The effect of nanoceramic materials on the tribological properties of technological lubricants

E G Berdichevsky
Yaroslav-the-Wise Novgorod State University, ul. B. St. Petersburgskaya, 41 173003 Veliky Novgorod, Russia
E-mail: berse@mail.ru

Abstract. The effect of some nanotechnological materials such as boehmite and β-sialon on the tribological characteristics of technological lubricants has been studied. It is shown that even a low percentage of nanocermics used for doping mineral oils can significantly improve the tribological situation in the zone of boundary contact friction. Technical and economic characteristics of the considered nanocermics suggest them promising components in the development of innovative technological lubricants for heavy duty friction.

1. Introduction
The possibility of improving the tribological properties of lubricants by doping them with nanocomponents has been shown in many studies. So in [1] it was established that such nanoproducts as fullerene black, fullerene soot and other nanocarbons increase the functional – tribological properties of lubricants operating under conditions of heavy friction contact. There is a lot of information about the successful use of nanocarbons in motor and transmission oils [2], in plastic deformation of metals [3], in boundary sliding friction [4]. However, carbon nanopowders have high cost, instability in lubricants and low heat resistance. As a result, carbon friction nano-modifiers are not widely used in practice.

2. Nanocermics
It is interesting and promising to consider nanoceramic materials as alloying components of technological lubricants. Nanocermics are much cheaper and thermostable than nanocarbons. Many nanomaterials have a layered disulfide and molecular structure, like graphite and molybdenum disulfide, and in this case they can actively exhibit antifriction properties [5]. Nano- and finely dispersed powders of layered silicates added to various oil compositions significantly improved the tribological situation in many friction sites. The achieved tribo effect was explained by the interaction on friction surfaces of broken atomic bonds of particles of compositions with active bonds. Initially, the composition consists of solid-dispersed basic particles of layered silicate with a dimension of 0.5 ÷ 20 microns with thin from 10 to 500 nanometers marshallite inclusions.

Silicate contains siloxane (bridged) Si-O-Si bonds. Due to high-tech fine grinding, bonds are broken so that the number of uncompensated broken bonds is as large as possible. Broken siloxane bonds are active hydrogen acceptors. When they interact, compensated Si-OH silanol groups are created. Thus,
by adding finely divided layered silicate into the lubricant, which has a large specific surface and a large number of broken siloxane bonds, we create at their expense the conditions for binding active hydrogen in the friction zone, i.e. prevent its interaction with the metal and prevent hydrogen wear of the latter.

The presence of marshall inclusions stimulates, according to the opinion of developers, the adhesive interaction of geo-silicate friction modifier with the metal surface of the friction unit, contributing to the formation of anti-friction sliding surfaces film. In addition, marshallites also adsorb bound hydrogen.

The authors of the composition note that the use of layered silicate powders as an additive to lubricants is especially effective when high temperatures and contact pressures are present in the friction zone. In this case, the thermal decomposition of silicate occurs with the formation of new chemical products that actively interact with each other and the metal of the rubbing pair. As a result of numerous transformations, disintegrations, transformations, repeated interactions on the friction surfaces a mineral film of high density, hardness and adhesion to the substrate is formed. Mineral film provides a significant reduction in wear, prevents surface chips.

3. Doping with nanoceramic boehmite

Of great scientific and applied interest is the study of the tribological properties of lubricants doped with nanoceramic boehmite.

Boehmite belongs to the hydroxide subclass and has the form $\gamma$-AlOOH. The mineral represents an aluminum hydroxide and is one of the main components of bauxite. The composition of boehmite is similar to the diaspora, isostructural. The basis of the layered crystalline structure of boehmite is the alternation of packs of two internal oxygen and two external hydroxyl layers with aluminum atoms located in voids.

Boehmite is insoluble in acids, does not melt in front of the blowpipe, splits cleavage. The density of boehmite is 3.02–3.06 g/cm$^3$, the hardness on the Mohs scale is 3.5. The mineral contains impurities of various oxides: Fe$_2$O$_3$, SiO$_2$, TiO$_2$, and others.

Nanocrystalline boehmite is produced according to the technology of hydrothermal synthesis from quartzite. During the synthesis, aluminum particles of up to 10 microns in size are transformed into nanocrystalline boehmite. The stable properties of the initial aluminum powders and developed technological process make it possible to synthesize boehmite powders with constant properties. Unlike additives based on natural raw materials, this allows for greater stability of the properties of artificial tribomodifiers [6].

Tribological effectiveness of lubricants doped with boehmite was evaluated on the SMT-1 friction machine according to the roller-to-block scheme. The list of tested compounds is given in table 1.

| Name of tested additive | Additive concentration in oil M-10DM |
|-------------------------|------------------------------------|
| Boehmite from ZAO “Concern Nanoindustry” with surfactant after ultrasonic treatment | Boehmite 0.08 g/l, surfactant 0.3–0.5 % |
| Boehmite produced by GOSNITI with surfactant after ultrasonic treatment | Bemite 0.08 g/l, surfactant 0.3–0.5 % |
| Boehmite produced by GOSNITI with silica powder and surfactant after ultrasonic treatment | Boehmite and silicon oxide at 0.04 g/l, Surfactant 0.3–0.5% |
| Potassium polititanat and surfactant after ultrasonic treatment | Potassium polititanat 0.08 g/l, surfactant 0.3–0.5 % |

SAS (surface-active substance) – surfactant – based on fat soluble acids. The predominant particle size of boehmite is 2–3 microns, the maximum – up to 10 microns. Aggregates of particles were crushed by ultrasound.
Figure 1 shows the dependence of the friction coefficient on the load for the tested compositions and for pure M-10 DM oil.

Tests have shown that the minimum friction and temperature optimal concentration of boehmite is 0.5%, at that the coefficient of friction is reduced by one third.

The best results showed lubricants with surfactants and ultrasonic treatment. Each group of lubricant compositions has its own ranges of optimum concentration in oils and loads in friction units, at which their greatest efficiency is ensured.

Tribological properties of boehmite were studied as an doping component of the emulsion. 3% emulsion of standard emulsol was accepted as a model composition. 5%, 10% and 15% boehmite was introduced into the emulsol with mechanical mixing. Dispersion of emulsol in water was carried out first with a propeller stirrer, then by ultrasound. The lubricating properties of the emulsions were evaluated on a four-ball friction machine. Coefficient of plastic friction was determined on the stand by plane-symmetric sink of aluminum rings by the method described in [3]. The test results are shown in table 2.

| Boehmite concentration in emulsion, % | Bedding load, $R_b$, N | Welding load, $R_s$, N | Wear spot diameter, mm | Coefficient of plastic friction (bench tests) |
|-----------------------------------|----------------------|----------------------|-----------------------|---------------------------------------------|
| 0                                 | 210                  | 280                  | 5.6                   | 0.38                                        |
| 5                                 | 240                  | 320                  | 4.8                   | 0.32                                        |
| 10                                | 270                  | 360                  | 4.1                   | 0.28                                        |
| 15                                | 300                  | 410                  | 3.7                   | 0.24                                        |

From the results it follows that an increase in boehmite concentration in emulsion and in emulsion leads to a systematic improvement of all tribological properties considered. The load of breaking lubricating film at 15% of the content of boehmite increased by almost 50%, the load of welding balls – by 40%. Nanocrystalline boehmite modifier made it possible to reduce friction coefficient by almost 80%. It was established that emulsions containing boehmite are more dispersed, stable, and less prone to foaming. It is likely that boehmite particles, being adsorbed on the boundary between the oil and water phases, impede the coalescence of oil phase droplets, i.e. have a separating-stabilizing effect.
4. Nanosized β-sialon powder

In addition to boehmite, nanosized β-sialon powder is promising. Nanoparticles have an average size of 50 microns, show rounded shape and represent Al₂O₃ and AlN solid solution in β-Si₃N₃ with the general formula \( \text{Si}_{6x}\text{Al}_x\text{O}_x\text{N}_{8x} \) (where \( x = 0.8-4.2 \)) obtained by the plasma-chemical method. Medium-viscous industrial oil I-40 thickened with cerisin was used as a lubricant base.

The results of testing lubricant compositions doped with nanopowder β-sialon are presented in Table 3. The tests were carried out on four-ball friction machine by standard method [3].

Table 3. Tribological characteristics of lubricating compositions doped with β-sialon.

| Lubricating composition                      | Bedding load, \( R_k \), N | Welding load, \( R_s \), N | Chips index, \( C \) | Friction coefficient |
|---------------------------------------------|-----------------------------|-----------------------------|---------------------|---------------------|
| Oil I-40 + 1% cerasin                        | 65                          | 122                         | 26                  | 0.17                |
| Oil I-40 + 1% cerasin + 1% β-sialon          | 110                         | 204                         | 54                  | 0.15                |
| Oil I-40 + 1% cerasin + 2% β-sialon          | 188                         | 276                         | 69                  | 0.14                |
| Oil I-40 + 1% cerasin + 3% β-sialon          | 290                         | 414                         | 90                  | 0.14                |
| Oil I-40 + 1% cerasin + 3% β-sialon + 2% colloidal graphite | 306                         | 420                         | 90                  | 0.12                |

Analysis of test results showed that introduction of nano-sized doping ceramic component made it possible to increase bearing capacity of friction pair by 4.5 times, significantly increase the load of lubricant film breakthrough (3.5 times), and slightly reduce friction coefficient. The addition of the classic antifriction additive – graphite – insignificantly improved the tribological indicators on the background of nanoceramic modifier. The obtained positive results can be explained by complex transformations of β-sialon on friction surfaces, which, under the influence of nanoceramics, change not only their microgeometry and morphology, but also elastoplastic properties [7].

“Concern Nanoindustry” (Russia) has produced preparation for doping transmission and engine oils based on nanoceramic of supersonic grinding. The advantages of lubricating oils with nanopowders compared with oils doped with traditional additives are shown in Table 4.

Table 4. Comparison of advantages of oils doped with nanoceramics and traditional additives.

| Characteristics                      | Traditional additives                     | Nanoceramic modifier “Stribile”                  |
|--------------------------------------|------------------------------------------|-------------------------------------------------|
| Friction surface hardening           | Not happening                             | Happening                                       |
| Microrelief alignment                | Not happening                             | Optimum clearance is being added                |
| Compatibility with used oils         | Requires careful selection                | Compatible with all oils                         |
| Friction coefficient                 | Not less than 0.015                       | 0.008–0.03                                     |
| Vibration                            | Declining                                 | Declining                                       |
| Anticorrosion resistance             | Low                                       | High                                            |

Note that the discussed nanoceramic product showed significant efficiency in friction pairs with relatively soft and spare loads (transmission, internal combustion engines, gearboxes).
5. Conclusion
Nanoceramic powder materials used for doping technological lubricants have positive effect on tribological situation in contact friction zone. Due to the low cost and thermal stability usual for all ceramics, nanoceramics can serve as the basis for creating innovative tribological lubricants for heavy regimes of boundary friction. Physical-chemistry of behavior of the products such as boehmite and β-sialons in lubricating compositions needs further study.

References
[1] Berdichevsky E G 2018 Friction Process Control in Forging and Hot Stamping Technologies IOP Conf. Ser.: Mater. Sci. Eng. 441 012010
[2] Pogodaev L I 2006 Structural and energy models of materials reliability and machine parts (SPb: ATPF Publ) p 608
[3] Berdichevsky E G 2011 Friction and lubrication during plastic deformation (Veliky Novgorod: NovSUPubl) p 184
[4] Ginsburg B M at al 2000 Effect of fullerene C60, fullerene soot and other carbon materials on the boundary slipping friction of metals Technical Physics 70 (12) p 87–97
[5] Davydov N A and Slitsky B U 2009 Practical implementation of effectiveness of new nanotechnological materials for rolling equipment tribological systems of railway transport Collection of scien. papers of the IX intern. conf. “Tribology and Reliability” (SPb) p 96–101
[6] Almyasheva O V, Korytkova E N at al 2005 Synthesis of aluminum oxide nanocrystals under hydrothermal conditions Inorganic Materials 41 (5) p 80–91
[7] Kostetsky B 2014 The structural-energetic concept in the theory of friction and wear (synergism and self-organization Wear 159 p 1–15