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Mechanics

Features of the Formation of Self-Organized Secondary Structures on the Surfaces of Steel Parts during Rolling Friction in Oil Environment Modified with Carbon Nanotubes Doped with Clusters of Fe-Atoms

Giorgi Abramishvili[*], Elguja Kutelia[**], Tamaz Natriashvili[§], Jumber Iosebidze[*], Besik Eristavi[**], Malkhaz Khvedelidze[*], Konstantine Beradze[*]

[*] *Department of Road Transport and Logistics, Georgian Technical University, Tbilisi, Georgia*
[**] *Republic Center for Structural Research, Georgian Technical University, Tbilisi, Georgia*
[§] *Academy Member, Department of Road Transport and Logistics, Georgian Technical University, Tbilisi, Georgia*

The formation of self-organized secondary structures on the friction surfaces of steel during rolling friction in the medium of oil modified with Fe-atom cluster-doped CNTS, was investigated using the methods such as scanning electron microscopy (SEM), energy-dispersive X-ray microanalysis (EDX) and Auger-electron spectrometry (AES). It is shown that on the surfaces of high-carbon steel tribo-pair friction in the medium of oil-based nanolubricant with 5wt.% of Fe-atom cluster-doped Carbon nanotubes (CNTS) as an additive, at the end of the running-in stage, a thin ($\leq$ 1000Å) self-organized film is formed in the form of a dissipative ordered film. The film is composed of a mixture of nanoparticles of carbon allotropic forms (graphite, diamond-like carbon, graphene) and iron carbide additionally generated due to the conversion of additive nanoparticles using tribosynthesis. This heterophase continuous film, with self-organized secondary structures, having a feature of the minimum entropy production rate in the self-organized state, during the tribosystem (tribo-pair + intermedium layer) transition from the running-in regime to the stationary regime of friction (even in the case of load increase) leads to the reduction of wear and substantial shift of the destruction onset time above the protective film. *© 2024 Bull. Georg. Natl. Acad. Sci.*

friction surface, running-in, nanolubricant, Fe-atom cluster-doped CNTs

Steels, cast irons and iron-based alloys are, at this moment and obviously, will be in the near future, irreplaceable main constructional materials for manufacturing machines and assemblies where heavy-loaded tribo pairs are used. That is why the development of methods for creating wearless and low friction conditions for coupled sliding and rolling tribo pairs made of the mentioned materials is a high-priority task for modern mechanical engineering.

According to well-known criteria for provision of low external friction conditions [1-3], the key to this important scientific and technological problem lies in the development of effective lubricating nanocompositions that promote the formation at the tribo-pair surfaces of the film in the form of so-called intermedium layer with ultra-high wear resistance. At that, friction and wear are the classic examples of irreversible dissipative processes emerged due to combined structural and physical-chemical phase transformations taking place in the tribo-systems operating under conditions of both dry and lubricated condition.

In the case of dry friction of the tribo-pair (frictional / antifrictional material + counterbody) composed of different kinds of materials, such as, e.g. the pair of brake shoe / steel (cast iron) or polymer / steel (cast iron), formation of the intermedium layer is rather simpler to explain by the known mechanism of material (wear products) transfer from the surface of frictional / antifrictional body to the mating surface of the tribo-system counterbody [1-5].

In contradistinction from dry friction, in the case of liquid lubrication of the tribo pair, especially during friction of the same metal materials (steel/steel, steel/cast iron) in the medium of lubricating oil, the mechanism of formation of the working frictional film – intermedium layer at the friction surfaces is less evident, since in this case a mass transfer from the surface of one body to the friction surface of the other one is virtually impossible. It would be natural to assume that under conditions of liquid lubrication, a lubricating oil and its additives are the main sources delivering the substances necessary for formation of the intermedium layer to the friction surfaces. Therefore, selection of oil additive particles/nanoparticles takes on particular significance, since their nature, morphology, composition and physical-mechanical properties may have substantial impact on the course of processes of structural and phase transformation under lubricating conditions and on formation of adaptive secondary structures as protection films from destruction of steel friction pair base materials. From this viewpoint, over the last two decades special attention of researchers has been given to elemental carbon and its new nanoforms.

In our previous work [6], there was demonstrated the opportunity of receipt of a new composition of highly-efficient transmission oils with amorphous finely-dispersed carbon (AFC) additives in order to reduce friction and wear of heavy loaded steel tribo-pairs. In particular, the phenomenon of tribosynthesis of micro/nanocrystallites of carbon allotropic forms, realized by friction of steels in the medium of oil containing AFC nanoparticles as an additive, has been observed first in the work [7]. The recent development of nanotechnology related to production of new carbon nanoforms (CNTS, CNPS) doped with different atom (Fe, Ni or Co) clusters [8, 9], such as nanocompositional hybrid additives for oils, has come up to new frontiers through creation of new generation of nanolubricants with superior performance, which are widely used in automotive, power and other industries.

In our recent work [10], for the first time there has been conducted the study of structural and phase composition of the boundary film (intermedium layer) formed on the steel surfaces during rolling friction in the running-in regime in the medium of oil, modified with Fe-atom cluster doped CNTS nanoparticles. It has been shown that a formed boundary film has a complicated multiphase composition as a mixture of inclusions in the amorphous matrix of nanoparticles with different carbon allotropies (graphite, DLC, diamond) such as products of tribosynthesis-induced conversion from the above-mentioned hybrid additive nanoparticles. This heterophase film makes a positive gradient of mechanical properties, which may ensure necessary conditions for normal external friction and wear without scuff up to origination of critical fatigue stresses.

It can also be noted that from the viewpoint of thermodynamics (non-equilibrium thermodynamics), formation of self-organized surface structures in the course of irreversible processes [11, 12] caused (accompanied) by structural and phase transformation during frictional interaction of solid state surfaces, clearly makes visible the signs of a new concept of friction, disclosure of implementation mechanisms of which still needs in-depth experimental studies at the micron, sub-micron and atomic levels using modern research methods.

Related to the abovementioned, the given work set a goal of study of formation of self-organized secondary structures on the heavy-loaded friction surfaces of steels (tribo-pair with the same steels) in the medium of oil modified with Fe-atom cluster doped CNTS during transition of tribosystem (tribo-pair + intermedium layer) from running-in regime to stationary mode of friction.

Experimental

According to the aim of this research, a thin oil based nanolubricant has been prepared for experiments, in which the oil consisted 5wt.% of Fe-atom cluster doped CNTs, as a hibrid nanocompositional modifying additive. Nanopowder composed of Fe-atom cluster doped CNTS particles has been obtained using the set-up described in [8], providing realization of the doping mechanism of a single CNTs with Fe-atom cluster [9]. The work [9] presents an SEM image of a nanopowder in a free-flowing state, consisting of CNTs doped with clusters of Fe atoms used as an oil additive, and the corresponding EDX spectrum. According to [9], a nanopowder consists of individual nanocomposite core-shell-type multi-walled carbon nanotubes (with several μm long and ≈ 250 nm in diameter), in which the Fe atomic cluster incorporated in carbon shell is mainly located at one end of the nanotube, namely in the inlet of MWCNTs channel.

The rolling friction of high-carbon steel ShKh-15 ball surfaces in the medium of the abovementioned nanolubricating oil has been simulated using four-ball tester of own design. The experimental technique includes preliminary running-in of balls friction surfaces at 3000 N axial load, 1800 min-1 rotation velocity and 20 min duration. After running-in a rolling of running-in surfaces was continued in stationary regime at 4500 N axial load during 100 min.

Right after friction tests, the morphology, composition and phase constitution of steel ball wear surfaces secondary structures have been examined using the scanning electron microscope JSM-6510LV (JEOL, Japan), with EDX spectrometer. The same samples after the SEM-EDX study were moved into the analytical chamber of the Auger-electron spectrometer RIBER LAS-2000 (France) with the primary electron beam energy $E_p = 5$ keV. The surface was sectioned by sputtering of the analyzed surface through its bombardment by the argon ions with an energy of 2 keV and a sputtering rate $\approx$ 10Å/min.

Results and Discussion

The comparative study utilizing SEM, EDX and AES methods of friction surfaces formed on the steel balls by the end of run-in regime at 3000 N axial load, as well as after working under conditions of stationary friction mode was conducted on the specimens passed the tribological test when rolling under the 4500 N load. The moment of run-in stage completion and system transition to the stationary mode of rolling was determined upon reaching of constant minimal value of friction coefficient established after decrease of its maximal value during rolling onset.

Figure 1 shows the SEM images (a, d) and respective EDX spectra (b, c) demonstrating a characteristic morphology and elemental composition of the steel ball surface with non-working area (right to the dashed line) and adjacent area formed during running-in regime with an axial load 3000 N for 20 min duration in the medium of developed nanolubricant oil (left to the dashed line). As is seen from SEM image in Fig. 1a, a transformation of steel ball initial surface morphology is clearly manifested during running-in process by its rolling friction in the medium of oil modified with nanoparticles of Fe-atom cluster doped with CNTs. In particular, a non-working area of the original steel ball surface, which is distinguished by characteristic rectilinear track of microscratches formed during finish mechanical machining (polishing), after running-in looks like a smooth-faced surface due to crumple and scuff of additive nanoparticles hitting the mated friction surface from nanolubricant volume (compare areas to the right and left of dashed line at SEM image, Fig. 1a).

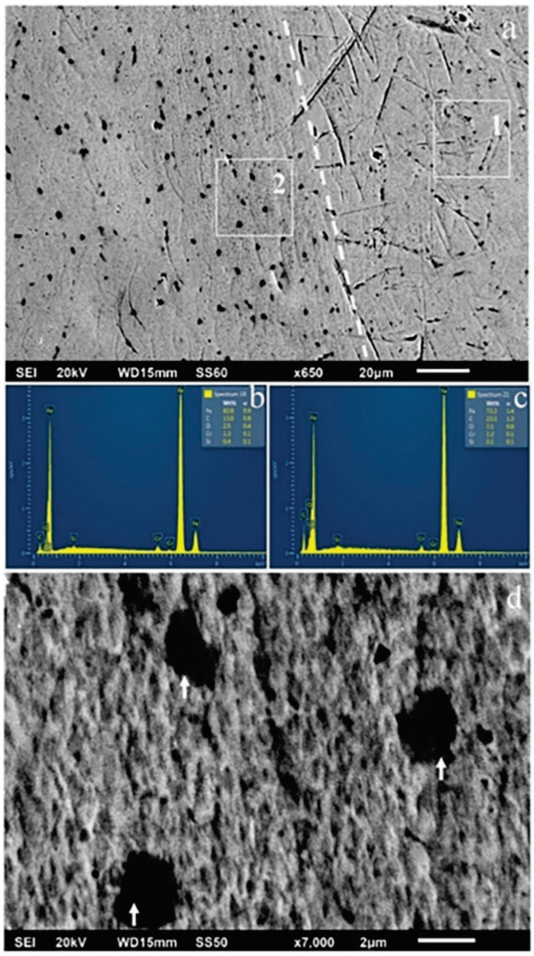

Fig. 1. SEM images of steel ball surface (a), demonstrated friction surface area, formed after running-in in medium of developed nanolubricant oil (to the left of the dotted line) and adjacent (to the right of the dotted line) non-working area of the original steel ball surface; (b) – EDX spectrum from the marked area-1, (c) – EDX spectrum from the marked area-2, (graphene/graphite, particles, marked by ⇑, indicate at the same time the direction of rolling).

EDX spectrum recorded for the non-working surface from the marked area-1 in Fig. 1a, is represented by peaks of elements (Fe, Cr, Si, C) with intensities corresponding their concentration in the used high-carbon chromium steel ShKh-15 (Fig. 1,b). Comparison of SEM images of steel ball surface non-working area and area after running-in points at the fact that during running-in process structural and phase transformations of hybrid additive nanoparticles hitting the friction pair surface from the nanolubricant volume due to tribosynthesis occur simultaneously with the above described morphological transformation of the initial friction surface [10]. This is evidenced by the contrast (observed at the SEM images in Fig. 1 a and d) from the particles (inclusions) of different dispersity, which are statistically uniformly distributed throughout the friction area. The magnified SEM image of the marked area 2 in Fig. 1a clearly shows that at the end of running-in regime there is formed on the friction surface the self-organized dissipative flow ordered film, composed of a mixture of products of tribosynthesis-induced conversion of different carbon modifications (graphite, DLC, graphene) and probably iron carbide nanoparticles, formed as a result of mechanochemical synthesis during interaction of iron and carbon clusters as the products of hybrid additive nanoparticles destruction. The EDX spectrum (Fig. 1c) recorded from the area 2, compared to the EDX spectrum of the area 1 (Fig. 1b) is represented by nearly double increased intensity of carbon peak, but at the same time by decreased intensities of peaks corresponding to the components of steel ball (Si, Cr). Therefore, taking into account the depth of penetration of the accelerated electrons by 20 KeV (≤1μ), generating the secondary X-Ray radiation, one may conclude that the thickness of the above-mentioned heterophase self-organized quazi solid state film formed on the friction surface together with the thickness of carbon absorbed from the atmosphere

(≤50Å) doesn’t totally exceed several hundreds of angstroms (≤1000Å).

This quazi solid state boundary film is a kind of plastic, viscous lubricant with inclusions of solid nanoparticles entered from the medium of nanolubricant oil at the stage of short-term running-in. Hereinafter, during tribo-system (tribo-pair + intermedium layer) transition to the prolonged (long-term) stage of stationary friction mode, a dissociation and regeneration of its forming components will uninterruptedly occur with continuous entry of the additive nanoparticles from nanolubricant volume that ensures improvement of its longevity during stationary friction mode thanks to formation of the secondary structure with a property of minimum entropy production [12].

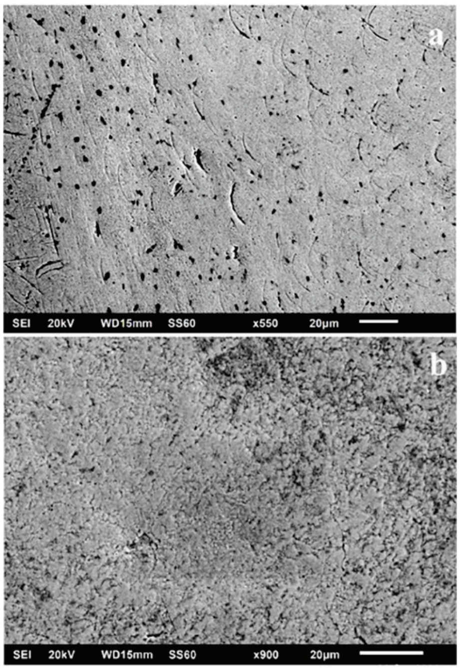

Fig. 2. SEM images of the friction surface on steel ball, formed after running-in with an axial load of 3000 N for 20 min in medium of developed nanolubricant (a), and SEM images of the same surface after prolonged friction in stationary mode (at a constant minimum value of the friction coefficient) for 100 min at an axial load 4500 N (b).

Figure 2 shows SEM images of the surface formed during rolling in run-in regime (a) and the same surface after prolonged friction in stationary mode at the increased axial load (b). Morphology of the surface formed at the end of run-in process, in addition to the presence of a contrast on graphite or graphene particles inclusions, is characterized by availability of paraboloidal scratches (tracks) of sliding and rolling of hard nanoparticles (DCL, iron carbide). A paraboloidal shape of observed tracks and their unilateral orientation (see Fig. 2a), along with bearing capacity in the direction of sliding, are caused by additional tangential component of a force emerged during rolling contact of steel balls having spherical curvature of surfaces. Well-defined traces of tracks point at the small thickness (≤1000Å) of the heterophase film, tribosynthesized at the end of running-in regime, which creates a positive gradient of mechanical properties prior to transition to the stationary friction mode, which will proceed for a long period at sharply increased bearing capacity of this frictional conjugation.

Comparison of SEM images of the friction surfaces after short-term running-in regime (Fig. 2a) and ensuing prolonged operation in the stationary friction mode (Fig. 2b) allows us to assume the further development of structural transformation processes during tribo-system transition from run-in stage to the stage of stationary friction mode.

Peculiarity of the above-mentioned adaptive self-organized film (as a intermedium layer in tribo-pair) is that in case of continued rolling under high load during stationary mode there may occur processes of continuous destruction (dispergation) and regeneration of its forming components and additive nanoparticles newly entering from the nanolubricant oil volume predominantly by a mechanism of mechanochemical synthesis causing to the certain extent a gain of thickness of continuous adaptive dissipative-ordered protective film that leads to reduction of wear and increase of destruction onset time of the above-mentioned intermedium layer film between mated surfaces of friction pairs.

In order to explain the revealed phenomenon of carbon nanoforms tribosynthesis-induced conversion to different allotropic transformations and to determine the type of carbon forms in the intermedium layer, the same samples examined by the SEM-EDX techniques, have been additionally tested using AES.

In Figure 3 the series (1-4) of peaks of carbon KLL differential Auger-electron spectra are shown, which were recorded after sputtering of 1 – 100Å, 2 – 300 Å, 3 – 600 Å and 4 – 1000Å surface films removed from the friction surfaces of steel balls, formed during running-in (a) and after prolonged friction in stationary mode (b).

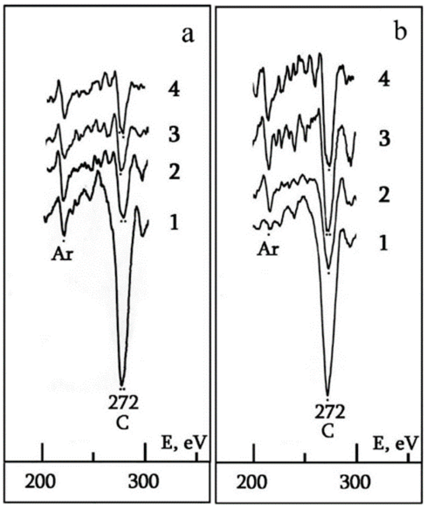

Fig. 3. Series of carbon KLL differential Auger-electron spectral peaks, recorded in the energy range of 200-350eV from friction surfaces of steel ball, formed after running-in (a), and after prolonged friction in stationary mode (b). Series of carbon KLL differential Auger-electron spectral peaks (1-4) were recorded in both cases after sputtering of surface layer: 1 – 100 Å, 2 – 300 Å, 3 – 600 Å, 4 – 1000 Å.

Characteristic features of the fine structure (shape, energetic displacement of main and plasmon peaks, satellite peaks caused by chemical effects) known for KLL peak of carbon atoms Auger-electron spectrum [13] allowed us to determine phase composition of tribosynthesized surface films on the steel friction surfaces in the medium of nanolubricant oil with Fe-atom cluster doped CNTS additive. Comparison of carbon Auger peaks given in Fig. 3 a and b clearly shows that tribosynthesized films (intermedium layer) formed in both considered cases on the steel ball friction surface consist of a mixture of carbon allotropic forms (sp2 state of hybridization) and iron carbide particles, just with different distribution and quantitative relationship in depth of mentioned films. In particular, a film located at 100Å depth from physical surface of the surface film formed as a result of running-in is a carbon phase (Fig. 3a, peak 1 is typical for graphite/graphene). Starting from 300 Å to 1000 Å depth carbon peaks shape is typical for iron carbide (Fig. 3a, peaks 2, 3, 4). The surface film (as a intermedium layer) formed in the process of prolonged operation in stationary friction mode consists of carbon phase (Fig. 3b, peaks 1 and 2 are typical for graphite and amorphous carbon). Starting from 600 Å to 1000 Å, a shape of carbon peaks is typical for iron carbide (Fig. 3b, peaks 3 and 4). At that, carbon peaks in carbide state represented in Fig. 3b (peaks 3 and 4) have double more intensity than carbon peaks of carbide state shown in Fig. 3a (peaks 2, 3, 4). These results of Auger analysis are in good correlation with SEM-EDX analysis results and with our opinion expressed on their basis on the efficiency of a new nanolubricant used in the given work.

Conclusions

It is established that on the steel friction surfaces in the medium of oil based nanolubricant with 5% Fe-atom cluster doped CNTS as an additive, at the end of the running-in regime, a thin (≤1000Å) self-organized quazi solid state film is formed in the form of dissipative ordered film composed of a mixture of nanoparticles of carbon allotropic forms (graphite, diamond-like carbon, graphene, diamond), and iron carbide additionally generated due to the conversion of hybrid additive nanoparticles and its ultra-dispersed destruction products using tribosynthesis during the transition of the tribosystem from the running-in regime to stationary mode of friction.

Based on the theoretical foundations of the process of converting nanodispersed carbon into diamond nanocrystals, formed on the basis of data and previous studies, in order to optimize the composition of lubricating oils, it is advisable to use carbon CNTs doped with ferromagnetic clusters as an additive, since tribosynthesized self-organizing (containing a phase of diamond nanoparticles) in them in the environment, the heterophase secondary surface structure characterized by the properties of high dissipative order and minimal rate of entropy production; this leads to a corresponding adaptation of the tribological properties of the oil to new conditions during the transition of the friction unit from the running-in mode to the stationary mode and with increasing loads and, as a consequence, to a significant reduction in wear and friction.

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მექანიკა

Fe-ატომების კლასტერებით დოპირებული ნახშირბადის ნანომილაკებით მოდიფიცირებული ზეთის არეში გორვით მოხახუნე ფოლადის დეტალების ზედაპირებზე თვითორგანიზებული მეორეული სტრუქტურების ფორმირების თავისებურებები

გ. აბრამიშვილი*, ე. ქუთელია, თ. ნატრიაშვილი§, ჯ. იოსებიძე*,**
ბ. ერისთავი, მ. ხვედელიძე*, კ. ბერაძე***

** საქართველოს ტექნიკური უნივერსიტეტი, საავტომობილო ტრანსპორტისა და ლოგისტიკის დეპარტამენტი, თბილისი, საქართველო*
*** საქართველოს ტექნიკური უნივერსიტეტი, სტრუქტურული კვლევების რესპუბლიკური ცენტრი, თბილისი, საქართველო*
§ აკადემიის წევრი, საქართველოს ტექნიკური უნივერსიტეტი, საავტომობილო ტრანსპორტისა და ლოგისტიკის დეპარტამენტი, თბილისი, საქართველო

შესწავლილია თვითორგანიზებული მეორეული სტრუქტურების ფორმირება ფოლადის გორვით მოხახუნე ზედაპირებზე, Fe-კლასტერებით დოპირებული ნახშირბადის ნანომილაკების (CNTs) დანამატებით მოდიფიცირებული ზეთის არეში, მასკანირებელი ელექტრონული მიკროსკოპის (SEM), ენერგოდისპერსიული რენტგენული მიკროანალიზის (EDX) და ოჟე-ელექტ-

რონული სპექტრომეტრიის (AES) მეთოდების გამოყენებით. ნაჩვენებია, რომ მაღალნახშირბადიანი ფოლადისგან დამზადებული ტრიბოწყვილის მოხახუნე ზედაპირებზე, რომლებიც მუშაობენ 5% (მას.) Fe-კლასტერებით დოპირებული ნახშირბადის ნანომილაკების (CNTs) დანამატებით მოდიფიცირებული ზეთის არეში, მიმუშავების ეტაპის დასასრულს წარმოიქმნება თხელი (<1000Å) თვითორგანიზებული ფენა დისიპაციურად მოწესრიგებული აფსკის სახით. ეს აფსკი შედგება ნახშირბადის ალოტროპული ფორმების ნანონაწილაკებისა (გრაფიტი, ალმასის მსგავსი ნახშირბადი, გრაფენი) და რკინის კარბიდისაგან, რომლებიც დამატებით წარმოიქმნება ტრიბოსინთეზით, დანამატის ნანონაწილაკების ტრანსფორმაციის შედეგად. ჰეტეროფაზის ეს უწყვეტი შრე (აფსკი), თვითორგანიზებული მეორეული სტრუქტურებით, რომელსაც ახასიათებს ენტროპიის წარმოების მინიმალური სიჩქარე თვითორგანიზებულ მდგომარეობაში, ტრიბოსისტემის (ტრიბოწყვილი + შუალედური ფენა) მიმუშავების რეჟიმიდან სტაციონარული ხახუნის რეჟიმში (თუნდაც დატვირთვის გაზრდის შემთხვევაში) გადასვლისას განაპირობებს ტრიბოსინთეზირებული აფსკის რღვევის დაწყებამდე დროის მნიშვნელოვან გადიდებას – დაღლილობითი ცვეთის შემცირებას.

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