FRICTION BEHAVIOR OF IRON-CARBON ALLOYS IN COUPLES WITH PLASMA-ELECTROLYTIC OXIDE-CERAMIC LAYERS SYNTHESIZED ON D16T ALLOY

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We study the tribological behavior of 45 steel, U8 steel, and SCh 21-40 cast iron in couples with plasma-electrolytic oxide-ceramic layers synthesized on D16T alloy in I-20 mineral oil and in the same oil with an addition of aqueous solution of glycerol. It is shown that, in the case of friction interaction of steel with plasma-electrolytic oxide-ceramic layers in oil-glycerol mixture, we observe the realization of the modes both of the selective transfer and of the transformation of elements in the contact zone. It is discovered that these contact couples preserve their serviceability up to specific loads higher than 10 MPa.

Keywords: light alloys, plasma-electrolytic oxide-ceramic layers, friction, wear, selective transfer, transformation of elements, friction coefficient, steel, cast iron, glycerol.

Light alloys are not used in friction units under standard conditions of thermal treatment due to their low wear resistance. Hence, it is customary to modify their working surfaces. At present, the most efficient synthesis of plasma-electrolytic oxide-ceramic (PEO) layers in subalkali electrolytes is realized under high electric voltages. As a result, the metal surface is transformed into a composite oxide-ceramic layer characterized by the strong adhesive bonding with the metal substrate, elevated hardness, and higher wear and corrosion resistances as compared with the intact metal [1–4].

However, the tribological behavior of synthesized PEO layers is poorly studied, which restricts the implementation of these technologies in the industry. Therefore, it is necessary to create new approaches, which would enable us to understand the course of tribochemical processes in the zone of friction contact because they differ from the processes running in the case of friction of the metal surfaces [3, 4].

Under the influence of corrosion factors, the oxide ceramics or PEO layers are chemically stable. At the same time, in the friction interaction, they are reactive. The friction interaction itself leads to fundamental changes in the behavior of ceramics, which becomes more sensitive to the separating medium than the metals [5].

The behavior of oxide ceramics under the conditions of boundary lubrication is also studied insufficiently. In the case of lubrication with traditional oils intended for metal contact couples, the behavior of ceramic couples subjected to friction contact is different. Clearly, in this case, it is necessary to develop new approaches. In particular, it is necessary either to create alternative oils for the friction couples of ceramic materials or to form contact couples for the existing oils, e.g., metal–ceramics. In our opinion, it is especially efficient to

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combine metals and ceramics or PEO layers synthesized on aluminum alloys in the same friction unit because, in this case, the wear rates both of the metal and of the ceramics are lower than in the metal–metal or ceramics–ceramics contact couples. It was discovered that if we combine the oxide ceramics with the metal in a single contact couple, then the process of wear of the metal becomes slower than in the ordinary metal–metal joint by about two orders of magnitude [5]. The causes of this behavior remain unclear. However, it may serve as an argument for the importance of the correct choice of materials for the triad [2, 5].

At present, it is customary to use oils with ecologically pure admixtures in friction couples. Thus, in particular, it is possible to use aqueous solutions of glycerol, which are well mixed with traditional mineral oils. These mixtures have better lubricating properties than pure oil and the friction coefficient and wear of metal contact couples under the conditions of boundary lubrication decrease by an order of magnitude [6].

In the present work, we study the tribological behavior of iron-carbon alloys in couples with PEO layers synthesized on D16T alloy in I-20 mineral oil and in the same oil with an addition of aqueous solution of glycerol under different contact loads.

Experimental Procedure

We studied the tribological behavior of contact pairs formed by plasma-electrolytic oxide-ceramic layers synthesized on D16T alloy and iron-carbon alloys (dielectric–conductor) according to the "disk–shoe" testing scheme (plane contact) in an SMTs-2 machine according to GOST 23.224-86. The ratio of the areas of contact surfaces in the case of friction interaction was equal to 0.125. In the course of the tests, to fasten the immobile specimen (shoe), we use a self-adjusting device guaranteeing the constancy of the contact area and strict mutual location of the contact surfaces in the course of friction interaction, which enables us to correctly estimate the changes in the tribological parameters of the joint. During the tests, we simultaneously recorded the changes in friction moments by a contactless inductive transducer fastened on the shaft of the installation and the temperature of friction heating of the counterbodies by a chromel-alumel thermocouple mounted in these bodies at a distance of 0.5 mm from the contact zone. The computer recording of the electric signals caused by the changes in the measured parameters was carried out with steps of 0.25 sec in millivolts. The sliding velocity was equal to 0.67 m/sec. The contact load was equal to 4 MPa and the duration of the tests to 4 h. As separating media, we used the I-20 industrial oil (GOST 20799-88) and the same oil with an addition of 1% of a 2.5% aqueous solution of glycerol.

The "disk" specimens with a thickness of 10 mm were made of D16T alloy. The PEO layers were synthesized on their cylindrical surface in a 3 g/liter KOH + 2 g/liter Na_2SiO_3 electrolyte by pulse current with a frequency of 50 Hz in the cathodic-anodic mode. The ratio of currents was $(I_c/I_a) = 1$ and current density constituted 20 A/dm^2. The thickness of the layer after synthesis was ≈ 250–300 μm. Prior to the tribological tests, the PEO layers were ground by a diamond wheel to a size $d = 42 \pm 0.02$ mm and a roughness $R_a = 0.6$ μm. The parameters of grinding were as follows: The rotation frequency of the specimen was equal to 3.17 sec^{-1}, the linear velocity to 30 m/sec, and the table feed to 0.3 m/min.

The "shoe" specimens were made of 45 steel, U8 steel, and SCh 21-40 cast iron with the same internal diameter and thickness. The steel specimens were preliminarily annealed in a vacuum at 800°C for 1 h. Their wear was determined by the gravimetric method on a Radwag WAA-160 analytical balance with a measurement error of ± 0.0001 g. The macrostructure of the surfaces after friction was studied in a Zeiss Stemi-2000c microscope, whereas their microstructure and elemental analysis were carried out in an EVO-40XVP (Carl Zeiss) scanning electron microscope equipped with an INCA-Energy system for X-ray microanalysis.

Experimental Results

The phase composition of the PEO layers synthesized on aluminum alloys is the main factor specifying their mechanical and tribological characteristics. These layers mainly consist of α-Al_2O_3 and γ-Al_2O_3 phases, mullite $(3Al_2O_3 \cdot 2SiO_2)$, and an insignificant amount of amorphous aluminum oxide. The α-Al_2O_3 phase and mullite are stable, while the γ-Al_2O_3 phase is metastable and can be transformed into the α-Al_2O_3 phase in the course of heating within the temperature range from 800 to 1200°C under stationary conditions [3, 4]. The temperature of the phase transformation may also change due to the friction interaction when the crystal lattice of aluminum oxide contains admixtures of other elements. The γ-$Al_2O_3 \rightarrow \alpha$-$Al_2O_3$ transformation may run through the δ- and θ-Al_2O_3 phases. Therefore, the γ-, δ- and θ-phases are regarded as phases with similar structures.

This series of transitions is usually represented in the form of the following simple transformation:
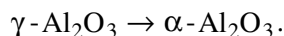
$$\gamma\text{-}Al_2O_3 \rightarrow \alpha\text{-}Al_2O_3.$$

However, there exists one more β-phase (mixed aluminum and sodium oxides), which is transformed into α-Al_2O_3 and the oxide of the corresponding metal at 1600–1700°C.

In the PEO layers synthesized on alloys with elevated contents of copper [in particular, on D16T (3.8–4.9 wt.% Cu], the concentration of the α-Al_2O_3 phase varies within the range 60–70%, whereas the γ-Al_2O_3 phase is predominant on alloys with elevated magnesium content [in particular, on AMg-6 (5.8–6.8 wt.% Mg)]. In the PEO layers synthesized on D16T alloy, we also reveal insignificant amounts of the metastable γ-phase, which may cause a catalytic effect in the zone of friction interaction, in particular, the dissociation of water into oxygen and hydrogen [3, 4].

In the PEO layers, the hardness of the α-Al_2O_3 phase is equal to ≈ 26 GPa, the hardness of γ-Al_2O_3 to 17 GPa, the hardness of mullite to 10.5 GPa, and the hardness of anode-formed amorphous aluminum oxide to 7 GPa. The PEO layers formed mainly of α-Al_2O_3 are characterized by the highest abrasive wear resistance [2–4].

The data of by X-ray phase diffraction analysis of the PEO layers synthesized on D16T alloy demonstrate that, parallel with aluminum oxides, they also contain copper and Cu_2O oxide (Fig. 1). This is also confirmed by the results of electron-microscopic investigations (Fig. 2). Copper is formed in the synthesized layer in the course of synthesis, when the aluminum and copper oxides are formed simultaneously. The excess of aluminum in the plasma discharge partially reduces copper oxide to pure copper [2].

The tribological investigations of the PEO layers in couples with counterbodies of 45 steel, U8 steel, and SCh 21-40 cast iron in the I-20 industrial oil and in the same oil with an addition of 1 vol.% of a 2.5% aqueous solution of glycerol show that the wear of counterbodies made of iron-carbon alloys in the glycerol mixture becomes almost five times weaker (Fig. 3). The friction coefficients and the temperatures of tribological heating are also lower (Fig. 4).

We also determined the influence of the addition of an aqueous solution of glycerol on the changes in the tribological parameters under different specific loads (Fig. 5). As a result, we detect a sharp decrease not only in degree of wear but also in the friction coefficients and temperatures of the tribological heating of contact couples. Thus, the friction coefficient of 45 steel in couple with the PEO layer or with cast iron becomes about 40 or 15 times lower, respectively, while the temperature of tribological heating becomes about four times lower.

The structures tribologically synthesized on the surfaces of counterbodies were analyzed by the electron-microscopic method. It was discovered that they are different after testing in oil and in oil-glycerol mixtures. According to the concept of selective transfer, if, in the course of friction interaction in the indicated mixture,
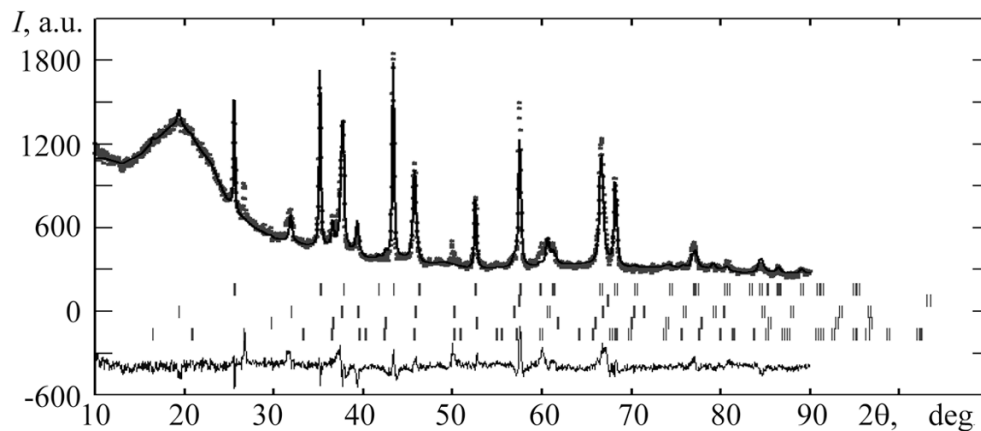
Fig. 1. X-ray phase diffraction analysis of the PEO layers synthesized on D16T alloy by the Rietveld method of full-profile analysis with the use of the Fullprof program.
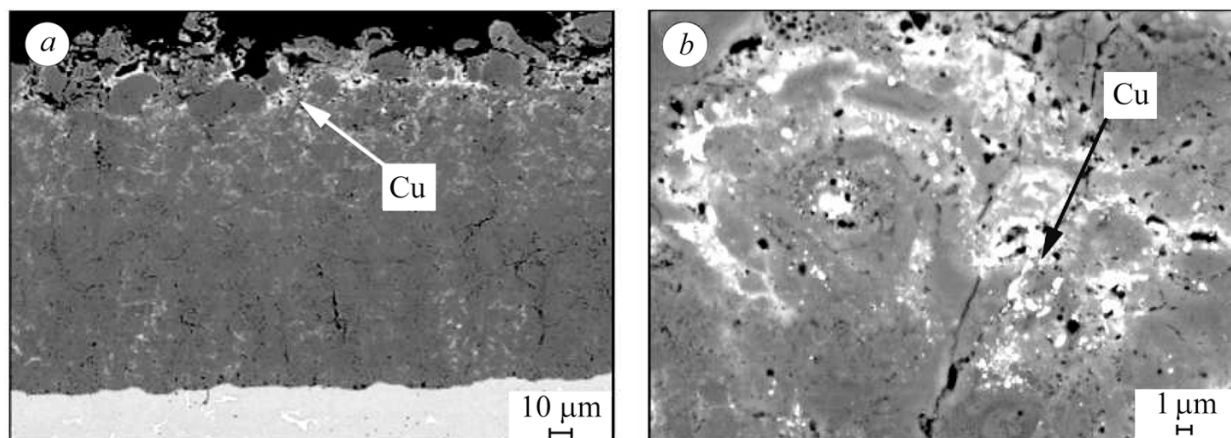

Fig. 2. Typical microstructures of the PEO layers synthesized on D16T alloy: (a) cross section, (b) friction surface.

Table 1. Lattice Parameters and the Fractions of the Phases in the PEO Layers

Phase	a	b	c	SG[1]	wt.%
α - Al_2O_3	4.7591(1)	4.7591(1)	12.9908(6)	R - $3C$	56.26
Al_3O_4	7.9319(1)	7.9319(1)	7.9319(1)	FD - $3M$	37.08
Cu	3.6227(3)	3.6227(3)	3.6227(3)	FM - $3M$	2.45
Cu_2O	4.2538(4)	4.2538(4)	4.2538(4)	PN - $3M$	2.93
SiO_2	4.9285(1)	4.9285(1)	53954(1)	$P32$	1.28

Comment: 1. SG stands for the space group.
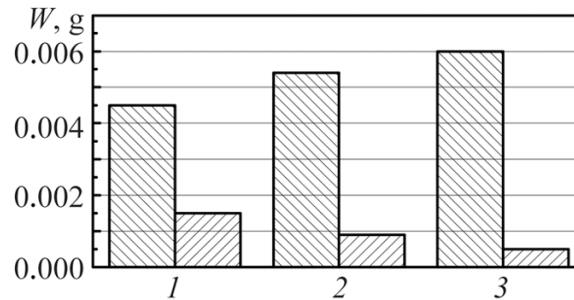
Fig. 3. Wear of counterbodies of 45 steel (1), U8 steel (2), and SCh 21-40 cast iron (3) in couples with PEO layers synthesized on D16T alloy in I-20 m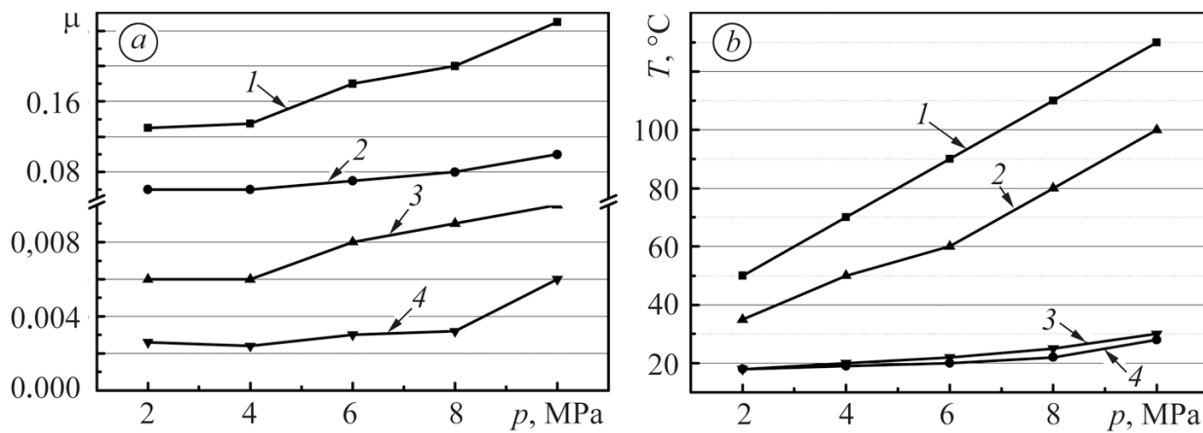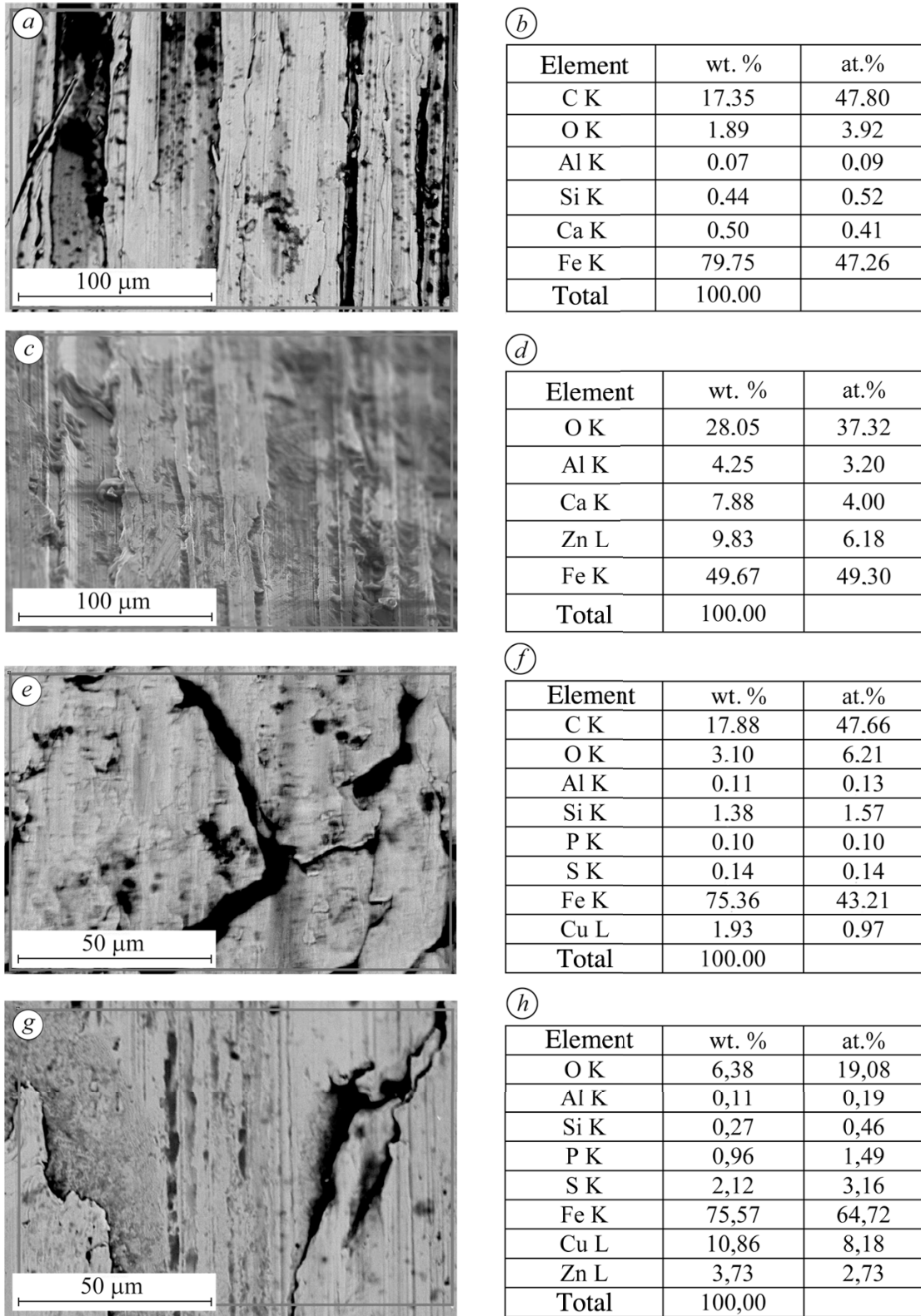ineral oil and in the same oil with an addition of 1% of a 2.5% aqueous solution of glycerol (under a specific load of 4 MPa for a testing time 4 h).
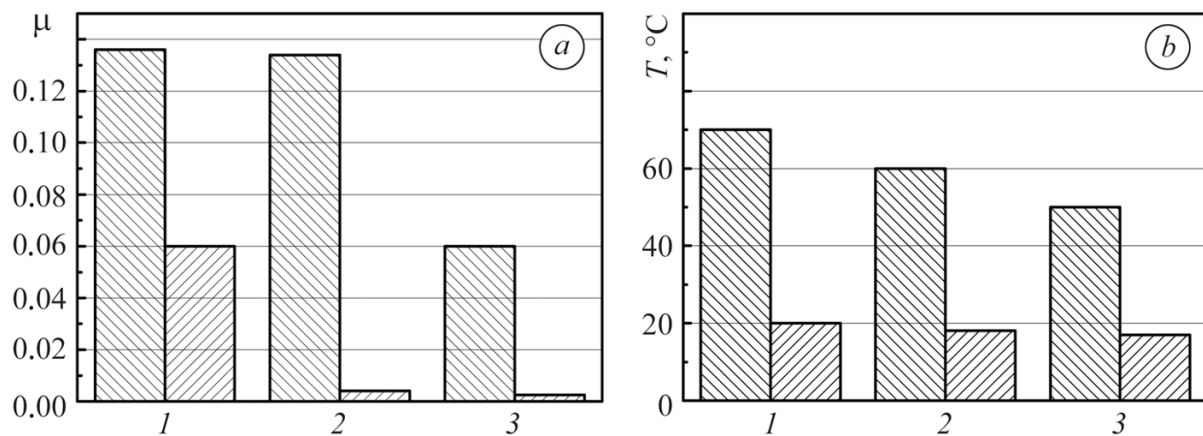
Fig. 4. Mean values of the friction coefficient (a) and temperatures of tribological heating (b) in friction couples of PEO layers synthesized on D16T alloy with: (1) 45 steel, (2) U8 steel, and (3) SCh 21-40 cast iron in I-20 mineral oil and in the same oil with an addition of 1% of a 2.5% aqueous solution of glycerol (under a contact load of 4 MPa for a testing time of 4 h).

Fig. 5. Mean values of the friction coefficient (a) and temperatures of tribological heating (b) in frictional couples of PEO layers with iron-carbon alloys: (1, 3) 45 steel; (2, 4) SCh 21-40 cast iron under different contact loads. Separating media: (1, 2) I-20 mineral oil; (3, 4) mineral oil with an addition of 1% of a 2.5% aqueous solution of glycerol (for a testing time under each load of 4 h).

Element	wt. %	at.%
C K	17.35	47.80
O K	1.89	3.92
Al K	0.07	0.09
Si K	0.44	0.52
Ca K	0.50	0.41
Fe K	79.75	47.26
Total	100.00	

Element	wt. %	at.%
O K	28.05	37.32
Al K	4.25	3.20
Ca K	7.88	4.00
Zn L	9.83	6.18
Fe K	49.67	49.30
Total	100.00	

Element	wt. %	at.%
C K	17.88	47.66
O K	3.10	6.21
Al K	0.11	0.13
Si K	1.38	1.57
P K	0.10	0.10
S K	0.14	0.14
Fe K	75.36	43.21
Cu L	1.93	0.97
Total	100.00	

Element	wt. %	at.%
O K	6,38	19,08
Al K	0,11	0,19
Si K	0,27	0,46
P K	0,96	1,49
S K	2,12	3,16
Fe K	75,57	64,72
Cu L	10,86	8,18
Zn L	3,73	2,73
Total	100,00	

Fig. 6. Microstructures (a, c, e, g) and elemental analysis (b, d, f, h) of the tribostructures formed on the friction surfaces of counterbodies made of 45 steel (a–d) and SCh 21-40 cast iron (e–h) after testing in couples with PEO layers synthesized on D16T alloy in the I-20 mineral oil (a, e) and the oil-glycerol mixture (c, g) (testing time 4 h; contact load 4 MPa,).

the surface of iron-carbon alloy operates in contact with the copper surface, then we observe the transfer of copper to this surface. However, after tests, we discovered zinc (instead of copper) on the steel surface (note that zinc is absent both in the chemical compositions of the contacting surfaces and in oil). At the same time, on the friction surfaces, we also recorded significant differences between the contents of the other elements after testing in these two separating media. In particular, the amount of aluminum increases from 0.09 at.% after testing in oil to 3.20 at.% after testing in the oil-glycerol mixture, while the amount of calcium increases from 0.41 to 4.0 at.%, respectively. Silicon disappears but the oxygen content changes from 3.92 to 37.32 at.%.

The elemental compositions of the friction surfaces of the counterbodies of cast irons after testing in these media are also different. Unlike steel counterbodies, in this case, we detect copper and its amount increases from 0.97 at.% after testing in oil to 8.18 at.% after testing in the oil-glycerol mixture. However, in the case where glycerol was added to oil, we discovered on the surface of the cast-iron counterbody not only copper but also zinc (2.73 at.%). The amount of oxygen increases from 6.21 to 19.08 at.%, the phosphorus content increases from 0.1 to 1.49, and the sulfur content increases from 0.14 to 3.16 at.%. The aluminum content remains practically invariable: 0.13 at.% after testing in oil and 0.19 at.% after testing in the oil-glycerol mixture. The amount of silicon decreases from 1.57 to 0.46 at.% (Fig. 6).

Hence, at present, we cannot correctly explain the friction behavior of the triads formed by the PEO layers synthesized on D16T alloy, iron-carbon alloys, and oil-glycerol mixtures on the basis of the generally accepted concepts of friction and wear. We can formulate only certain assumptions. According to [7], the selective transfer and hydrogen wear are caused by the influence of hydrogen ions (H^+) because just these ions are responsible for the transfer of copper ions from the copper-containing alloys onto the friction surfaces of iron-carbon alloys. In the course of friction interaction, hydrogen is formed in the contact zone as a result of destruction of the separating hydrogen-containing medium, when the reactions with the participation protons take place on the friction surfaces. Furthermore, the catalytic action of juvenile surfaces of the transition metal (iron) with the formation of monatomic oxygen is also possible. The atoms of oxygen may interact with monatomic hydrogen, which leads to the synthesis of water in the contact zone and, hence, to endothermic reactions. The outlined course of the process is possible for temperatures of tribological heating of the contact zone of up to $\approx 65°C$. At higher temperatures, we observe the intense wear under the action of hydrogen.

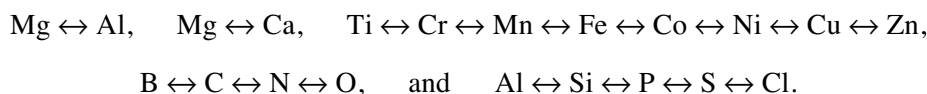In the process of tribodestruction of glycerol, hydrogen ions (H^+) can reduce both copper and iron oxides and also promote the formation of friction polymers, i.e., glycerates of both copper and iron [2, 10]. However, the friction polymers are formed only in the case of triboemission of electrons. The most powerful emitters of triboelectrons are oxide surfaces, namely, oxide ceramics or the PEO layers synthesized on aluminum alloys [2, 7]. High local temperatures on the microasperities of the contact surfaces caused by the friction interaction may activate the emission of triboelectrons, which leads to tribochemical reactions according to the NIRAM (Negative-Ion-Radical-Action-Mechanism) concept [5] as a result of which the reactivity of the surfaces increases.

As a result of the friction interaction of contact couples in the active separating medium, copper oxide from the PEO layers is reduced to pure copper, which is transferred to the friction surface of counterbodies made of iron-carbon alloys and (completely or partially) transformed into zinc. We also detected changes in the quantitative fractions (at.%) of the other elements transferred to the friction surfaces from the PEO layers. These changes can be explained with the help of Kervran's hypothesis about the transformations of chemical elements [7]. However, it was formulated only for biological objects [8, 9].

For the friction triads, there are different approaches that enable one to describe or comprehend the transformations of elements. Indeed, for the friction activation of the contact zone, it is possible to detect the generation of local temperature flashes leading to the tribochemical reactions on the nanolevel according to the NIRAM [5], NAE (Nuclear Active Environment), LENR (Low-Energy Nuclear Reactions), and LANR (Lattice-

Assisted Nuclear Reaction) concepts. Under the action of the active monatomic medium (H^+ ions) in the course of friction interaction, one may observe low-energy reactions (cold fusion) caused by the deformation of the crystal lattice of transition metals and leading to the transmutation or transformation of some elements into other elements [10–12]. These transformations occur at low energies (1–4 eV) due to the addition of one or more protons to the nuclei or, in the course of thermal fusion, as a result of liberation of electrons from the nuclei. If a proton penetrates into the atomic nucleus, then another element (or another isotope of the same element) is formed or this element becomes unstable and disintegrates into two or more elements.

These transformations are realized only under the mechanical influence, in particular, of friction, when the crystal lattice of transition metals deforms under the action of monatomic hydrogen at relatively low energies (1–4 eV), and indicate the possibility of changes in the nature of chemical elements, e.g.,

$$Mg \leftrightarrow Al, \quad Mg \leftrightarrow Ca, \quad Ti \leftrightarrow Cr \leftrightarrow Mn \leftrightarrow Fe \leftrightarrow Co \leftrightarrow Ni \leftrightarrow Cu \leftrightarrow Zn,$$

$$B \leftrightarrow C \leftrightarrow N \leftrightarrow O, \quad and \quad Al \leftrightarrow Si \leftrightarrow P \leftrightarrow S \leftrightarrow Cl.$$

This process is known as the K-capture when a proton (p) captures an electron (e^-) from the K-shell and transforms into a neutron (n) with the emission of energy (ν):

$$p + e^- = n + \nu.$$
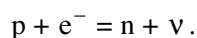
This phenomenon takes place with the minimal energy losses if the atomic masses of the initial and final nuclei are equal. In this case, only free electrons are necessary. The newly formed vacancies in the K-shell are filled with electrons from the outer shell without radiative transitions. The Auger transition is, in this case, most probable. Hence, the phenomenon of K-capture can be used to describe the transformation of elements with relatively low amounts of energy. This process is connected with low energy losses and takes place at energies by about 25 orders of magnitude lower than in thermonuclear reactions and only free electrons are necessary. The oxide surfaces (in particular, oxide ceramics) and also plasma-electrolytic oxide-ceramic layers synthesized on light alloys are the most powerful emitters of free electrons in the contact zone [10, 12].

CONCLUSIONS

We study the tribological behavior of conductor–dielectric contact couples on the example of PEO layers synthesized on D16T alloy operating in contact with iron-carbon alloys, namely, 45 steel, U8 steel, and SCh 21-40 cast iron. As a result of tribological investigations, it is shown that, as a result of the addition of an aqueous solution of glycerol to I-20 mineral oil, the tribological behavior of the triad formed by the PEO layers synthesized on D16T alloy, iron-carbon alloys, and separating medium undergoes substantial changes. Thus, the friction coefficient and the temperature of tribological heating become about 20 and 5 times lower, respectively. Moreover, we observe the realization of the mode of selective transfer and transformation/transmutation of elements in the tribolayers formed on the counterbodies.

REFERENCES

1. P. S. Gordienko, *Formation of Coatings on the Anode-Polarized Electrodes in Aqueous Electrolytes under the Break-down and Sparking Potentials* [in Russian], Dal'nauka, Vladivostok (1996).
2. M. M. Student, V. M. Dovhunyk, M. D. Klapkiv, V. M. Posuvailo, V. V. Shmyrko, and A. R. Kytsya, "Tribological properties of combined metal-oxide-ceramic layers on light alloys," *Fiz.-Khim. Mekh. Mater.*, **48**, No. 2, 55–64 (2012); *English translation: Mater. Sci.*, **48**, No. 2, 180–190 (2012).

3. V. Dehnavi, *Surface Modification of Aluminum Alloys by Plasma Electrolytic Oxidation,* Electronic Thesis and Dissertation Repository (2014).

4. V. Dehnavi, X. Y. Liu, B. L. Luan, D. W. Shoesmith, and S. Rohani, "Phase transformation in plasma electrolytic oxidation coatings on 6061 aluminum alloy," *Surf. Coat. Tech.,* **251,** 106–114 (2014).

5. C. Kajdas, *General Approach to Mechanochemistry and Its Relation to Tribochemistry.* http://dx.doi.org/10.5772/50507.

6. Y. Shi, I. Minami, M. Grahn, M. Bjorling, and R. Larsson, "Boundary and elastohydrodynamic lubrication studies of glycerol aqueous solutions as green lubricants," *Tribol. Int.,* **69,** 39–45 (2014).

7. D. N. Garkunov, G. I. Suranov, and Yu. A. Khrustalev, *Triboengineering. Hydrogen Wear of Machine Parts* [in Russian], UGTU, Ukhta (2007).

8. L. Kervran, *Biological Transmutations and Modern Physics,* Maloine, Paris (1982), rexresearch.com.

9. M. Arghirescu, *The Cold Genesis of Matter and Fields,* Science Publishing Group (2015). http://www.sciencepublishinggroup.com.

10. G. J. Molina, M. J. Furey, A. L. Ritter, and C. Kajdas, "Triboemission phenomena: electronic and photonic outputs from surface modification and its use as novel probes for the dynamics of surface processes," *Wear,* **249,** 214–219 (2001).

11. G. J. Molina, *Triboemission from Ceramics: Charge Intensity and Energy Distribution Characterization,* Blacksburg, Virginia (2000).

12. E. Storms, "An explanation of low-energy nuclear reactions (cold fusion)," *J. Condensed Matter. Nucl. Sci.,* **9,** 1–22 (2012).

13. N. Knorr, *Squeezing out Hydrated Protons: Low-Frictional-Energy Triboelectric Insulator Charging on a Microscopic Scale.* http://dx.doi.org/10.1063/1.3592522.