Mechanics

Investigation of Structural and Phase Transformations of Steel Surfaces during Sliding Friction in the Environment of Oils Modified with Carbon Nanoform Particles

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(Presented by Academy Member Tamaz Natriashvili)

The research aim of the present paper was thorough investigation of structural and phase transformations of steel surfaces during sliding friction in the environment of two new lubricating oils with suspended (additive) amorphous fine carbon (AFC) nanoparticles and Fe-cluster doped CNTs using the methods of scanning electron microscopy (SEM), energy-dispersive x-ray microanalysis (EDX) and Auger electron spectrometry (AES). Simulation of sliding friction on the surfaces of high carbon steel balls in two new high performance lubricating oils with suspended amorphous fine carbon nanoparticles (AFC) and Fe-doped carbon nanotubes (CNT) was realized using a four-ball tester. It is shown that at the running-in stage, a thin (~1 µm) amorphous film (practically without roughness) is formed on the mating friction surfaces, consisting of the products of the conversion of oil additives to graphite (sp^2 state), diamond-like carbon (characterized by a mixture of states sp^2 and sp^3) and pure diamond crystallites (sp^3 state) by tribosynthesis. *© 2022 Bull. Georg. Natl. Acad. Sci.*

amorphous fine carbon (AFC), Fe-cluster doped CNTs, graphite, diamond, friction surface

When a tribological pair (tribopair) operates in the environment of lubricating oils, a selection of oil additive particles/nanoparticles takes on particular significance, since their nature, morphology, composition and physical-mechanical properties may have a substantial impact on the course (dynamics) of structural and phase transformation processes in case of friction under lubricating conditions and formation of adaptive secondary structures in the surface layers, as screening protection from friction pair base material destruction [1, 2]. Therefore, the tribological pair surface modification directly in the running-in regime in the environment of lubricating oils using interaction with different additive particles/nano-particles suspended in oil, is an effective approach

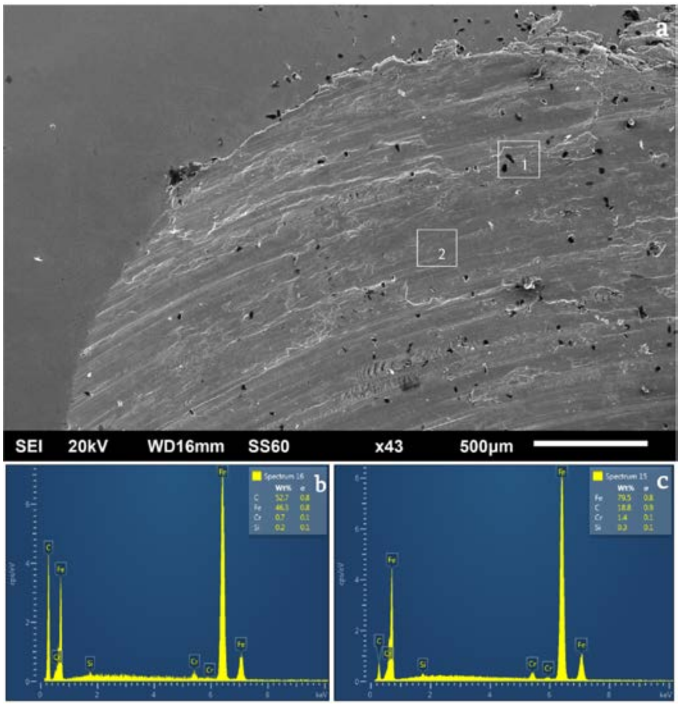

Fig. 1. SEM image of ¼ part of friction surface on the steel ball formed after sliding in area of oil 1J modified with nano-particles of ultradispersive amorphous carbon (a) and respective EDX spectra from selected areas 1 – (b) and 2 – (c).

to improvement of wear resistance of metallic materials that has been successfully adopted for enhancement the damage resistance ability in case of heavy-loaded friction. In this regard, a search for new materials and development of technologies of their entering into oil as non-sedimentating additive aimed to create new generation of lubricating compositions is a relevant objective of tribonics [3, 4]. From this viewpoint, over the last two decades a special attention of researchers has been given to elemental carbon and its new nanoforms.

In [4, 5] it was demonstrated the possibility of obtaining new composition of highly-efficient transmission oils with AFC additives in order to reduce friction and wear. In particular, the phenomenon of graphite and diamond crystallites' tribosynthesis realized by friction of steels in the medium of oil containing suspended of amorphous carbon nanoparticles has been observed [5].

The research aim of the given paper was investigation of structural and phase transformations of steel surfaces during sliding friction in the environment of two new lubricating oils with suspended (additive) AFC nanoparticles and Fe-cluster doped CNTs using SEM, EDX and AES methods.

Experimental

Two oil compositions based on the same thin oil have been prepared for experiments, from which the oil of the first composition (marked as 1J) consisted 5% of AFC particles ~200÷500Å in size as an additive, which was obtained from acetylene production waste, while Fe-cluster doped CNTs nanopowder, prepared according to the technology described in [6, 7] has been entered in 5% quantity as an additive into the oil of the second composition (marked as 1G).

The sliding friction of high-carbon steel (ShKh-15) ball surfaces in the environment of the above-mentioned lubricating oils has been simulated using four-ball tester of our own design [8]. Experiments have been conducted at 150 MPa load, rotation velocity: 1500 min^{-1}, duration: 10 sec. at room temperature. Right after friction tests, the morphology, composition and phase constitution of steel ball wear surfaces have been examined using the scanning electron microscope JSM-6510LV (JEOL, Japan) with EDX spectrometer.

Element and phase distribution at physical surface of friction and in depth from free surface of investigated specimen after SEM-EDX experiments has been exposed to the Auger-electron spectrometry (AES) examination, carried out using spectrometer LAS-2000 (RIBER, France) with primary electron beam energy E_p = 5keV.

Results and Discussion

Fig. 1 gives SEM image of the steel balls friction surface formed during sliding in run-in regime in the environment of oil 1J modified with AFC (a) and respective EDX spectra from selected areas 1 (b) and 2 (c). It is seen that by the end of run-in regime a mirror-like surface with roughness signs of the plastic flow type is already formed all across the round friction spot. At the same time, there are observed graphite particles inclusions (see Fig. 1, a selected area 1) formed due to AFC nanoparticles conversion taking place during tribosynthesis. Indeed, comparison of EDX spectra in Fig. 1, b and c, recorded for selected areas 1 and 2, respectively, shows that the inclusions with a black contrast observed in area 1 represents graphite particles, since the carbon peak in EDX spectrum (Fig. 1,b) has several times higher intensity than the similar peak in the spectrum recorded from area 2 (Fig. 1, c), where inclusions are not observed. Though, the carbon peak intensity in the latter EDX spectrum exceeds several times the expected carbon peak intensity in case of the respective carbon concentration in the tested steel. This fact may be caused by the enrichment of the surface (evidently amorphized) layer (formed by friction) with AFC nanoparticles, which was not subject to the conversion into graphite.

SEM image of the steel ball friction surface formed during sliding in run-in regime in the environment of oil 1G modified with Fe-cluster doped CNTs (a), and respective EDX spectra from selected areas 1 (b) and 2 (c) is presented in Fig. 2. The friction surface formed during sliding in run-in regime on steel ball in the environment of oil 1G

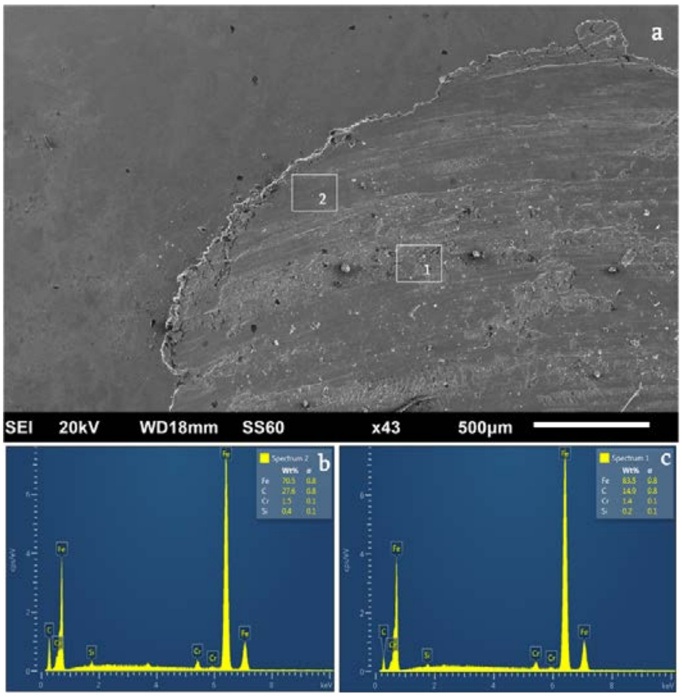

Fig. 2. SEM image of ¼ part of friction surface on the steel ball formed after sliding in area of oil 1G modified with Fe-cluster doped CNTs (a) and respective EDX spectra from selected areas 1 – (b) and 2 – (c).

represents a mirror-like surface virtually without roughness signs of the plastic flow type (Fig. 2, a). In addition to the foregoing, the given surface is distinguished by much smaller number of observed inclusions with black contrast (graphite particles) and prevailing of inclusions with white contrast (diamond microparticles) (Fig. 2, a) in contradistinction from the surface shown in Fig. 1. Comparison of carbon peaks intensity in EDX spectra recorded for selected areas 1 and 2, respectively (Fig. 2, a) makes clear that the carbon peak in the spectrum obtained from the area 1 (Fig. 2, b) is twice higher than that formed from area 2 (Fig. 2, c) that is caused by the presence of particles with white contrast in the selected area 1.

A hundredfold increased SEM image of the area 1 presented in Fig. 3 that is marked in Fig. 2, a demonstrates the availability of tribo-synthesized diamond microcrystal (white contrast) (area 1) on the friction surface and of nano-film in the form of islands made of CNTs destruction products (grey contrast) (area 2). The ratio of carbon and iron intensity peaks (close to 1) observed in EDX spectrum recorded for the selected area 1 (Fig. 3, b), explicitly points at that the given diamond microcrystal has been synthesized due to nucleation exactly on Fe-cluster (~100 nm), associated with CNT and moved to the friction surface during boundary lubrication. Increased value of carbon peak intensity in EDX spectrum from selected area 2 (Fig. 3, c) in comparison with the expected carbon peak intensity from tested carbon steel confirms that the observed nano-film (islands with grey contrast) (Fig. 3, a) is formed from CNTs destruction products (and probably from the oil itself).

The above-cited results make evident that identified differences in morphology, structural and phase composition (against the background of common features) of friction surfaces formed such as of thin film during run-in regime on steel surfaces under conditions of sliding friction during boundary lubrication in the environment of oils 1J and 1G are explicitly associated with peculiarities of structure, morphology, size, composition and

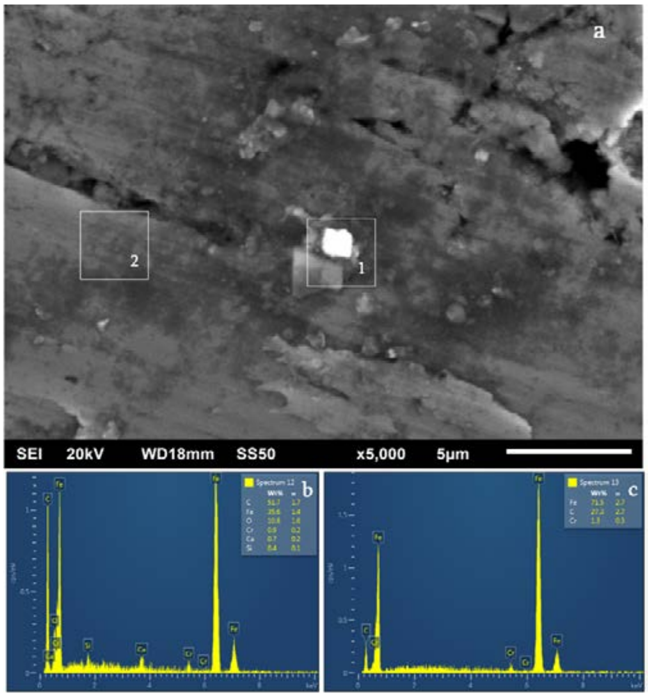

Fig. 3. Magnified SEM image of selected area 1 in Fig. 2. a demonstrated tribosinthesized diamond microcristall, on the steel ball friction surface, formed in area of oil, modified with Fe-cluster doped CNTs (a) and the respective EDX spectra from selected areas 1 – (b) and 2 – (c).

physical-mechanical properties of additive particles used for oil modifying. In order to verify this hypothesis, the trends of carbon allotropic transformation during steel surfaces friction in the environment of oils modified above have been investigated using AES methods.

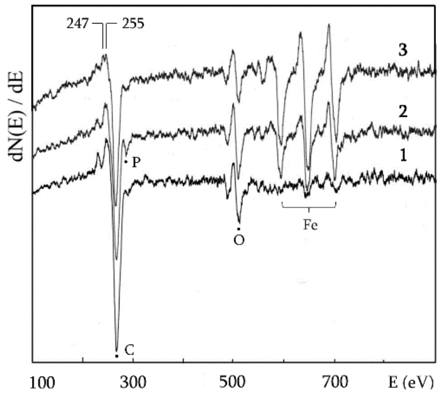

Fig. 4. Differential Auger-electron spectra of the friction surfaces of steel balls after sliding in area of oils modified with nanoparticles of ultradispersive amorphous carbon (curve 1 and 2) and Fe-cluster doped CNTs (curve 3). Spectra 1, 2, 3 were recorded after sputtering of surface layer: 1 – 0 Å, 2 – 1000 Å, 3 – 1000 Å in thick by bombardment using argon ions with the 2KeV energy.

The differential Auger-electron spectra recorded in the 100÷900eV energy range for the steel balls friction surface after sliding in the environment of oils modified with AFC nanoparticles (curves 1 and 2) and Fe-cluster doped CNTs are given in Fig. 4 (curve 3). Curve 1 presents the Auger-spectrum of the steel balls friction surface (prior to initiation of bombardment by argon ions), formed during sliding in the environment of oil 1J (shown in Fig. 1, a). Auger-spectrum recorded prior to bombardment by argon ions for friction surface formed during sliding in the environment of oil 1G (shown in Fig. 2, a) was entirely identical to curve 1. Occurrence of only intense peaks of carbon (272 eV) and oxygen (503 eV) atoms in the given Auger-spectrum, in presence of disappeared intensities of triplet peaks of L_3VV Auger-transitions of iron atoms (marked by arrow in Fig. 4) confirms the availability on the investigated friction surface of a layer adsorbed from the atmosphere, the effective thickness of which does not exceed ~50Å and which exists at the top of any solid loaded from the air. The Auger spectra identified for the surfaces formed during sliding friction in the environment of oil 1J and 1G after removal of the sputtered layer ~1000Å in thickness is demonstrated in Fig. 4, curves 2 and 3, respectively.

As one can see, the observed difference between Auger-spectra recorded prior to and after removal of adsorbed layer is that in the latter case Auger-spectra (curves 2 and 3) are represented by intense peaks: triplet peak of L_3VV Auger-transitions of iron atoms, oxygen atoms $KL_{23}L_{23}$ Auger-transition peak and carbon atoms KLL Auger-transition peak, which are shifted to less energies (270 eV) and has a changed shape due to appearance of plasmon peaks from the side of less energies (247 eV and 255 eV) and more energies (plasmon peak P on the curve 2, Fig. 4). A definite difference of intensity ratio and forms of iron and oxygen Auger peaks detected when comparing spectra 2 and 3 in Fig. 4, confirms the different oxidation degree of iron atoms (probably their different amount per unit of volume) consisting formed thin surface layers (described in Figs. 1 and 2) during friction in the environment of oils modified with nanoparticles of different carbon nanoforms. It is obvious that atomic iron clusters incorporated in CNTs and covered by multiwall graphene layer from oil 1G volume in the course of the mentioned surface layer formation enter into its volume without oxidation, while iron atoms of the steel ball interact with oxygen and undergo oxidation.

As a short-range ordered configuration of carbon atom groups, which can exist in sp^3, sp^2 and even in the linear sp electronic hybridization, may simultaneously be realized in the disordered structure of AFC nanoparticles, this amorphous additive material during tribosynthesis will be respectively distinguished by polyvariety of crystallization trends of many phases (graphite (sp^2), diamond (sp^3) and DLC (mixture of sp^2 and sp^3), whereas nanocomposite additive material – Fe-atomic cluster doped CNT during tribosynthesis will initially experience conversion of sp^2-bonded carbon (CNT) into sp^3-bonded carbon (diamond), as far as it contains catalyst in the form of Fe-atom cluster, facilitating the abovementioned type of conversion.

Conclusions

- The structural and phase transformations on the surface layers of steel during sliding friction in the environment of oils modified with carbon nanoform particles (CNFs) have been holistically investigated by the methods of scanning electron microscopy (SEM), energy-dispersive X-Ray microanalysis (EDX) and Auger electron spectrometry (AES).
- Thus, the comparative study of the fine structure of carbon KLL Auger-transition peaks (the shape, energy disposition of main and plasmon peaks and ratio of their intensities) showed that the thin surface layers formed on the steel balls in run-in regime during sliding in the environment of oils modified with different CNFs additives (AFC and Fe-cluster doped CNTs) have a complicated multiphase composition as a mixture of inclusions in the matrix of nanoparticles with different carbon allotropies (graphite, diamond, DLC), such as conversion of tribosynthesis products from initial CNFs additive and part of non-converted initial additive nanoparticles.

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მექანიკა

ნახშირბადის ნანოფორმების ნაწილაკებით მოდიფიცირებული ზეთის არეში სრიალით მოხახუნე ფოლადის ზედაპირების სტრუქტურული და ფაზური ტრანსფორმაციების კვლევა

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მასკანირებელი ნანოფორმების ნაწილაკებით მოდიფიცირებული ზეთების არეში სრიალის ხახუნის დროს, მიმუშავების ეტაპზე, შეწყვილებულ ფოლადის ხახუნის ზედაპირებზე ტრი-

ბოსინთეზის გზით წარმოიქმნება თხელი ამორფული შრე (პრაქტიკულად სიმქისის გარეშე), რომელიც შედგება ზეთის დანამატების გარდაქმნის პროდუქტებისგან, როგორიცაა გრაფიტი (sp^2 მდგომარეობა), ალმასის მსგავსი ნახშირბადი (ხასიათდება sp^2 და sp^3 მდგომარეობების ნარევით) და სუფთა ალმასის კრისტალიტები (sp^3 მდგომარეობა).

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