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RESEARCH OF THE COMPOSITION AND STRUCTURE OF PROTECTIVE FILMS SELF-GENERATED ON THE TRIBO SURFACES OF THE EPOXY COMPOSITE MATERIALS

Summary. The article presents the results of the study of the chemical composition and structure of the protective copper films formed on the tribo surfaces of epoxy composites. Epoxy composites are reinforced with copper oxide particles and discrete carbon fibres. The distribution of chemical elements in the cross section of the epoxy composites is presented. The correlation between the chemical composition of the epoxy composite and the structure of the protective films, formed as a result of a selective transfer during the friction, is established.
Keywords: epoxy composite, frictional interaction, chemical composition, structure, protective film, discrete carbon fibres.

BADANIE STRUKTURY I SKŁADU CHEMICZNEGO WARSTW GENEROWANYCH NA POWIERZCHNI WYBRANYCH KOMPOZYTÓW EPOKSYDOWYCH W OBSZARZE TARCIA W PARACH KINEMATYCZNYCH TYPU KOMPOZYT-STAL

Streszczenie. W artykule przedstawiono wyniki badania składu chemicznego i morfologii warst wierzchnich pojawiających się w strefach tarcia ślizgowego na kompozytach epoksydowych zbrojonych włóknem węglowym. Przedstawi ono rozkład pierwiastków chemicznych w przekroju kompozytu i w obszarze warstwy powstającej w procesach tribologicznych. Określono korelacje pomiędzy składem wymienionych wyżej warstw a składem chemicznym kompozytu.
Słowa kluczowe: kompozyt epoksydowy, interakcja cierna, skład chemiczny, struktura, warstw wierzchnich, włókna węglowe.

Introduction

As a result of physicochemical transformations in the process of frictional interaction, occurs the structural transformation of composites tribo layers with the formation of secondary products in the form of a protective film. The formation of the film is connected with structural self-organization and depends on the conditions in which frictional interaction occurs [1, 2].

The contradiction in views on nature and the mechanism of selective transfer of material in the process of frictional interaction is explained to the lack of sufficient quantity experimental data about the influence of individual factors on the formation of film on tribo surface. The determination of the patterns and mechanisms of formation of protective films on the contact surfaces requires the study of the structure and properties of the surface layers, the morphology of the transfer products, the evaluation of the influence of the temperature-times and load-speed parameters. Therefore, the simulation and analytical description of the process of generation and frictional behaviour of film, as well as finding methods for control of the frictional transfer of material determine the range of the main tasks of studying the friction processes and wear of polymer composites on epoxy resin based [3-6].

The increase of duration of the friction interaction (at moderate speed and specific loads) for most epoxy composites provides a reduction in the intensity of wear due to the selective transfer of the recovered copper from the tribo surface of the epoxy composite to the steel surface of the counter body. Because of this effect a protective film on the tribo surfaces of epoxy composites and counter body begins to form. Film layers are easily slipped, destroyed and restored in the process of tribo interaction [3, 7]. On the tribo surface of the epoxy composites, the formation of the fragments of the protective film occurs in places of localization of copper oxide particles. The morphology of these particles is determined by the composition of the epoxy composite material [8]. The process of copper recovery and it's intense transfer to the counter body is fixed for epoxy composites with a higher content of copper oxide powder. As a result occurs stabilization of the frictional interaction process, which is accompanied by reduce in the intensity of wear [9-14].

The purpose of the work is to analyse the structure of the tribo surface of the epoxy composites and to establish correlation relations between the chemical composition and the intensity of wear of the developed epoxy composites.

Experimental

As the matrix of the developed epoxy, composite materials were used epoxydyan resin ED-20 and the low-temperature hardener polyethylene polyamine. The following fillers were used for reinforce of epoxy polymers: fluoroplastic powder, graphite in the form of flakes, copper oxide powder (CuO), discrete carbon fibres.

The structuring of the epoxy composites lasted for 24 hours under normal conditions, followed by heat treatment in step mode: 50 °C and 100 °C with exposure 1 hour, followed by 120 °C with exposure 4 hours.

Determination of wear resistance was carried on a friction machine SMC-2 under the scheme "disk - block" in conditions of friction lubricating free. The mass of samples was determined on analytical laboratory scales of the type AVIV S / 3-3 with an accuracy of 0.0001 g.

The investigation of microstructure of tribo surface of the epoxy composites was performed on an optical microscope (Axio Lab A1). Chemical and morphological analysis was performed on a raster electron microscope (EVO 50).

Results and discussion

The analysis of the surface layer in the tribocontact zone was to identify the structural elements and to determine the size of the fragments of the formed protective films on the surface of the epoxy composite. To identify the structure of tribolayer was chosen epoxy composite material filled with copper oxide powder and discrete carbon fibres.

At points 1 and 2 (Fig. 1) high carbon value was fixed (43.87% and 47.56%, respectively) (Table. 1). At the given points, the content of oxygen is the highest. These areas can be identified as fragments of the epoxy polymer matrix. The copper content is relatively small and amounts to 33.81% and 30.25% respectively. These points to the redistribution of copper atoms, which fell on the investigated areas from the tribo surface of counter body because of a selective transfer.

Points 3 and 4 are found on particles of copper oxide powder. This corresponds to the obtained value of high copper concentration 60.83% and 62.56% respectively. Oxygen content is low. Carbon content is the lowest among the studied points. This indicates of the presence of macromolecules of epoxy polymer on the surface of particles of copper oxide powder. They are fell on the study surface as a result of the frictional interaction or were impregnated during the formation of the system. Groups of macromolecules of epoxy polymer are easily fixed in the volume of copper oxide particles, because these particles have high porosity (Fig. 2).

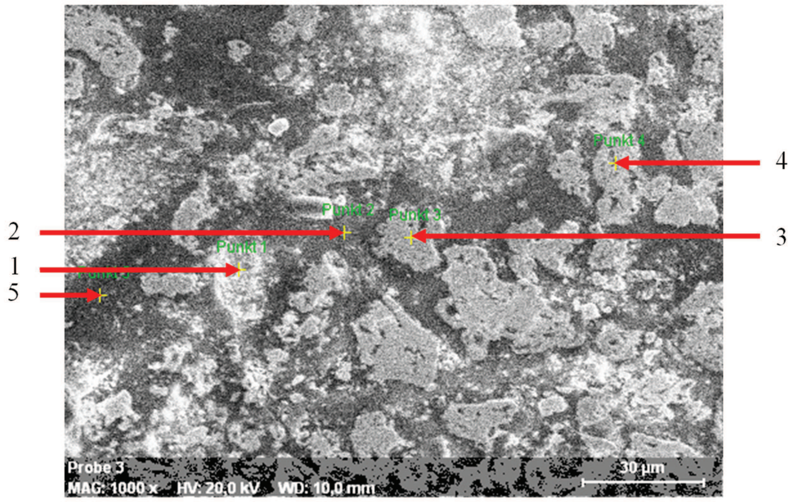


Fig. 1. Microstructure of tribo surface of epoxy composite filled with discrete carbon fiber and copper oxide powder

Point 5 corresponds to the highest carbon content (56.71%) and the lowest copper content (24.47%). Oxygen content is in intermediate value compared to other points. The presence of other chemical elements is accidental on the friction surface, where they can get from counter body or products of wear. The concentration of these elements is low, so their influence on tribotechnical researches can be ignored.

Table 1. Chemical analysis of tribo surface of the epoxy composite material

Points	**Chemical elements, %**					
	C	O	Cu	Si	Cl	Fe
Point 1	43,87	21,16	33,81	0,22	0,36	0,58
Point 2	47,56	20,99	30,25	0,24	0,31	0,65
Point 3	20,13	17,93	60,83	0,22	0,19	0,69
Point 4	21,39	14,86	62,56	0,23	0,27	0,68
Point 5	56,71	17,59	24,47	0,32	0,25	0,66

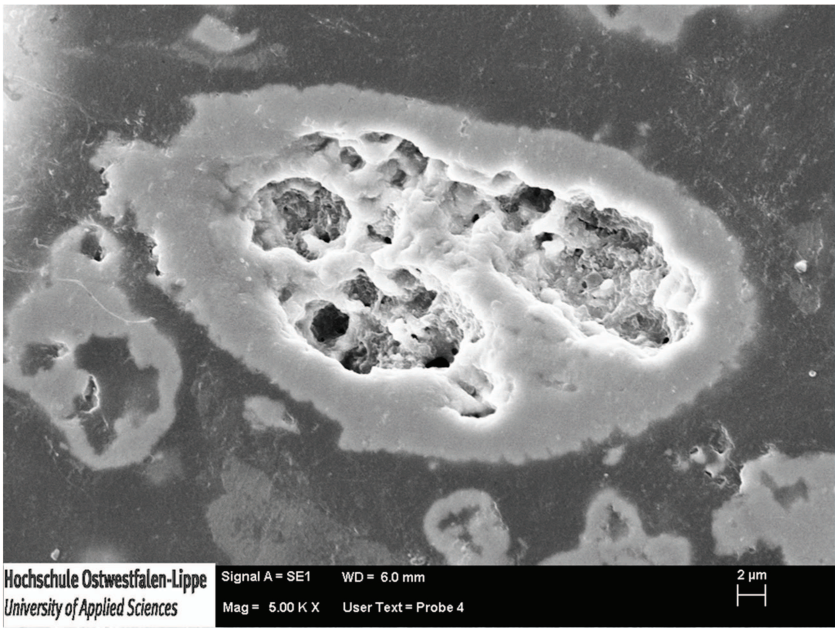
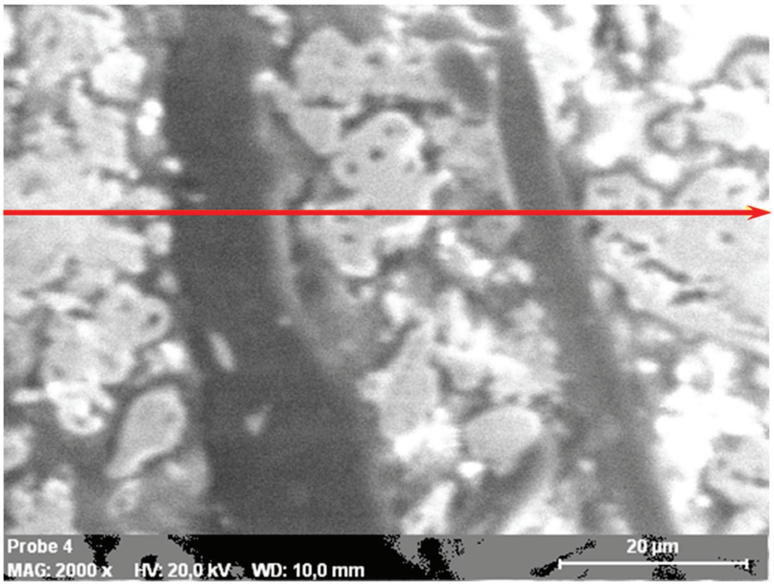


Fig. 2. The microstructure of the particle of copper oxide powder, × 5000

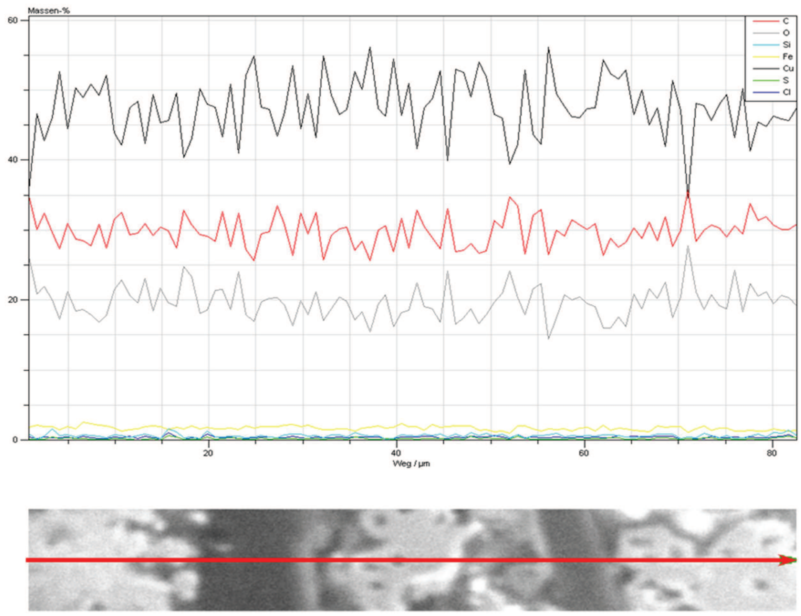
The carbon content on the surface of the epoxy composite material (Fig. 3), filled with copper oxide powder and carbon fiber, ranges within 26...36% and oxygen ranges within 19...28%. Copper is present in the largest quantity of 34...56%, which is primarily due to the high content of copper oxide powder (200 mass part) in the epoxy composite material.

The dependence of the concentration of carbon, oxygen and copper in the surface tribolayer of the epoxy composite material is interisting. Carbon with copper oxide restores copper with the following removal of carbon in the monoxide form. Therefore, for these chemical elements is characteristic the inverse mechanism of redistribution, in which the growing of copper concentration is accompanied by decreasing of carbon and oxygen concentration.

It has been experimentally established that for moderate modes of tribo-load (forces of the pressure P=1.5 MPa, V=2.3 m/s), the low wear intensity has epoxy composites of the original composition with optimal content of graphite, fluoroplastic powder, discrete carbon fibre and copper oxide powder (5,4 mass part). Studies at a higher speed sliding V=3.6 m/s have shown that the wear intensity increases several times, especially for composites with graphite free. Under this load regime, the temperature in the contact zone is very high, which leads to thermal destruction of the epoxy polymer matrix.



a



b

Fig. 3. The change of the chemical composition along the vector on the surface of the epoxy composite material: (a) microstructure of the surface; (b) change of the chemical composition

Epoxy composites containing graphite have a higher wear resistance because graphite is the solid lubricant and is more resistant to elevated temperatures. With an increasing of specific load up to 2 MPa with sliding speed V=3.6 m/s the content of copper oxide powder performs main function. The intensity of wear increases almost in 3 times for the epoxy composite of the original composition with 5.4 mass part of copper oxide powder. The intensity of wear increases almost in 1.5 times for the epoxy composite of a similar composition with a high content of copper oxide powder (200 mass part).

The epoxy composites of the origin composition on the tribo surface have a small area of copper film of 12.09% (Fig. 4, a), which is due to the low content of copper oxide powder (CuO = 5.4 mass parts) (Fig. 4, b). For a composite filled with graphite, fluoroplastic powder, copper oxide powder (200 mass parts) and discrete carbon fiber, the protective film is formed in the form of small fragments (Fig. 4, c). These fragments are evenly distributed on the tribo surface of the epoxy composite. These fragments represent thin layers of copper atoms on the surface of particles of copper oxide (Fig. 4, g). These layers are formed as a result of copper recovery from copper oxide. The increasing of copper film is complicated, because graphite and fluoroplast prevent the fixation of the transferred particles of copper on the tribo surface of the epoxy composite.

The elevated temperatures that occur during the friction interaction contribute to the oxidation and reduction reactions on the surface of the epoxy composites in the tribocontact zone. There is a local recovery of copper from particles of copper oxide (CuO) during their interaction with carbon. Then the particles of the recovered copper from the surface of the epoxy composites and are transferred to surface of counter body and connected to it with the formation of adhesive bonds. During the frictional interaction, there is also a reverse process of transfer of copper atoms to the surface of the epoxy composite material in places of localization of particles of copper oxide powder. These particles are centres of formation and growth of fragments of protective copper film. Therefore, the process of forming of fragments of a copper film with a larger area is more intense for epoxy composites with a higher content of copper oxide powder. For epoxy composites filled with copper oxide powder (200 mass parts) and discrete carbon fibre, the area of the copper film is larger (21.84%), which is confirmed by decreasing in the intensity of wear by 13-15%.

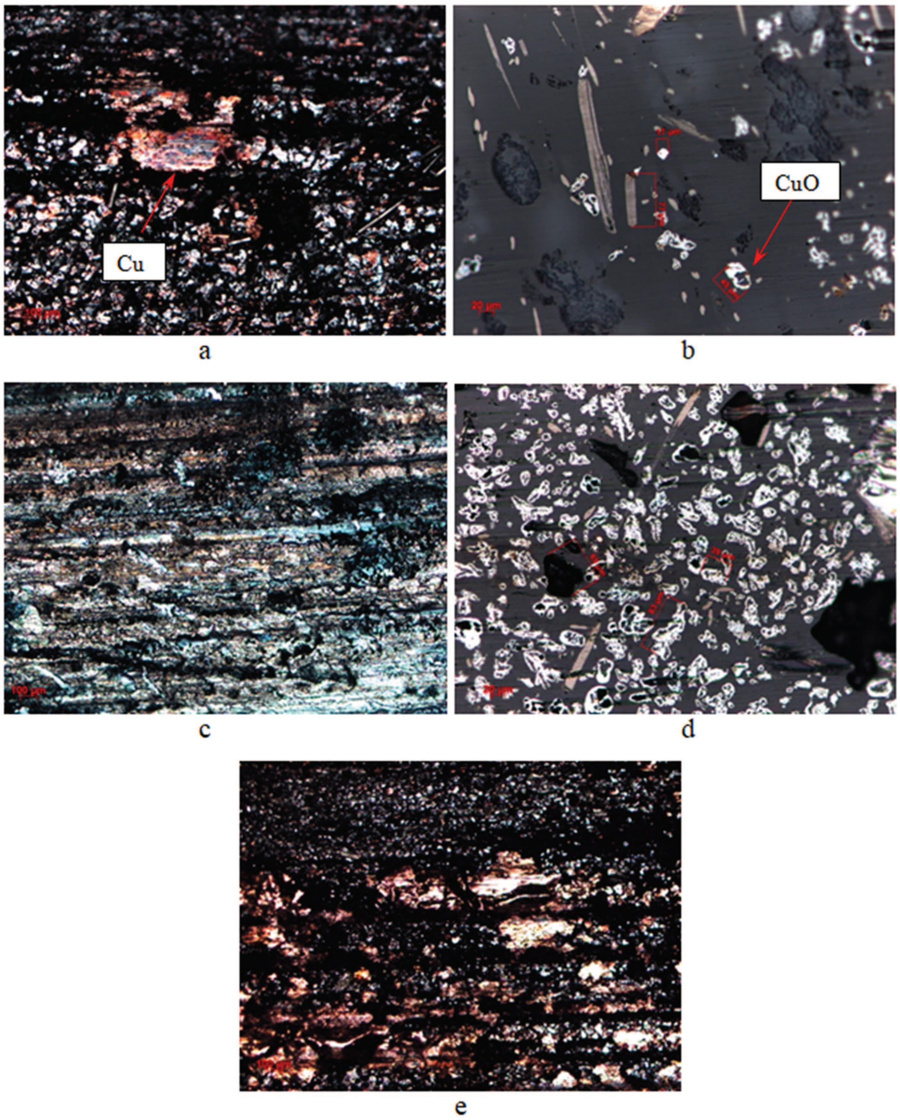


Fig. 4. The structure of the tribo surface of the epoxy composites (a, c, e) and microstructure of the epoxy composites (b, d) is filled: (a, b) with copper oxide powder (5.4 mass part), fluoroplastic powder, graphite in the form of flakes, carbon fibre; (c, d) with copper oxide powder (200 mass part), fluoroplastic powder, graphite in the form of flakes, carbon fibre; (e) with copper oxide powder (200 mass part), carbon fibre

Conclusion

High copper concentration (up to 62.56%) on the tribological surface of the epoxy composite indicates on the presence of fragments of a copper film. As a result of long-term tribotechnical research, the intensity of wear of epoxy composites is reduced by 2.1...3.2 times, which indicates the ability of the material to self-organizing of structure during frictional interaction. Developed epoxy composite materials can be operated in conditions of static load and lubricating free in the range of modes of triboload: with a sliding speed of up to 2 m/s (forces of the pressure P=1.5...1.8 MPa), with a sliding speed of up to 4 m/s (forces of the pressure P=1,2...1,5 MPa), with sliding speed up to 5 m/s (forces of the pressure P=0.9...1.2 MPa).

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