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THE ROLE OF SELF-ORGANIZATION AND SELECTIVE TRANSFER IN FRICTIONAL COATINGS FORMATION

Emilia ASSENOVA

Society of Bulgarian Tribologists, Sofia, Bulgaria, emiass@abv.bg

Abstract: The adaptation to the variable and complicated conditions of contact interaction in the tribocouples can be realized by self-organization and synergy mechanisms. One of the phenomena of the most important acts of self-organization in contact systems is the selective transfer of materials between the friction surfaces and the microtribological (physico-chemical and mechano-chemical) processes that take place during friction under conditions of selective transfer. Reduced wear and friction result after the formation in the contact zone of non-oxidized thin film formed as friction protection coat during sliding. The paper overviews quickly self-organization and the selective transfer as self-organization phenomenon depending on interface energy and the material exchange. Generation of the frictional coating requires special combination of materials of the contact surfaces, as well as special lubricant between them.

Keywords: self-organization, selective material transfer, frictional coatings.

1. INTRODUCTION

Transferring the models and methods of the well-ordered classical sciences, e.g. the Newtonian mechanics, into the basics of new interdisciplinary sciences is difficult, suspicious and mostly inadequate. The main difficulty is in the generalization of the concepts and the formulation of the tasks, which should permit the usage of well-known classical procedures. As a result the real and complex system is normally being replaced by a simplified model, just assumed to be equivalent, but whose behavior rarely corresponds to the observed behavior of the real complex system.

In the middle of the last century the notion of complexity was ranked; scientists from different disciplines started to study phenomena in complex systems that seemed to be governed by inherent creativity, by the spontaneous appearance of novel structures or the adaptation to a changing environment. The new concepts have slowly started to combine into a new approach, the knowledge of self-organization and adaptation [1-4].

The ability of a system "to forget" the external perturbations is related to a specific organization of the system - self-organization [2,3]. Far from equilibrium, due to the flow of mass, energy and information towards and from the system, arise new structures dissipative structures, clusters, nano-clusters, etc. It is as if the system of molecules arranges itself into a more ordered pattern. It was noted that such a phenomenon contradicts the mechanistic world view. The formation of these new structures is characterized by spontaneity. Furthermore, their formation is intentional, not fully arbitrary. The aim of the system is to survive in spite of the external perturbation. The latest only stimulates (unlocks) internal mechanisms in the system as a result of which the new structures are formed.

As concerns tribology, a basic conception is that friction and wear are most easily monitored by means of the behavior of the thin material layer - the third body - which divides and unifies sliding, rolling and impacting bodies. If the original contact pair does not possess a separate intermediate layer, its formation can be evoked by the contact processes themselves. The adaptation to the variable and complicated conditions of contact interaction of the tribo-couples is realized by self-organization and synergy mechanisms. In its essence, self-organization is the spontaneous creation of a coherent pattern out of the local contact interactions between initially independent elements. Synergy corresponds to the mutual work of two or more agents working together to produce a result not obtainable by any of the agents independently [5-14].

Using favorable friction phenomena of selforganization (selective transfer, abnormally low friction in a vacuum, etc.) plus wide introduction of new methods for combating harmful phenomena related to the increased entropy production, could offer considerable potential economic benefits. One of the phenomena of the most important acts of selforganization in contact systems is the selective transfer of materials between the friction surfaces and the microtribological (physicochemical and mechano-chemical) processes that take place during friction under conditions of selective transfer. Reduced wear and friction result after the formation in the contact zone of non-oxidized thin film induced during sliding. The selective transfer is a unique phenomenon of active self-adaptation, which is exhibited in friction of solids and minimizes losses (of material, energy and information) in this interaction. It has much in common with friction of animal and human joints, and many other phenomena from the living nature.

The present paper presents a quick overview of the advance of studies on selforganization and selective transfer related to tribology and contact science.

Following these lines, the paper seeks to bind down tribology, reliability, quality and safety [15-20] in the application of selective transfer processes in friction couples based on the review of self-organization in tribology [5,6,20-27]. Consideration is given to the selective transfer phenomenon in friction couples consisting of copper cooperating with steel in the medium of special lubricant and to the creation of a secondary protective layer, namely a self-formed layer serving to prolong the life of the friction unit. The selective transfer friction prevents dislocation accumulation in surface layers [5,6]. The coat formed directly on the rubbing surface leads to low friction and highly improved wearresistance with implications in combustion engine cylinders (even racing car engines), heavy loaded friction units, aircraft units, etc.

2. TRIBOLOGY AND SELF-ORGANIZATION

The non-equilibrium open systems are characterized with their interaction with the environment and the exchanged mass-, energyand information flows. These systems are the so-called "immersed systems" [2], i. e. their behavior becomes informative if only they are regarded as imbedded into their milieu. Accordingly, these systems are accentuated "contact systems", because of the unfeasibility to consider them as isolated objects, separately of their contact with all other elements of their environment. Viewed in this larger sense, tribology as a science of contact is anchored in the deep essence of things. Tribosystems as systems for the behavior of which contact has the most crucial importance, are also open nonequilibrium systems. They may exist only due to their embedding in the environment. Friction, a typical contact process, can be seen as resistance/opposition of environment against system behavior. If we set aside the sense of contact as topological property, contact represents the possibility for the third body to be regarded as a multi-phase system with specific properties and behavior.

In non-equilibrium open systems, as well as in contact systems, the ability to extinguish

external disturbance is due to dissipation and, under given conditions, relies to the specific organization, the self-organization. Nonequilibrium becomes a source of ordering: a new space-time organization of the system and new structures, the dissipative structures, may appear.

As regards the tribosystems, their state is determined external conditions by (surrounding medium - elements, pressure, temperature; motion velocity; contact pressure, etc.), and by internal conditions (properties and specifics of the contact body). Impact on the system and changes in the external conditions, could improve output parameters, i.e. improve effectiveness. At the same time for unchanged external situation non-equilibrium system each attempts towards self-organization on the account of internal options and mechanisms, choosing for process progression ways with minimum loss energy price of (the is sometimes recompensed by feasible entropy production).

Are there enough good reasons for using the concept of self-organization in tribology?

Investigators are used to bind selforganization with the living nature. Although not much popular, the study of the role of selforganization in friction and wear processes has a special significance.

The major features significant for the ability of self-organization to be ascribed to the contact zone are as follows. On one hand, the properties of the contact body are structuresensitive; the structure follows the dynamic nature of the contact, forming and destroying during friction. On the other hand, in this dynamics, the contact structure exhibits a multiscale organization with marked hierarchy allowing encouraged adaptation and selforganization in the contact zone. It is this organization that brings the tribosystem far equilibrium through destabilization from during the friction and wear processes encouraging the formation of such protection structure patterns in order that the system could survive; destruction is combined with restoration, i.e. self-organization processes are available.

Moreover, there is close relation between tribology and synergetics [9,13,14,26,28]. Tribological systems exhibit behavior and characteristics, which are typical for synergetic e.g. well-expressed nonlinearity systems, [9,28,29], auto-catalysis, feedback function, energetic and materials heterogeneity, training ability, etc., plus some particular attributes, like energetic and materials heterogeneity, memory, learning capability. Further, friction is a distinctive dissipative process based on many different grounds on lower level of matter: adhesion, elastic and plastic deformation, fretting, fracture. On the macroscale friction remains general energy dissipation and resistance acting opposite to movement and displacement. The structure-sensitivity and hierarchy functions, the features related to synergetics and the universality of friction also suggest tribosystems' consideration under selforganization principles.

Tribology history knows a number of examples about the studies of selforganization in tribology, related to the named of great scientists which left significant traces and schools, like D.N. Garkunov, B.I. Kosteckii, G. Polzer, L.I. Bershadskii, N.A. Bushe, M. Nosonovsky, B. Bhushan, G. Shpenkov, etc. [5-7,9,12,14,21,30-31].

Most of the studies of self-organization in tribology are connected with experimental and production investigations. Few of the works deal with theory developing models of selforganization in triboprocess related to thermodynamic entropy generation in the irreversible processes friction dissipation and wear degradation [9,32-34].

Another important tribological conception is that friction and wear are most easily monitored by means of the behavior of the thin material layer – the third body – which divides and unifies sliding, rolling and impacting bodies. If the contact pair needs a special intermediate layer during friction, its formation can be evoked by the contact processes themselves through self-organization in contact.

Relying on above reflections and on the previous experience, following formulation could be extracted:

Having in view Tribology, and especially Green Tribology, two environmental pollution trends result from the basic tribological processes friction and wear. Friction and wear are both irreversible dissipative processes; the first one - as irreversible energy dissipation, and the second one - as irreversible mass dissipation. During the process of friction heat is generated in the contact of the interacting surfaces; the bigger part of the generated energy is irreversibly dissipated in the environment, polluting thus the environment with increased temperature, resp. increased entropy, i.e. trend toward energy disorder is observed. During the process of wear related with friction surfaces deterioration, the increase of entropy, resp. of the disorder state, is due to the mass flow of the wear debris from the surface to the environment, i.e. again pollution process increasing entropy.

The fight for friction and wear reduction, i.e. against increased entropy production, accounting also material, energy and environment saving, can be found in several approaches of contact preparation, roughly gathered in two groups:

- 1. Manipulation of the intermediate layer, the third body, using contact zone optimal lubrication [17,35,36] and/or surface materials treatment through appropriate surface coatings and layers [7,18,37,38].
- 2. Providing conditions, under which the interacting frictional surfaces adapt to the changes and form spatial and temporal patterns acting as protective structures during self-organization [9,20,21,24,32,39].

3. SELF-ORGANIZATION AND SELECTIVE TRANSFER IN TRIBOSYSTEMS

In tribology are known many effects connected to self-organization: the effect of extremely low friction after irradiation of the surfaces with alpha-particles or ultrasound; the effect of selective transfer of material between the contacting surfaces; the effect of surface-active additives in lubricants which

cause decrease of surface strength; the effect of autovibrations, etc. In all cases formation of new structures is observed - these are secondary protective surface structures. The study of the secondary protective surface structures is a central question in the study of self-organization in contact systems. It is important to make use of the possibilities to optimize tribosystems behavior by employing the conception of self-organization. For example the problem of optimizing the tribosystemis is related to the possibility of optimizing the conditions, under which the system is introduced in operating regime through the purposeful affect for forming the secondary protective surface structures. Generally, the affect is on the working surface (material, preliminary structure) and on the conditions of the process, in such way that the internal for the system factors of its selforganization could be switched on [21,40].

One of the phenomena of most important acts of self-organization in contact systems is the selective transfer of materials between the friction surfaces and the microtribological (physico-chemical and mechano-chemical) processes that take place during friction under conditions of selective transfer. Highly reduced wear and friction result after the formation in the contact zone of frictional coating formation. The selective transfer minimizes losses of material, energy and information in the contact interaction.

The phenomenon of friction transfer is observed for nearly all materials (metals, polymers) ceramics, and and their combinations. According to N.K. Myshkin, polymers are most disposed to friction transfer when rubbing both against metals and polymers. Considering friction between PTFE and PE was discovered that PTFE is transferred in the form of small flakes, the thickness of the transferred layer increasing monotonically and then oscillating about a mean value depending especially on load and sliding velocity [22].

Having in view the nature of tribology as interdisciplinary science, the progress in investigations on contact interactions of solids under friction, especially in the new phenomena such as selective transfer, is only possible if based on advances in the physics of solids surfaces, thermodynamics, contact phenomena and mechanics of damage, electro- and mechanochemistry, materials technology, etc. [21]. Particular attention is to be paid to the quality of surface preparation and to the interaction between lubricants and metal surfaces.

4. EXAMPLES ON SELECTIVE TRANSFER

An interesting example comes from the experience of the Space Research Institute of the Bulgarian Academy of Sciences together with the Tribology Centre – Sofia. Properties of antifriction materials adaptable to the friction conditions were studied. One important material for reducing friction in vacuum is lead bronze (Fig. 1) [41]. The structure of the material is on copper basis (solid solution of α -copper and Cu₃P, alloyed with Mn and P), and contains lead configurations in the form of globular clusters. Friction and wear properties were studied by means of the developed by the team vacuum tribometer [41,42].



Figure 1. COF *f* vs. vacuum degree for various couples; 1: lead bronze/Ti alloy; 2: Fe/Pb; 3: graphite bronze/Al; 4: Cu/Steel; 5: Be

During friction, lead comes on the surfaces and forms thin intermediate layer, acting as a lubricant. The X-ray microanalysis of the surface shows that under atmospheric conditions the friction layer contains Pb oxide, and under vacuum - it is a friction layer of metallic lead. The antifriction properties result by the quantity, distribution and form of lead components. At vacuum was obtained a significant decrease of friction and wear intensity. The contact pressure has been found, at which the surrounding atmosphere cannot manage with the formation of regenerated secondary structures on the surface after their abrasion, and the system enters the pathological regime.

Next example (Fig. 2) shows the influence of electric current in the course of action of selective transfer. Diverse processes, which take place on contact surfaces as a result of the selective transfer, become more complicated under the effect of electric current. Experiments show that electric current in the initial stage makes surfaces covered with an extremely thin copper layer [43]. The copper film formation rate and its thickness are functions of the current density and direction. Overall said, electric current intensifies the selective transfer.



glycerin as lubricant [43]

The surface passivation in selective transfer accompanied by formation of a plastic copper film on both copper alloy and steel is determined to greater extent а bv electrochemical processes of selective dissolution of the copper alloy and transfer of dispersed copper particles to the steel surface. In this case also synergy effect of both agents - surface material and lubricant - is observed. A favorable combination of materials of contact pairs (bronze-steel) and lubricant (glycerine, oils with surfactant additives) results spontaneous origination in of intermediate layers on the contact surfaces, which produce the minimum friction.

The example below shows a procedure to increase of the antiwear properties of lubricants. The quantitative transition from rough- to ultradispersion of copper particles in the lubricant leads to considerable qualitative changes of the maintenance properties of metal-plating lubricants. This is a new generation of multifunctional additives on the basis of copper and its oxide of colloidal dispersion.

Fig. 3 shows results regarding the antiwear characteristics of the lubricant attained in the tests of the influence of additives on gear oils. While using the ultradispersed CuO additive in motor oils, redox reactions take place. Copper oxide reduces to free copper. Transfer and adhesion of their particles to the sliding surfaces occurs, particularly to surface defects and irregularities [21].





Another phenomenon studied by the Tribology Group in Schoenfels, Germany assisted also by the Tribology Centre – Sofia, is the study of selective transfer of material during friction of Cu-containing contact surface with special surface-active substances in alcohol-glycerin mixture. Characteristic is the formation of the secondary layer with low shift resistance in the contact: a frictional coating. This protective layer cannot accumulate dislocations and is highly antifrictional. The self-organization phenomena in this case depend on the interface energy and the material exchange. Generation of that layer requires special combination of materials of the contact surfaces, as well as special lubricant between them. The good antiwear properties, saving fuel, oil, reducing temperature, wear-free friction and prevention of hydrogen wear of metals are characteristics for this process, which is closely related to the development of the tribology techniques of the Green Tribology. Finishing antifriction nonabrasive machining of friction surfaces and metalplating lubricants, allow making machines and mechanisms service life 3 to 5 times longer and reducing emissions of harmful substances, providing thus for energy, fuel and lubricants saving.

Some results of the studies and application in the area of copper frictional coatings are presented below.

The phenomenon of direct coating deposition is assisted by rubbing/deposition of brass under the special conditions of selective transfer of material. Different processes result. In the contact zones emerges reactive coating deposition with special properties: copper is rubbed on the steel friction surfaces with totally different electro-chemical potential, and secondly, not only the content but also the structure in the friction surfaces is being changed [23].

As a result, a tribological system appears which can bear higher loads at the influence of various processes. Different machines were designed, constructed and manufactured at the Department Tribotechnik in Zwickau' Higher Technical School, for application in rotating machines, for engine cylinders, for mining and road industries, etc. (Figs. 4 and 5).

The film forms on the friction surfaces in the bronze-steel tribocouple with glycerin lubrication passing firstly through dissolution of the bronze surface, where the glycerin acts as a weak acid. The atoms of the elements (tin, zinc, iron, aluminum) absorbed in bronze

outgo into the lubricant, as result the bronze surface is enriched with copper. Friction deformation of the bronze surface causes new passing of elements into the lubricant, so the bronze layer is purified and it nearly contains only copper. Its pores fill with glycerin. Glycerin is reducer for copper oxides, hence the copper film is free from oxides; it is very active with free ions and is highly adhesive for the steel surface. The steel surface is covered by thin copper layer. Self-organization and selective transfer of copper to steel take place. Before the stabilized selective transfer, the process goes on until steel and bronze are coated by 2 µm copper layers [5,6]. Mechanical and chemical transformations take place; e.g. formation of surface active substances on the friction surfaces; they interact chemically with the surfaces and form chemisorbed layers.



Figure 4. MBZ 3A Brass-coating device for sliding bushes (for application in lathes)

Generally said, most characteristic for the selective transfer in tribology applications is the fact that an inoxidable layer with low shift resistance is formed in the contact. This protective laver cannot accumulate dislocations and is highly antifrictional. The processes in this layer generate tight chemical bonds and form new antifrictional films. The self-organization phenomena depend on the interface energy and the material exchange with the environment. The generation of that layer requires special combination of materials and lubricant. Conditions for the continuous reproducibility of the layer are also needed

because of its short life in the contact body. Hence, synergy effect in the forming of new contact structures in the contact surface materials – lubricant appears to be desirable as optimization of the contact couple.



Figure 5. View of the brass-coating device MBZ 3A

By means of brass frictional coating in different constructions of steel and cast iron, can be obtained not only the 10-20% lowering of friction force, but also a changed wear distribution, which is to be seen, e.g., for the upper death point in engine cylinders of 2-cylinder- Otto-motors after various completed path lengths (Fig. 6).



Figure 6. Wear distribution in upper dead point of engine cylinder after different sliding paths: for cylinder with frictional brass coating (left) and uncoated (right)

5. CONCLUSION

An ambition of tribology is either to find out the optimal material – that third body, which to be put in the contact, or to predict the succession of events and phenomena by means of which the contact shall form its own protective layers using self-organization processes. A review is presented on the investigations of self-organization in the mode of selective transfer of materials, which have lead to the development of new lubricants, of selflubricating, wear-resistant and self-healing materials used in friction joints in normal and exposed operating conditions, as in aircraft, mining industry, space research, etc.

Consideration is given to the selective transfer phenomenon in friction couples consisting of copper cooperating with steel in the medium of special lubricant (glycerol or FPT1) and to the creation of "servovite" layer, namely a self-formed layer serving to prolong the life of the friction unit. The selective transfer friction prevents dislocation accumulation in surface layers. The coat formed directly on the rubbing surface leads to low friction and highly improved wearresistance with implications in combustion engine cylinders (even racing car engines), heavy loaded friction units, aircraft units, etc.

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