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RESEARCH

Investigation of Action Mechanism of Additives from Mineral Raw Materials

The structural changes of friction surfaces and assosiated changes of main tribological characteristics (coefficuient of friction, weight wear) taking place as a result of introduction of additive into the lubricating oil were investigated. It is shown that the mechanism of additive action is based on its specific composition and dispersity. The positive effect of the additive is demonstrated by structural examinations with the help of scanning electron microscopy (SEM), profile recording and microhardness measurements as well as by tribological tests conducted using the pair of "cast iron - chromium" (typical friction pair of the cylinder-piston assembly in the most modern engines).

Keywords: *coefficient of friction, wear, additive, lubricating oil, surface structure, scanning electron microscopy, profile recording, microhardness.*

1. INTRODUCTION

Lubricating oils with specialized and highly advanced additives made of mineral raw materials have wide distribution in the modern technological world. The use of such additives promotes the optimization of friction processes, reduces wear and friction coefficient, prevents the seizure of mechanisms, provides good running-in ability and, consequently, increases the service life of friction pairs, reduces fuel consumption and improves environmental impact [1]. There are two promising ways of such additive creation, namely, 1) use the various minerals (chiefly, having layered crystallographic structure) and their mixtures in dispersed state, and 2) use the powders of metals and non-metals oxides and salts obtained from mineral raw materials due to their specific treatment.

In the first case the improvement of the tribological characteristics, in particular, the coefficient of friction and wear-out decrease, is arisen from the ability of layered minerals to serve as boundary lubricants, specifically, to form so-called "slickensides" [2]. Such additives actually play the role of running-in coatings, which facilitate the processes of structural adaptation of metallic materials by formation of the surface structures that have boosted strength properties and hardness in comparison to the base metal.

In the second case, when the mixtures of salts and oxides of metals and nonmetals are used, the friction surface modification results from the formation of "servovite" (Latin: "servo" – conserve, vita – life, i.e., "life supporting") ceramic-metal films under the action of high temperatures and pressures in sites of friction parts contact.

The purpose of this study was to use both of the mechanisms at a time for improvement of tribological characteristics of friction pairs.

2. RESULTS

2.1 Additive composition and manufacturing process

The additives which action mechanism was investigated in this work were made by complicated manufacturing process.

The original composition of additive [3] includes the environmentally safe components each one playing the specific roles in realization of required qualities of the additive operation. The additive consists of a powder made by special processing of

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mineral natural raw materials having in their composition Aluminium, Silicon, Magnesium, etc., that capable to form ceramic-metal servovite films on the rubbing surfaces under the conditions taking place in friction zone. The additive composition also includes chlorides and silicates of Tin and Magnesium that additionally serve as a material for ceramic-metal film creation and carry out plating action, smoothing of working surfaces and protecting the juvenile surfaces of contacting parts.

The original multistage method of raw materials processing includes milling, annealing, mechanical activation, fine grinding and provides required properties of the additive at all stages of a friction process.

Investigated additive is the mixture of solid nano-particles of different types and compositions placed in viscous carrier (thickened mineral oil). Before introducing into friction zone, additive is admixed with lubricating oil (usually in concentration 1:1000).

2.2 Samples and test methods

To reveal the influence of additive on the coefficient of friction and wear we carried out the test using friction machines 2070 CMT-1 and СМЦ-2. Our testing method was similar to ASTM G77, Ranking Resistance of Materials to Sliding Wear, Modified.

The tribological tests were carried out using the friction pair “cast iron (moving disc) - chrome (chromium-plated fixed disc or block)”. This friction pair was chosen for test due to its wide usage in the friction nods, particularly, in the cylinder-piston groups of modern internal combustion engines.

Mobile specimens (discs) were made of the alloy grey cast iron castings. Microstructure was the pearlite with lamellar graphite and phosphide eutectic; hardness – HRB 100 - 105 (240 - 245 HB). To relieve stresses due to the mechanical processing the discs were tempered according to the following scheme: charging into a furnace at 300oC, heating at the rate 100o/hour to 600oC, soaking during 3 hours; cooling to 300oC at the rate 100o/hour, and further air cooling. This treatment regime is corresponded to the treatment regime for the cylinder sleeves of diesel locomotive engines.

We used testing schemes showed in Fig.1.

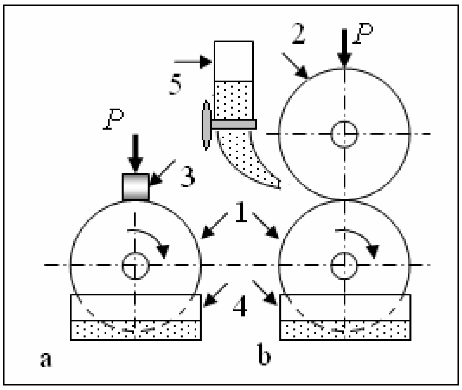

Figure 1. Test scheme: 1–moving disc, 2–fixed disc, 3–fixed block, 4, 5–containers for lubricating oil

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Immobile sample (blocks or disks) were of two types – either the segments of piston rings (Fig.1, a) or cast iron discs (Fig.1, b).They were made of the high-strength inoculated magnesium cast iron with spheroidal graphite (hardness HB 105 – 108). Their working surfaces were covered by chromium of the thickness 200-220 μm by means of electrolytic technique. Microhardness of chromium coating was HV_5 790-850 (7-7.5 GPa), $H_{\mu 100}$880-1000.

The working surface of the cast iron discs in the initial state was of the 8th surface finishing class (the average height of the roughness R_y was ~0.6-0,8 μm).

Lubricating was made by two methods: either by oil drops from upper container (Fig.1, b) or by dipping of moving disc into container (4 in Fig. 1) with oil.

The speed of moving disc (Ø 50 mm) was 1.3 mps. Frictional sliding was 25%.

The testing procedures were following:

- for coefficient of friction measurements: 15 min of run-in at the load of 0.2 kN, then 4 steps of loading (the step was 0.2 kN up to the load of 1 kN; 2 min on each step), off-loading and 15 min at 0.2 kN, and recycling;
- for wear measurements: tests during 1, 5 or 10 hours at the permanent loading of 0.5 kN.

For the friction torque registration the inductive data unit of friction machine СМЦ-2 was used. The coefficient of friction f was calculated according to the formula:

$$f = 2M/(d \cdot P),$$

where M is the friction torque, d is the diameter of mobile specimen, P is the loading magnitude.

The beginning of fretting was determined as the fast growth of the torque magnitude and the appearance of the scores on the working surfaces. The errors in torque and coefficient of friction determination were from 9% at P = 0.2 kN to 2% at P = 1.0 kN.

The wear magnitude was found by weighting on high-accuracy weighing machine before and after the tests with the accuracy ± 0.1 mg.

The investigation of the working surfaces was carried out by means of binocular microscope МБС-9 using the magnifications x8…50 and by means of scanning electron microscope (SEM) РЭММА 101-А in magnification range x30…1000.

Microhardness of the material was determined:

- on the friction surfaces in the zones with different failure level;
- on the surfaces situated far away from the friction zones (initial state).

Microhardness measurement was made by means ПМТ-3 device at the loading 50 g.

The surface topography analysis was performed on all tested specimens including the specimen not subjected to any friction, using TR200 profile recorder. The following measurements were taken: R_y – sum of the height of the highest peak and the depth of the biggest trench relating to the median in the base length limits; R_p – height of the highest peak relating to the median; R_m – depth of the deepest trench of the profile relating to the median.

2.3 Results of tribological tests

The typical dependences of coefficient of friction on the load during step loading for friction pair "cast iron – chrome" are shown in Figure. 2 and 3. Tests were carried out using mineral oil Shell Helix 15 W-40 (MO), synthetic oil Shell Helix Plus 5W-40 (SO) and these oils with additive in concentration (1000:1).

The average improvement of coefficient of friction due to additive introduction was about 8-11% depending on load level and oil type.

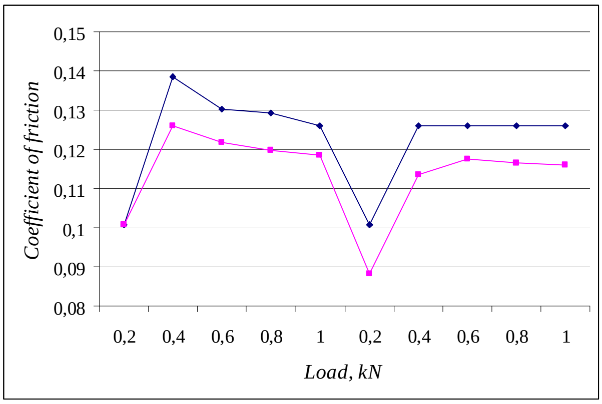

Figure 2. Coefficient of friction vs. load for step loading at friction in mineral oil with and without additive (lower and upper lines, respectively).

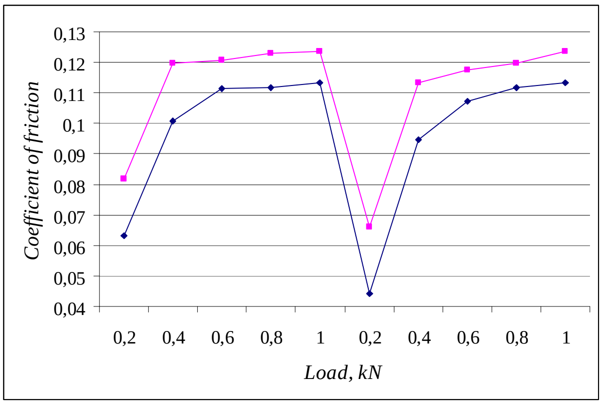

Figure 3. Coefficient of friction vs. load for step loading at friction in synthetic oil with and without additive (lower and upper lines, respectively)

The additive introduction into lubricating oil helps to reduce the weight wear both of the discs and blocks. The most clearly this effect was manifested at the analysis of total wear of friction pairs (Fig. 4), i.e. the sum of weight losses of disc and block.

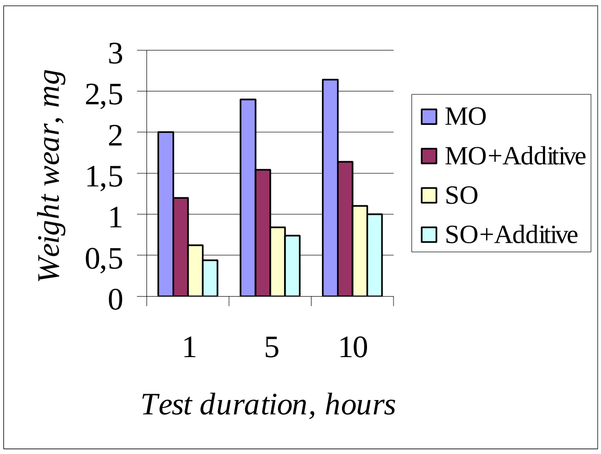

Figure 4. Total wear of friction pairs tested in mineral (MO) and synthetic (SO) oils with and without additive.

The obtained test results make the positive effect of additive introduction into lubricating oil obvious.

2.4 Changes of the surface structure and composition

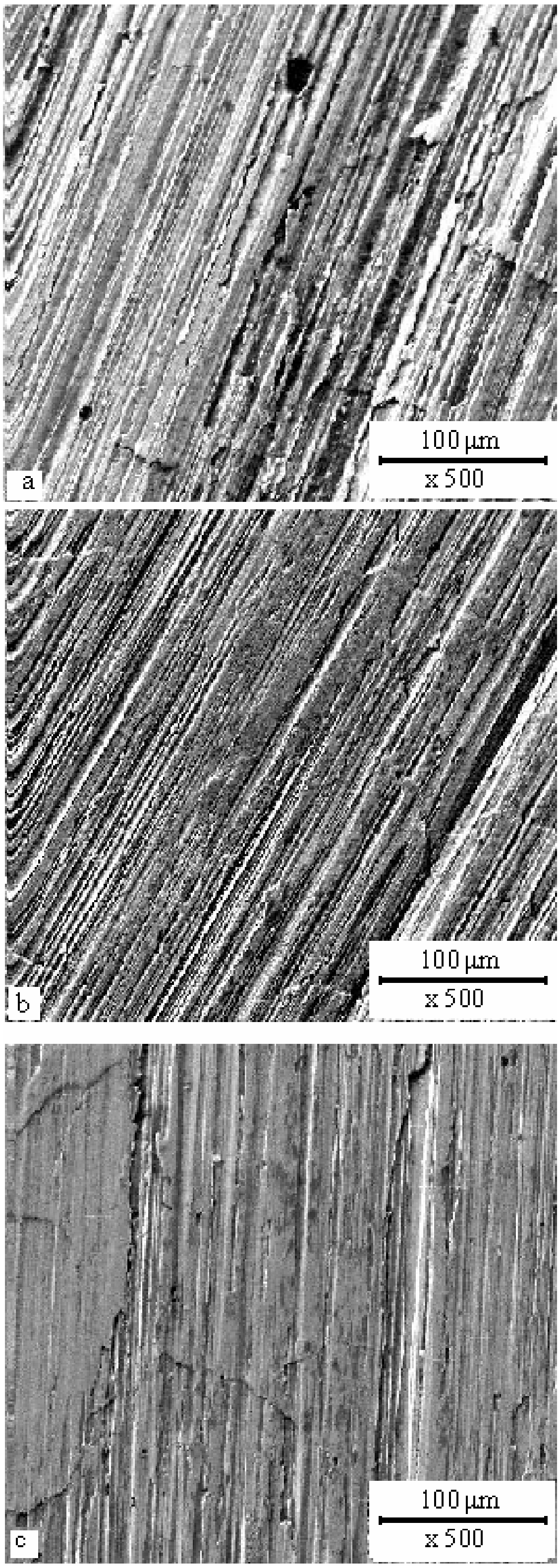

Figure 5. SEM images of initial surface (a) and surfaces after friction in oil (b) and in oil with additive (c)

To explain the reasons of friction characteristics improvement at additive introduction into lubricant the investigations of the friction surfaces and subsurface layers have been conducted. The carried out SEM investigations [4] showed that there are three types of surfaces: initial (untreated) surfaces and surfaces after friction in oil without and with additive (fig. 5). The surface of the initial untreated metal specimen is characterized by striation due to machining tool motion at machining work. There are two systems of striations: with small and big spacings (~300 and 5-20 µm, respectively). They can be seen on Fig. 5, a. Friction in oil (Fig. 5, b) shows the depletion of the surface topography, its smoothing out. However, the main features of relief formed by mechanical treatment, particularly, the systems of striations with different spacings are still present but they are less clearly defined. Interstriation spacings show significant dispersion.

Use of lubricating oil with additive brings on an intensive smoothening of the surface (Fig. 5, c). The relief of mechanical treatment can only be traced. Mainly the striations with large spacing are present. Large areas demonstrate the absence of contrast related to orientated ledges, and, what is more important, to trenches. The structure of these areas is similar to the surface structure of samples manufactured by powder metallurgy, i.e. by sintering of ultra-dispersive powders.

We believe that this surface secondary structure was formed also by sintering of nano-particles of additive.

The results of profile recording are demonstrated by bar graph (Fig.6). It was observed that additive utilization helps to reduce the roughness of the surfaces. Smoothing of the surface at additive use is realized not only for the mechanical cutting of the surface peaks but due to the filling of cavities by additive ingredients.

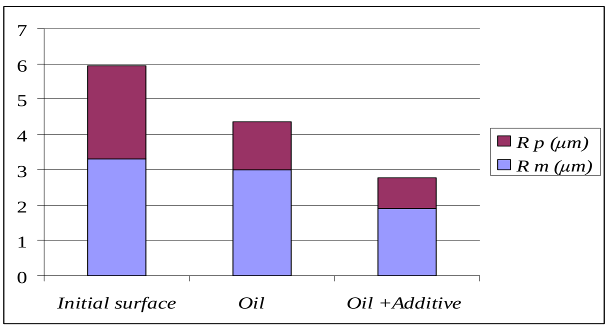

Figure 6. The relief measurements in tested specimens (blue – values for R_m, purple – values for R_p, bar height is the R_y value)

Measurements showed that microhardness of discs and blocks was increased after friction processes due to the mechanical hardening of rubbing surfaces (Table 1). The most significant increase of microhardness was revealed for tests in the lubricating oil with additive. We suppose that this fact reflects the contribution into the surface hardening process of the metal-ceramic film formed due to the additive action.

Table 1. Results of microhardness measurements

Lubricant	Microhardness, GPa			
	Disc		Block	
	before	after	before	after
MO	3.45	4.3	7.0	10.1
MO+Additive	3.50	6.8	7.2	15.2
SO	3.55	4.5	7.5	11.3
SO+Additive	3.4	7.1	7.3	16.8

2.5 Additive action mechanism

Conducted investigations found out that used additive consisted of at least two types of nano-particles: the particles of ingredient with the layered crystallographic structure and the particles of metals and non-metals salts and oxides. Each type of particles at getting into the friction zone plays the specific role. The particles with layered structure at the initial stages of rubbing act similar to classical layered modifiers of friction, for example, the graphite, facilitating the friction due to slickensides creation.

Another mechanism of additive action based on the process of surface modification. The dispersive particles of metals and non-metals oxides and salts together with the lubricating oil get into the friction zone. During the friction pair operation these particle presence leads to the course of the following processes:

- removal of adsorption and oxidation products from the friction surface;
- activation of the surface layers of the rubbing parts;
- mechanical activation of solid particles of additive;
- baking (sintering) of the additive particles under the action of the high temperatures and pressures in the friction zone and, as a result, the formation of the servovite ceramic- metal film.

The optimal complex of the secondary structure properties is stipulated by the composition and dispersity of additive particles. It is very important that the dosed introduction of Mg- and Sn-containing components provides the plastic properties of forming film. The presence of Cl-containing component provides the protective function of chloric films in the instants and in the sites of destruction of metal-ceramic film that prevents the contact of juvenile surfaces and development of dripping processes. Ultra-dispersive state of the additive ensures easy flowing of the sintering process when the particles of oxides are baking at the temperatures and pressures that are realized occasionally in the sites of rubbing surfaces contact. Thin servovite ceramic-metal film (thickness about 0,10…0,15 μm) is in a dynamic state, i.e., it is intermittently formed and destroyed on the rubbing surfaces.

3. CONCLUSION

The additive created and tested in this investigation manifests several mechanisms of its action in friction zone. Due to that the following results of additive effect were observed:

- modification of the topography of friction surface, decrease of the roughness and smoothing of its relief;
- increase of the microhardness of the friction surfaces;
- minimization of the damageability of friction surface due to ceramic-metal film formation in comparison to the properties of secondary structures forming during the operation in the oils without additive;
- minimization of the wear processes: the hydrogen wear minimization – due to the decrease of temperature in friction zone and, as the consequence, of the oil decomposition process; the corrosion wear minimization - due to avoiding of intense oxidation of the rubbing materials; the abrasive wear minimization – due to the cermet-metal film formation, etc.

Introduction of investigated additive into the lubricating oils influences positively on the following operational characteristics of friction nods: coefficient of friction and wear, fuel consumption, working temperature in friction zone, and intensity of lubricating oils decomposition.

REFERENCES

[1] *Lubricant Additives: Chemistry and Applications*, Editor Leslie R. Rudnick, 2nd edition, Chemical Industries/124, CRC Press, Taylor &Francis Croup, NY, 2009.

[2] В.Н.Кузьмин, Л.И.Погодаев: *Смазочные материалы с добавками*, Трение, износ, смазка, Т.11, №38, 2009.

[3] Tananko D., Lyubchenko E., Aksyonova S., etc. *Nano-particle metal treatment composition for creating a ceramic-metal layer*. US Patent 7,304,020, 2007.

[4] Любченко Е., Аксенова С.: *Исследование морфологии поверхностей трения методом растровой электронной микроскопии*, Тезисы докладов XXIII Российской конференции по электронной микроскопии, Черноголовка, ИПТМ РАН, 2010, с.113.