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SELF-ORGANIZATION OF NANO-SIZED METAL-CONTAINING LUBRICANT ADDITIVES

Introduction

Effective lubrication between rubbing surfaces is required to reduce friction and wear. Conventional lube oils traditionally contain a package of additives that significantly improve their tribological properties. Antiwear and load-carrying additives improve boundary lubrication and reduce wear of the rubbing surfaces due to the formation of quasi-liquid crystalline layers on them [1]. Such structured layers with molecular ordering determine the tribological characteristics of the friction units [2,3].

Problem statement

Recently, significant improvement in the tribological performance of lube oils has been achieved with the application of nano-sized metallic powders [4,5]. Metal oxide nanoparticles form self-repairing, ultrastrong and ductile, antiwear and antifriction adhesive tribo-coats, characterized by excellent tribotechnical characteristics [6]. This is explained by the high specific surface energy of nano-sized materials that interact with the friction surfaces and form protective films. A highly effective wear protective gear, offered by Nanovit Research [7], contains nanoparticles of Al_2O_3, SiO_2 and C providing a combined cleansing, antiwear and additional lubricating effect [8].

Research analysis

Research, conducted on the marine diesel engines of a cargo ship [9], demonstrated an increase in the compression pressure, cleaning of the bearing shells from the deposits, a decrease in consumption of lube oil and fuel, and significant extension of the lube oil service life when NanoVit mixture had been added to the lube oil.

Despite the fact that effects from the use of nano-sized particles in lubricating fluids have been explained by the self-assembly of films, the mechanism of formation of the tribo-coats has not been sufficiently highlighted.

The **aim of this paper** is to describe the generation of nano tribofilms on the rubbing surfaces within the concept of self-organization in nonequilibrium systems [10].

Nanomaterial process

Practically all nanosystems are thermodynamically unstable; they are developed under conditions far from equilibrium. Substantial disequilibrium allows for spontaneous nucleation, while external action stops the growth and aggregation of the formed nanoparticles. The properties of nanomaterials depend to a large extent on the size of their parts. Thus, to obtain materials with good functional properties, it is necessary to use a fairly narrow distribution of the size of particles.

Methods for producing nanomaterials may be divided into several groups.

The first group includes mechanical-physical crushing methods (ball-milling) of production which allow obtaining nanoparticles during the decomposition of solids under the mechanical stresses, and during joint grinding of mutually insoluble components in planetary-type mills.

The second group consists of so-called high-energy methods based on the rapid condensation of vapors under conditions that preclude aggregation and growth of the formed particles. The process of nanomaterials in this group may vary depending on the method of evaporation and stabilization of nanoparticles. Evaporation can be performed using plasma excitation, laser ablation, electric arc, or thermal action. Condensation is carried out either in the presence of surfactants the adsorption of which on the surface of a particle slows down the growth (vapor trapping), or on a cold substrate when the growth of particles is limited by the diffusion rate, or in the presence of an inert component [11]. These methods allow obtaining nanomaterials of various sizes.

The third group comprises chemical methods. The most common methods are based on the formation of ultra-fine colloidal particles in solution as well as the production of nanomaterials using sol-gel synthesis.

It should be pointed out that the use of the materials, produced from free nanoparticles and nanostructures, is very difficult due to the metastability of a substance in a nanocrystalline state. This is related to an increase in the specific surface area of the nano-scale particles that results in the growth of the compound chemical activity and the intensification of the aggregation processes. To prevent the aggregation of nanoparticles and to eliminate the influence of external action (e.g. oxidation by atmospheric oxygen), the nanoparticles are embedded in a chemically-inert matrix.

Open thermodynamic system

According to the laws of classical thermodynamics, the evolution of a physical system should lead to an equilibrium state that corresponds to a complete system disorder.

For an isolated system

$$dS / dt \geq 0,$$

and in equilibrium, the entropy S reaches its maximum. Therefore, there is no spontaneous formation of an ordered structure in an isolated system on a macroscopic level as such a process corresponds to a decrease in entropy. Thus, the processes of self-organization cannot be described in the context of equilibrium thermodynamics [12].

However, ordering is observed for a number of non-equilibrium systems. To describe the processes occurring in such systems with sufficiently high accuracy, the concept of an open system has been introduced. The change in entropy of an open system consists of two components [10]

$$dS = dS_V + dS_S$$

where $dS_V > 0$ is the increase in entropy of a system due to the ongoing processes, and dS_S is the entropy flow caused by the exchange of energy or matter with the surroundings; this component does not have a definite sign. The decrease in the entropy of such an open non-equilibrium system is possible:

$$dS = \left(dS_V + dS_S\right) < 0$$

Hence, during the redistribution of energy between the elements of open thermodynamic systems, a fraction of energy may be expended on the increase of system ordering. It is should be emphasized that such a situation may develop only in non-equilibrium conditions, otherwise $dS_V = dS_S = 0$.

Processes in nonequilibrium systems

If a system in stable equilibrium is affected by external factors that bring it out of this state then, according to the Le Chatelier-Brown principle, the processes, counteracting the applied change, appear in the system. According to Onsager's hypothesis, with minor deviations from the equilibrium, there is a linear dependence between the generated flows and applied forces:

$$J = \sum_k L_{ik} X_i X_k$$

However, the thermodynamic system loses stability when deviating from the equilibrium state [10], and then small fluctuations can lead to self-organization resulting in the formation of new spatial and time structures that do not develop at the equilibrium. Such examples in hydrodynamics [11] are presented with the structuring of convective streams in cells (Rayleigh-Benard convection – Fig. 1), and with symmetric vortex structures at turbulent flow around a body (a Karman vortex street – Fig. 2).

A horizontal vessel filled with liquid is heated from below. A temperature gradient is created between the bottom and the surface leading to the fluid chaotic convective streams. When the threshold value of the temperature gradient is reached, chaotic flows self-organize into ordered structures (Fig.

1-a) resulting in a "honeycomb structure" on the surface of the liquid (Fig. 1-b).

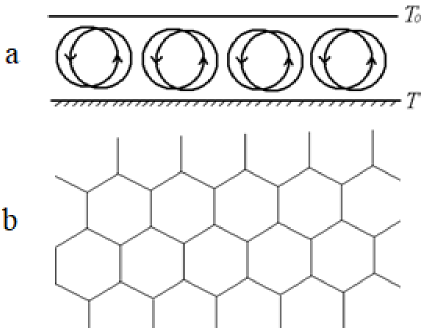

Fig 1. Rayleigh-Benard convection: a – self-organization of liquid chaotic streams (side view), b – "honeycomb structure" on the liquid surface (top view).

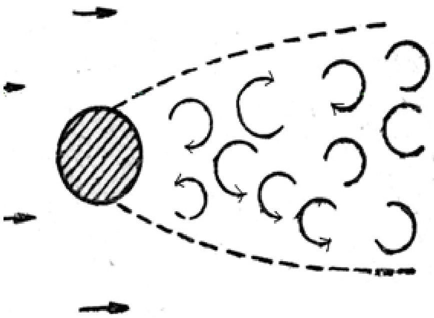

Fig. 2. Self-organization at the generation of Karman vortex street.

Such processes are only possible for the substances in a discernible nonequilibrium state, and formed structures continuously hold their form and retain the properties. Karman vortex streets are another example of self-organization associated with symmetric structures. Behind a slow-moving body chaotic flows arise; when a body speeds up, the point vortex pairs are generated in a staggered order at equal distances from each other.

It should be noted that structures may form, hold the shape, and retain their properties only in an open system that is far from the thermodynamic equilibrium.

Nanodispersed powder with the developed surface is characterized by the energy inhomogeneity that may be enhanced by the size reduction of the powder particles and other special techniques.

As a result of self-organization, the interaction between nano-additives and friction surfaces leads to the formation of a tribo-coats of superior contact strength, enhanced ductility, and good thermal conductivity. Besides that, at low speeds, such films reduce friction and wear, increase the actual contact area of interacting surfaces, and protect them from seizure.

Nanomaterials for tribological applications

Among the nanomaterials which are used for industrial applications and may, in particular, significantly increase the service life of ship's equipment, are molybdenum disulfide, nanodiamonds, and nanodispersed powders of metals and their oxides.

Molybdenum disulfide, formed by micron-sized polycrystals, is widely used as a solid lubricant [13] and lubricant additive due to its lamellar structure. The research revealed that molybdenum disulfide nanopowder may form tribo-coats on interacting surfaces [14].

The formed films exhibit high elasticity and ductility in a contact zone with the operating medium. Wear-resistance of interacting surfaces increases from 4 to 20 times (depending on the operating conditions) compared to micro-sized MoS_2 crystals due to the physical adsorption of MoS_2 particles caused by Van der Waals forces, and due to the mechanical implantation of nano-sized MoS_2 crystals into the metal surfaces. Similar results are observed for molybdenum and tungsten (MoW_2) coatings 4 nm thick.

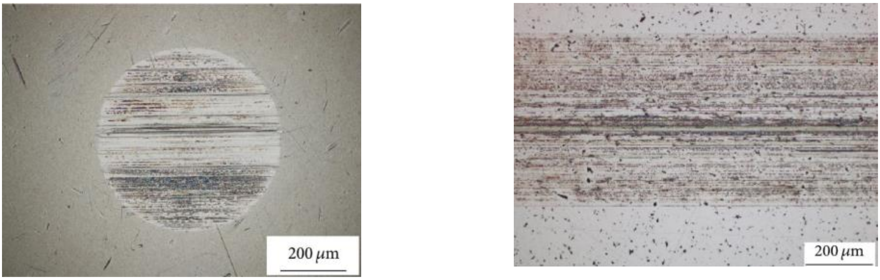

Fig. 3-a

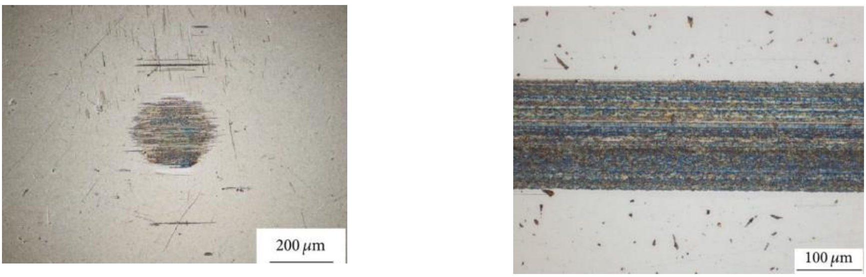

Fig. 3-b

Fig. 3. Optical micrographs of ball wear scars (top) and flat tracks (bottom):
a – base stock PAO, b – PAO + nano Al_2O_3. [20]

Nanodiamonds, formed by carbon atoms, are used for generation of wear-resistant coatings on interacting surfaces [15,16]. Besides that, nanodiamonds play an effective role in erosion reduction in engines [17].

Testing of a ‘supermaterial’ – nanotube fiber – proved that it is thousands of times stronger than steel. In addition, nanotubes are used as powder fillers for hardening in powder metallurgy. Only a few percent of nanotubes, introduced into aluminum powders, dramatically increase the strength of the elements compared to those made of steel.

Aluminum oxide Al_2O_3 nanopowder, introduced into the engine lubricating system, increases oil lifetime and reduces components wear rate [18, 19] by forming tribo-coats on friction surfaces.

Ball-on-flat wear experimental research [20], conducted using synthetic motor oil base stock polyalphaolefin (PAO) and its blend with Al_2O_3 (Fig. 3), showed a significant decrease in the wear of interacting surfaces: reduced contact spot and narrowed wear track.

Experiments carried out by NanoVit Research [9] have shown that nanoparticles of Al_2O_3, SiO_2 and C dispersed in the motor oil form antiwear and antifriction tribo-coats on the rubbing surfaces. The main features of the tribological experiments with motor oil 5W40, concentrated with 20 mg of NanoVit mixture (Fig. 4), are associated with the stable temperature in the friction zone and oscillations of the friction coefficient compared to the experiments with the lube oil that does not contain nanoparticles of Al_2O_3, SiO_2 and C.

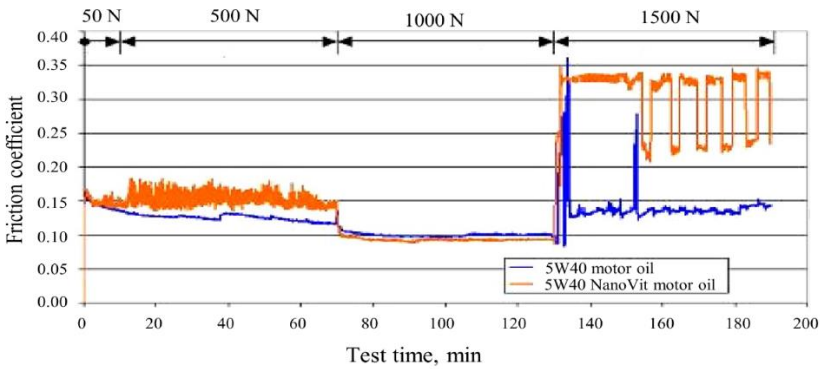

Fig. 4. Dependence of the friction coefficient on the test time at different loads for the conventional motor oil 5W40 and motor oil 5W40 with 20 mg of NanoVit mixture.

It should be noted that significant growth of the friction coefficient and appearance of the oscillations occur at the load of 1500 N. It can be assumed that starting from 1500 N the viscosity of the lube oil does not play a significant role in the lubrication, and tribological behavior of the friction triad is mostly determined by the properties of the frictional boundary layers. Therefore, the oscillations of the coefficient of friction for NanoVit motor oil can be associated with the decrease of the distance between the rubbing surfaces resulting in the wear of the protective nano tribofilms on the friction surfaces;

the heat dissipated due to the friction restores the protective coatings for an account of self-organization.

Conclusions

Self-organization of non-equilibrium systems has been described and analyzed within the concept of an open thermodynamic system. It has been shown that the protective antiwear and antifriction tribo-coats self-assemble on the surfaces of friction pair as a result of non-equilibrium processes occurring in the contact zone. Tribological behavior of nano tribofilms, associated with the oscillations of the friction coefficient between the mating surfaces indicated on the self-organization processes occurring in the contact area under load when energy is dissipated in the boundary friction state.

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