with surface-inactive lubricant. The resulting effect is related to the self-organization of friction surface. After deposition and wear resistance tests, the friction surface microstructure was analysed, as well as the surface and depth distribution of the elements.

Keywords: Self-organization, friction, coatings, hypoeutectic alloy

Praca dotyczy badań samoorganizacji powierzchni powłoki ze stopu eutektycznego Fe-Mn-C-B modyfikowanej Si, Ni, Cr, Cu przy tarceniu ze stalą C45. Powłoki otrzymano metodą napawania łukowego z użyciem drutu proszkowego. Badania odporności na zużycie przeprowadzono dla powłok eutektycznych z zastosowaniem węzła tarcia trzpień-tarcza w warunkach tarcia ślizgowego, w modelowych środowiskach smarnych. Zastosowano powierzchniowo-aktywny (olej glicerynowy) i nieaktywny (smar wazelinowy) środek smarny. Przeprowadzone badania tribologiczne wykazały, że współpraca powłoki ze stopu eutektycznego z przeciwpróbką ze stali C45 przy smarowaniu powierzchniowo-aktywnym środkiem smarnym powoduje znaczną poprawę właściwości tribologicznych niż przy smarowaniu powierzchniowo-nieaktywnym środkiem smarnym. Otrzymany efekt związany jest z samoorganizacją powierzchni tarcia. Po napawaniu i badaniach odporności na zużycie przeanalizowano mikrostrukturę powierzchni tarcia oraz powierzchniowy i głębokościowy rozkład pierwiastków.

1. Introduction

Properties of the surface layer have a decisive influence on the service life of products applied on cooperating elements of machinery and equipment [1, 2]. During operation, as a consequence of friction, so in result of physical and chemical changes of the surface layer, the friction node changes its properties [3-6]. This leads to wear and, in extreme conditions, to galling of the node and to its destruction. Wear in result of the friction causes the need for periodic regeneration or replacement of components, assemblies or machines. In many cases, the costs of stoppage of machinery and equipment needed for their renovation, greatly exceed the costs of materials and labour. One of the solutions to counteract this problem is to search for materials that during the friction process exhibit the self-organization of surfaces, increasing their durability and resistance to wear. Through self-organization or self-ordering, one understand

the processes in which components of the complex system are subject to spontaneous specified ordering.

The first attempts to examine and explain the process of self-organization of surface in the friction process has been taken in the 1970s. The first people to deal with the explanation of this issue were B.I. Kosteckii and L.I. Bershadsky [7]. They studied the formation of the so-called self-organizing “secondary structures” during the friction and regime of “structural scattering adjustment”. According to them, in the process of friction there is the formation of secondary structures that contribute positively to the process of self-organization of the surface. Usually, these are chemical compounds of non-stoichiometric composition. Their sizes, distribution, structure and chemical and phase composition can be different depending on the material, the lubricant used and the friction conditions [8]. N. Bushe and I.S. Gershman also claim that self-organization in the process of friction affects the formation of secondary structures on

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the surface, i.e. the formation of dissipative structures. These structures protect the materials of friction pair from the contact influence [9]. G. Totten and G.S. Fox-Rabinovich also point out that the phenomenon of self-organization of the surface involves the formation of secondary structures [10, 11]. On the other hand, D.N. Garkunov considers the discovered by himself “selective transfer”, also called “non-wear friction effect” to be self-organization of friction surface [12, 13]. Along with A. Polyakov, he suggested the concept of dynamically created tribological protective coatings (which they called “servovite coatings” or “surfing coatings”). These coatings are formed by chemical reactions caused by friction and they protect against wear, leading to a dynamic balance between wear and formation of protective coating.

The course of the friction process is also highly influenced by the surface segregation of atoms, which can also be classified as self-organization of the friction surface. This occurs, inter alia, in alloys of Fe-C, Fe-Al, Fe-Si, Cu-Al, Cu-Sn systems, in which the atoms of carbon, silicon and aluminium migrate to the surface in the friction process [14]. The above phenomenon was detected during the use of eutectic alloys based on based on Fe-Mn-C-B-Si, Fe-Mn-C-B-Si-Cr, Fe-Mn-C-B-Si-Ni-Cr systems. On the friction surface the carbon, boron and silicon atoms are segregated [15, 16].

Therefore, self-organization of the friction surface is connected with forming of new surface layers directly in the process of operation. The so-called operational surface layers (OSL) are formed, which separate the cooperating friction elements. They play an important role in the tribological system. Their aim is to reduce wear and prevent galling and creating films, which are more susceptible to abrasion in operational conditions. A perfect example of OSL may be the joints of living organisms that can operate practically for the whole life, with no visible signs of wear and with small resistances to motion. This is possible thanks to the continuous formation and renewal of the protective layers elements on the cooperating surfaces, minimizing the friction resistances. Therefore, it is advisable to search for materials which exhibit similar characteristics.

2. Methodology of research, material for research

The coatings were applied by arc GMA welding (MAG cover CO₂) with use of the elaborated flux-cored wires of the hypoeutectic weld metal Fe-Mn-C-B-modified with Si, Ni, Cr, Cu. The thickness of the padding welds was approximately 2-3 mm, and the hardness was 98 HRB. For surfacing, a wire with a diameter of 2.4 mm was used with filling of a metal strip around 33%. The chemical composition of the applied coating was the following: Mn-6.61%, C-1.45%, B-2.45%, Si-2.11% Ni-7.45% Cr-4.90%, Cu-4.91%, Fe-residue (mass %).

The coatings were subjected to structural analysis and phase composition. Structural analysis of the coatings was carried out using an Olympus GX71 a light microscope (magnification to x1000). Metallographic cross-sections of the deposited layer were examined. After treatment in heat-strengthening phenol resin, cross-sections were ground and polished mechanically. The samples were ground abrasive

paper with grits from 240 to 2000 pm and then polished on the faces of the felt using an aqueous suspension of aluminum oxide. For the disclosure of the structure, the sections were chemically etched with a 5% HNO₃ alcoholic solution. The phase composition of the coating was examined with a Empyrean X-ray diffractometer. The radiation source was a ceramic X-ray tube with a copper anode 3 kW. The study was conducted in monochrome radiation. Registration was performed by scanning stepper angular range $2\theta = 5-110^\circ$. Step scan was 0.05° and the exposure time at the point 3-5 seconds.

The coatings were subject to tribological studies. The studies used a modified tribotester of Amsler type. The tester allows to conduct research in accordance with the methods set out in the PN-79/H-04329, PN-82/H-04332 standards. The tribological studies were implemented with the following parameters:

- contact: distributed (pin-on-disc),
- type of movement: sliding,
- pin diameter: φ 7 mm,
- disc diameter and thickness: φ 50x8 mm,
- sliding velocity: 0,4 m/s,
- contact load: 20 MPa,
- sliding distance, in each test: 5700 m,
- lubricated contact: glycerine oil, grease Vaseline,
- number of repetitions: 3-5,
- time of one trial: 6 hours,
- ambient temperature: $23\pm 1^\circ\text{C}$.

The friction node consists of fixed pin (sample) pressed with the required force to the disc rotating with a set speed (counterbody). The samples made of hypoeutectic alloy of Fe-Mn-C-B modified with Si, Ni, Cr, Cu were used for studies. The counterbody was made of C45 steel. Its hardness after heat improving was 52-54 HRC. Wear of the samples and counterbodies were determined by weighing to the nearest 0.1 mg (weight series Radweg WPS/110/C). Mass loss was measured after 15, 30, 60, 90, 120, 180, 240, 300, and 360 minutes.

The surfaces of the samples and counterbodies were subjected to additional tests. The measurements of roughness were conducted, the microstructure of the friction surface and the surface and depth distribution of elements was examined, and their possible structures were evaluated. Measurement of surface roughness of surface layers (before and after tribological tests) was made using a needle profilometer Surtronic 3+ by Talyor Hobson. The device is equipped with a diamond needle. The measurements were conducted perpendicularly to the direction of processing marks and sliding distance for a distance of 4 mm with a measurement accuracy of $\pm 0.02 \mu\text{m}$. As the value describing the surface roughness, the Ra parameter was adopted, according to PN-EN ISO 4287:1999 standard. For the evaluation of the friction surface microstructure, metallographic microscope Nikon Eclipse MA 200 was used. The images were obtained in a digital form and processed using NIS-Elements program. In order to obtain higher magnifications, friction surfaces were also observed with a scanning electron microscope SEM. The scanning electron microscope of Quanta

3D FEG type by FEI company was used. SEM studies were performed in a high vacuum (pressure $<6 \cdot 10^4$ Pa) using a secondary electron detector ET SED (Everhardt-Thornley Secondary Electron Detector). For high vacuum, the resolving power of the microscope at an accelerating voltage of 30 kV was 1.2 nm.

The use of X-ray photoelectron spectroscopy XPS allowed for the surface and profile deep-seated analysis of the surface layer (change of participation of individual elements into the material). The multi-chamber UHV analytical system by Prevac company was used for studies. The surfaces of hypoeutectic alloy samples with dimensions of $\phi 7 \times 4$ mm and surfaces of counterbodies with dimensions $8 \times 8 \times 7$ mm were subjected to studies. The pressure inside the chamber during the measurement with the spectrometer was $\sim 5 \cdot 10^{-9}$ mbar. To collect the broken electrons, the electrons energy analyser Scienta R4000 was used. During the study, the surface and depth analysis was conducted. The analysis was performed at depths of 5, 10, 15, 20, 50, 100, 200, 600 nm from the surface. The layers were consecutively removed by ion etching (argon ions Ar^+ with an energy of 2 kV). During the etching, the pressure in the chamber was $\sim 5 \cdot 10^{-6}$ mbar.

3. Research results and discussion

The microstructure of the hypoeutectic coatings is shown in fig. 1. Dendrites of various sizes, creating the coating matrix, form during welding. The morphology varies across the thickness of coatings. Austenite dendrites (bright in photos) grow from the fusion zone perpendicularly to the heat dissipation gradient. The coatings are characterized by adequate fusion (adhesion) with the base material (~ 500 MPa).

The coatings primarily consist of doped austenite γ -(Fe, Cr, Ni) (base), carbide $\text{Fe}_{0.4}\text{Mn}_{3.6}\text{C}$ (strengthening phase), and a small amount of dispersive phases, Fe_2B , Fe_3C , and Cr_7C_3 , CrSi_2 , Cr_2B , Cu, α -Fe.

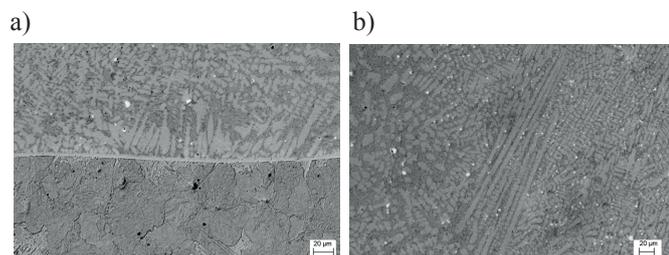


Fig. 1. Microstructure of the coating Fe-Mn-C-B-modified with Si, Ni, Cr, Cu

Figure 2 shows the results of measurements of the average mass loss of the coatings and the corresponding counterbodies after 6 hours of the process of friction with the lubrication with glycerine oil and Vaseline grease. The average mass loss of coatings with glycerine oil lubrication was 4 mg and 3.25 mg for counterbodies. In contrast, with Vaseline grease lubrication, the average wear of coatings was 77 mg and 67 mg for counterbodies.

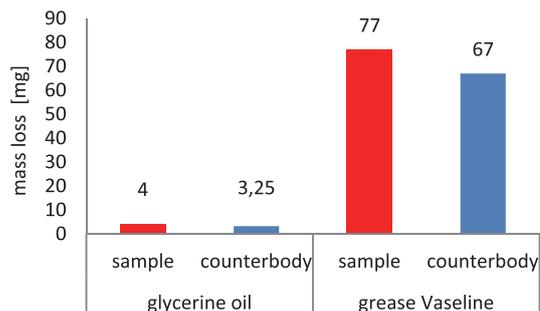


Fig. 2. Summary of mass loss of coatings and counterbodies after the tribological tests with a unit pressure of 20 MPa and glycerine oil and Vaseline grease lubrication

For better illustration of the process of friction, the results of measurement of the average mass loss of the coatings and the corresponding counterbodies was presented as a function of time of friction (Fig. 3) (for glycerine oil and Vaseline grease).

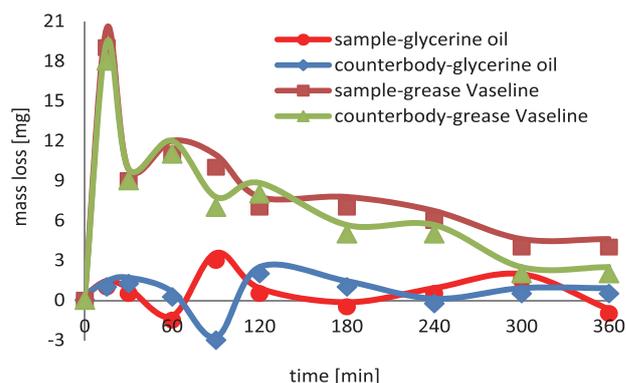


Fig. 3. Curve of mass loss of coatings and counterbodies with friction in glycerine oil and Vaseline grease with unit pressure of 20 MPa

Analysis of the obtained results (Fig. 2 and 3) showed that in case of lubrication with the surface-active lubricant (glycerine oil) throughout the entire period of testing there is a variable wear of components (gain and loss of weight). This phenomenon can be explained by the fact that there is a material transfer from one surface to the other and back. This can lead to the formation on the friction surfaces of a thin layer (film), having specific properties. The layer fulfils the task of protection of friction surfaces from direct contacting, contributing to the reduction of the material wear rate and lower coefficient of friction. This explains the noticeable effect of slight wear of the cooperating elements. However, in case of lubrication with Vaseline grease, the above phenomenon was not observed. There is a visible increase in the wear of the cooperating elements compared to the lubrication with glycerine oil. The coefficient of friction in case of lubrication with glycerine oil for the analysed couplings was 0.011 and 0.026 with Vaseline grease lubrication.

The conducted tribological studies clearly demonstrated that cooperation of hypoeutectic alloy coatings with counterbody of C45 steel with glycerine oil lubrication results in a significant improvement in tribological properties,

compared to Vaseline grease lubrication. Therefore, for further evaluation and analysis, the coatings after tribological tests lubricated with glycerine oil were adopted.

In the next stage, the microstructure of friction surface was examined. The friction traces generated on the surface of the hypoeutectic alloy coatings and surface of counterbodies lubricated with glycerine oil were subjected to observation (Fig. 4). Friction surface is almost completely covered with tribochemical products. The operational surface layer (OSL) was formed. The furrows and scratches practically disappear (surface is very smooth) - see fig. 4b. One can see a significant decrease of surface roughness. The surface roughness of the coating before the process of friction was 1.382 μm and 0.493 μm after the tribological tests.

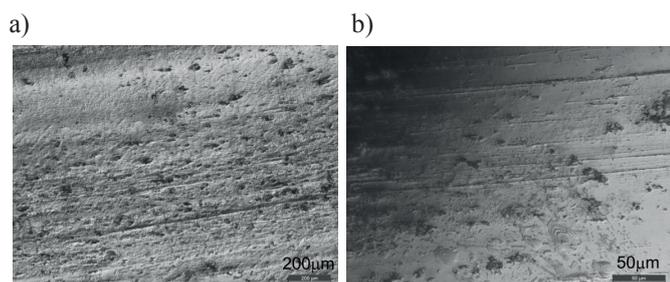


Fig. 4. View of the surface of friction traces on the hypoeutectic alloy coating after tribological testing with unit pressure of 20 MPa and glycerine oil lubrication

The SEM view of the friction traces formed on the hypoeutectic alloy coating lubricated with glycerine oil at various magnifications are shown in fig. 5. The friction surface is characterized by a flake-layer structure (Fig. 5 a). There are visible differences in the shape and size of layers and flakes. The individual layers and flakes are on different levels and overlap each other. They also have visible plastic deformations. One may notice exfoliated secondary structures. In case of magnifications x500 000 (Fig. 5 b), there are visible spherical structures with size of 15 nm. According to H. Kuźmin et al. [17], the flake-layer structures can be formed, provided that the friction node elements contain substances which facilitate the formation of layers in result of tribochemical reactions.

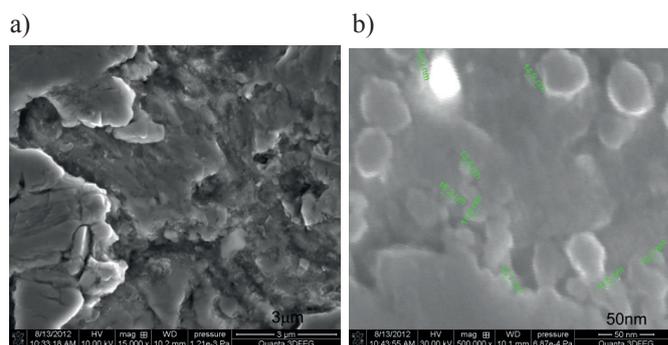


Fig. 5. Pictures of the friction traces formed on the hypoeutectic alloy coating with lubrication with glycerine oil

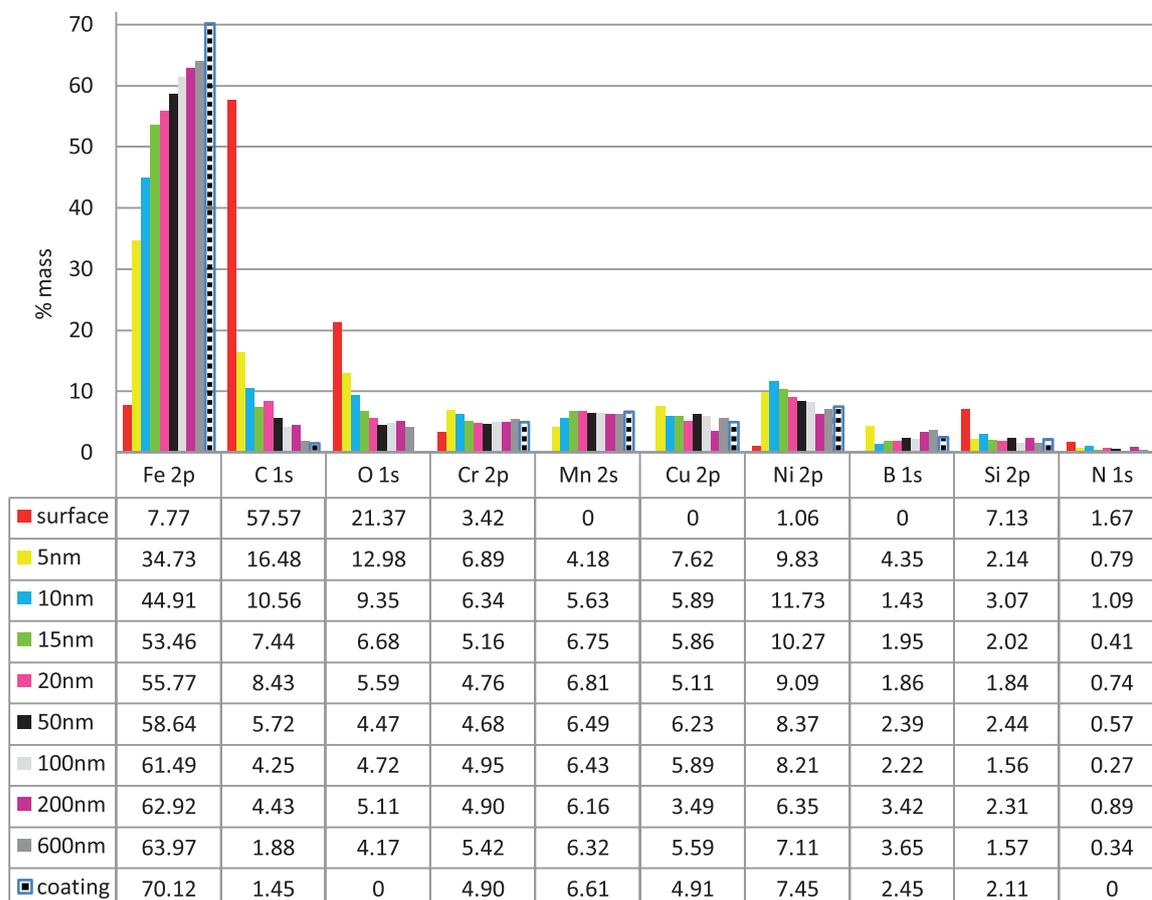


Fig. 6. The content of the chemical elements on the surface of the hypoeutectic alloy coating and at depths of 5, 10, 15, 20, 50, 100, 200, 600 nm after tribological testing at a unit pressure of 20 MPa and with the glycerine oil lubrication, expressed in mass %.

The content of the chemical elements on the surface of the hypoeutectic alloy coating and at the depth of 5, 10, 15, 20, 50, 100, 200, 600 nm (after the tribological tests) identified by X-ray photoelectron spectroscopy (XPS) is shown on fig. 6.

While analysing the content of elements on the basis of the graph (Fig. 6), it is visible that the carbon is present in a large amount on the surface (57.6% wt). Then, its content decreases. At a depth of 600 nm it is 1.9% wt. The oxygen content is similar. On the surface it amounts to 21.4% wt. At a depth of 5 nm it increases to 13.0% wt., and then decreases amounting at depth of 600 nm to 4.2% wt. The silicon content is also the highest on the surface 7.1% wt. The content is also high at a depth of 10 nm (3.1% wt.), 50 nm (2.4% wt.) and 200 nm (2.3% wt.). Its content decreases with depth. At a depth of 600 nm it is 1.6% wt. The iron content changes in a totally different manner. On the surface it is relatively low, and increases with depth. On the surface it is 7.8% wt., and at a depth of 600 nm, up to 64.0% wt. In the case of chromium and nickel, the amount on the surface is trace. Then, at a depth of 5 nm it increases and is maintained at a similar level. The chromium content varies in the range of 3.4-6.9% wt., and the nickel in the range of 1.1-11.7% wt. Manganese, copper and boron were not observed on the surface. At a depth of 5 nm, boron content is growing rapidly 4.3% wt. At a depth of 10 nm it decreases to 1.4% wt., and then increases to 3.6% wt. at a depth of 600 nm. In case of manganese, at a depth of 5 nm its content is 4.2% wt, and at a depth of 10 nm (5.6% wt.). At the other depths, it remained at a similar level. The copper content at a depth of 5 nm is 7.6% wt. At other depths it varies within the range of 6.2 to 3.5% wt..

The exemplary review spectra XPS recorded on the surface and a depth of 10 nm after the process of friction with a load of 20 MPa and the glycerine oil lubrication are shown in fig. 7.

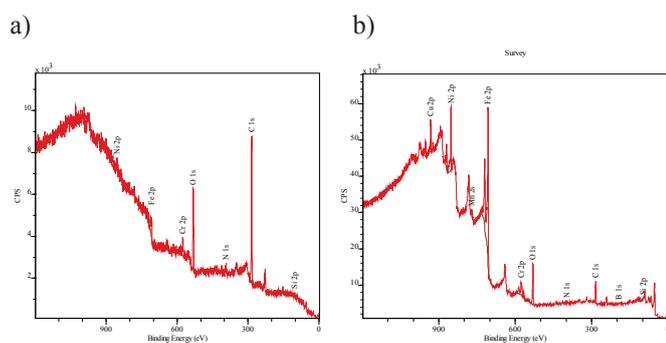


Fig. 7. The exemplary review spectra XPS recorded on the friction surface (a) and at a depth of 10 nm (b) after tribological tests with a unit pressure of 20 MPa and glycerine oil lubrication

XPS spectrum recorded on the surface is significantly different from the others. In this spectrum, there was no spectral lines for boron B 1s, manganese Mn 2s, copper Cu 2p and nitrogen N 1s. Between the spectra recorded at different depths there are also visible differences. In these spectra there are spectral lines characteristic for the elements included in the coating obtained from the hypoeutectic alloy (Fe, C, B, Cr, Ni, Si, Cu), and lines derived from oxygen and nitrogen. Manganese Mn 2s lines coincide with the Auger lines for iron and are difficult to interpret. The form of spectral line of iron Fe 2p indicates that it is present in metallic form and in the

form of iron oxides (FeO, Fe₃O₄, Fe₂O₃). In turn, the spectral lines of carbon C 1s indicate that this element is in the form of a carbide (Fe₃C, Cr₇C₃). The lines of boron B 1s indicate that it is present in the form of boron oxide (B₂O₃) and borides (FeB, Fe₂B, CrB₂). Chromium Cr 2p is present in metallic form, in form of oxides (Cr₂O₃) and chromium carbide (Cr₇C₃). Silicon Si 2p is present in metallic form and in the form of silicon oxide (SiO₂). Nickel Ni 2p in metallic state and in form of the nickel oxides (NiO). In contrast, spectral lines of oxygen O 1s indicate that it is present in the form of oxides (SiO₂, NO₂, CuO, B₂O₃, NiO, Cr₂O₃, FeO, Fe₃O₄, Fe₂O₃) and nitrogen N 1s in the form of nitrides (BN, Si₃N₄) and nitrogen oxides (NO₂).

4. Conclusions

The conducted tribological research clearly demonstrated that cooperation of hypoeutectic alloy coatings with counterbody of C45 steel in case of lubrication with surface-active lubricant (glycerine oil) results in a significant improvement in tribological properties, compared to the lubrication with surface-inactive lubricant (Vaseline grease). The resulting effect is related to the self-organization of friction surface. It was found that in the surface layer in the process of friction, tribochemical changes occur. Friction surface is almost completely covered by tribochemical products. A new OSF was formed. Friction surface of coating has a flake-layer structure. Phase and quantitative composition of material of the surface layer varies with the depth, which was confirmed by XPS studies. In the surface layer of Fe-Mn-C-B coating modified with Si, Ni, Cr, Cu, there is a presence of compounds such as oxides (B₂O₃, SiO₂, Cr₂O₃, FeO, Fe₃O₄, Fe₂O₃, CuO, NiO, NO₂), carbides (Fe₃C, Cr₇C₃), borides (FeB, Fe₂B, CrB₂), as well as nitrides (BN, Si₃N₄).

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