HETEROSTRUCTURED ANTIFRICTION AND ANTISCUFF ADDITIVES FOR LUBRICATING MATERIALS WITH REGULATED TRIBOLOGICAL PROPERTIES

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Abstract: *Antifriction, antiscuff and antiwear properties of lubricating materials produced on the base of standard greases containing additives of new heterostructured nanopowders were investigated. Heterostructured nanopowders were synthesized by intercalation of some transition metals (Cu, Ni, Zn, Mn, Co, Cr) in the layered matrix of the potassium polytitanate and following low temperature treatment. It was recognized that the introduction of heterostructured additives intercalated with Zn, Cu and Mn allowed obtaining the greases characterized with tribological properties significantly superior to the greases produced with additives of nanoscale particles of corrersponding metals and commercial analogists based on MoS_2 additives.*

KEYWORDS: *LUBRICATING MATERIALS, ANTIFRICTION ADDITIVES, NANOPARTICLES, TRIBOLOGICAL PROPERTIES*

1. Introduction

Lubricaiting compositions are widely used in different technical areas including ball and sliding bearings, sliding members, ball-screw and spur gears of different type, friction assemblies, ball-and-socket joints in all kinds of carriers and transport systems, screw couplings etc. It is well known that high antiwear and antiscuff properties can be obtained by the use of molybdenum disulfide (MoS_2) as a component of lubricating systems. Its application promotes reduced consumption of greases as well as low wear. Nowadays, almost all leading manufacturers of lubricating oils and greases apply MoS_2 as an antifriction admixture (Shell, Mobil, Esso, Castro, etc.). However, in spite of its advantages, MoS_2 is an expensive material and cannot be used in all areas of its potential application as a lubricant due to relatively high corrosion activity and generation of abrasion particles of molybdenum oxide during exploitation [1].

On the other hand, there is a lot of other antifriction admixtures proposed last decade and recommended to apply in the composition of greases and oils due to their perfect tribilogic characteristics. The substances consisting of nanoscale particles are of great interest because of highe tribilogic properties in comparison with microscale particles of the same composition. However, synthetic nanoparticles of this type (WS_2, fullerenes, carbon nanotubes, nanodiamonds, ZrO_2, ZnO, Al_2O_3, different metals etc.) [1-6] are characterized by high cost; whereas interesting natural antifriction analogs, i.e. natural serpentinites, contain abrasive admixtures (silica sand, magnetite, pyroxenes, etc.) and their benefication dramatically increases a price) [7-9].

2. Preconditions and means

The authors have developed the technology to produce a new kind of material (potassium polytitanate, PPT) which is promising for its application as a cheap analog of MoS_2 [10]. The potassium polytitanate has a layered platelet structure. Each layer is presented by polyanion constructed by titanium-oxygen octahedra; the K^+ cations as well as hydronium ions and H_2O molecules are located between the layers of polyanion. The quasi-amorphous structure of PPT particles is similar to the crystalline structure of lepodocrocite; however the distance between the layers is very irregular. The K^+ content and [H_2O] depend on PPT synthesis conditions and can be regulated in a wide range [11]. The PPT particles are characterized with some properties important for the antifriction additives, such as high mechanical strength (Young's modulus of about 280 MPa), low friction coefficient (similar to MoS_2) and high thermal stability (up to 750-800 ^oC).

Taking into account the abovementioned comments the authors of this paper proposed to introduce the PPT in the composition of some well-known commercial lubricating compositions instead of MoS_2 additives. Such investigations realized with different types of basic oils and greases have shown [10, 12] that an exchange of the molybdenum disulfide and potassium polytitanate is possible in all standard lubricating materials and pastes which are produced in Russia and abroad. On the other hand, it was demonstrated that a correct selection of the surfactants applied to obtain stable dispersions of PPT particles in the basic oils allowed increasing the main tribology properties of lubricating compositions up to the level better of similar compositions based on MoS_2 additives [13].

However, the tests realized before have shown that the antiwear effect of the potassium polytitnate additives is not so high as in the case of MoS_2 or metal (Cu, Zn, Pb) nano-sized additives. That is why, the *objective* of this research was to define a possibility to produce the heterostructured nanoparticles consisting of the layered potassium polytitanate matrix and nanoparticles of some transition metals promoting cladding of rubbed steel surfaces. It was assumed that such particles could promote twin effect combining high antifriction properties of the potassium polytitanate modified by organic surfactants and high antiwear properties of metal nanoparticles.

3. Solution of the examined problem

The basic potassium polytitanate (PPT) powder was synthesized in accordance with [11]. The TiO_2 powder (anatase, Aldrich, purity of 99%, average diameter of particles of 7 μm) was treated in the molten mixture of KOH and KNO_3 (weight ratio of 1:1:8) at 500 ^oC for 2 h in the alumina crucible. The obtained product was washed with distilled water (20 weight parts of H_2O for 1 weight part of the product), separated from the aqueous solution by Whatman paper filter (No40) and dried in the oven at 60^{o}C for 4h. The obtained product was characterized with a chemical composition corresponding to the molar ratio of TiO_2: K_2O = 4.1.

To produce heterostructured particles, the basic PPT powder was dispersed in the distilled water (1:10) containing admixture of non-ionic surfactant (trade-mark OP-10, 0.1%) at the room temperature using the ultrasonical treatment. Further, the salts of different transition metals were introduced into the obtained aqueous dispersion in quantity corresponding to the ratio of 10 g of PPT to 0.01 mol of the salt. The sulfates of Ni, Co, Zn, Cu, Cr and Mn were applied for the treatment during 6 h, corresponding to the equilibrium in the system obtained. After the treatment the modified PPT powder was separated from the solution by filtration (paper Whatman No42), thermally treated at 90 ^oC for 4h in the oven and further used to produce lubricating compositions.

The modified PPT powders obtained in accordance with abovementioned method were investigated to identify their chemical composition and structural features using the following methods. The morphology and size of the particles were measured with a Hitachi H-600 Transmission Electron Microscopy, 200 kV. XRD spectra of the nanoparticles were measured with a Philips X'Pert X-ray diffractometer, Cu target, voltage: 40 kV; chemical composition - with a SEM Philips MP-3, equipped with the EDS analyzer EDAX Pegasus) .

The TEM images of the particles of some modified potassium polytitantes and their X-ray diffracograms are presented in fig.1. The obtained products can be classified as powders consisting of heterostructured particles. Each particle has a matrix formed by the basic PPT layered structure; at the same time, the ions of the metals, intercalated into the interlayer space of PPT particles, due to a high reduction activity of the potassium polytitanate [14] are transformed into an atomic species and form the nanocrystals (diameter of 5-50 nm).

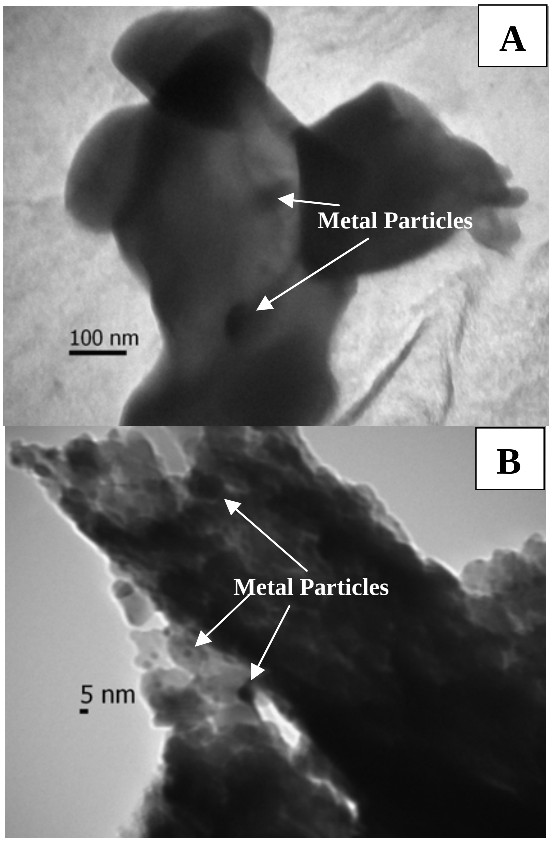

Fig.1. TEM images and XRD patterns of the PPT/Ni (A) and PPT/Zn (B) particles.

Table 1. Chemical composition of the PPT powders doped by different metals.

PPT/Me	K_2O	TiO_2	Me
PPT	18.9	81.1	-
PPT/Cu	9.9	80.2	8.9
PPT/Zn	10.0	81.4	6.6
PPT/Mn	9.2	83.7	7.1
PPT/Cr	9.8	84.3	5.9
PPT/Ni	9.1	82.6	8.3

Such small size of the crystals does not support obtaining the XRD patterns typical for crystalline structures of the metals. The X-ray diffractograms don not change their character typical for amorphous (semicrystalline) potassium polytitanates. The chemical composition of heterostructured PPT/Me powders, obtained by intercalation of Me ions from the salts and further used as antifriction/antiscuff additives, are reported in table 1.

To produce lubricating compositions, the heterostructured PPT-based powders were dispersed in the basic oil (I-20) in presence of oleophylic surfactant (monohydro-citrate of diethylamin-glizeride) admixture (0.1%), which, as a result of sonification, allowed obtaining stable 50% dispersions with average size (diameter) of platelet particles equal to 380 nm (data obtained with the particle size analyzer Shimadzu 2201). The obtained dispersions were used to manufacture model greases. These lubricating compositions were produced on the base of the universal Russian grease of the Litol-24 trademark (RF Standard GOST 21150-87) traditionally applied in different types of bearings. The model greases were prepared by mixing of Litol-24 with oil dispersions of the PPT/Me nanopowders in proportion, which allowed obtaining the greases containing 3 wt.% of the modified PPT. This concentration of antifriction and antiwear admixture was selected taking into account that a most part of the commercial greases of this type (including Megaplex XD3 used in comparative tests) are characterized with 3 wt.% admixture of the MoS_2 powder). The homogenization of the lubricating composition was realized in the UPPS-1 grease stirrer for 1h (controlled with the Micromed C-11 optical microscope).

Taking into account that the modified PPT powders consisted of the potassium polytitanate matrix and metal nanocrystals, some model greases only containing nanoparticls of different metals, including intercalated into the PPT/Me particles, were also prepared to compare their influence on tribology properties of the same Litol-24 basic grease. The metal nano-powders applied to prepare the greases (Ni, Cu, Zn) were produced by spark-plasma method [15] and characterized with average size of particles equal to 20 nm. The content of metal nanopowder in the greases was selected in accordance with the paper [16], in which the admixture of 1.6 wt.% of the metal nano-powder was recognized as optimal.

The maximum nonseizure loads (PB) and other tribilogical characteristics of the investigated greases were evaluated, according to ASTM D2783, on a modified four-ball CM-1 tribotester, equipped with ZET 210 - ZET 410 tenzometric complex, at 1435 rpm and room temperature. The balls (12.7 mm in diameter) in the test were made of ШХ-15 bearing steel (RF standard GOST 801-78). A dependence of the wear-scar diameter on friction time was selected as antiwear characteristic and measured under a constant load of 100 N after 1 h testing. The wear-scar diameter and friction force torque (friction coefficient) were measured after a given time limited by 1 h with a step of 3 min; the whole process was repeated several times. Each test was realized with a new portion of the corresponding grease and new balls.

The ball after the four-ball test was cleaned using an ultrasonic bath in ligroin and then in distilled water for 5 min. EDS analyses of the elements on the wear scar were conducted on a SEM (MIRA 2 LMU) equipped with the EDS analyzer (INCA Energy 350) using pass energy of 20 eV and Cu Ka line excitation source. The wear scar diameter (d_{ws}) was measured with an optical microscope (BMI-1) for each of three down balls obtained after 3 testing series; the measurements were done in two perpendicular directions. The resulted d_{ws} was estimated as average value of 18 measurements (3 balls of 3 series in 2 perpendicular directions).

4. Results and discussion

The kinetic data on a change of the friction force torque value with a testing time of Litol-24 basic grease containing different PPT/Me and Me additives is presented in fig.2. The obtained results demonstrated the following features:

1) The PPT/Me additives promote reduced friction for all types of heterostructured PPT/Me particles.
2) The antifriction properties (equilibrium friction force torque values) of the PPT/Me additives are similar to that obtained with corresponding Me nanoparticles applied as additives. M_{fr}(PPT/Ni) ≈ M_{fr}(/Ni). M_{fr}(PPT/Cu) ≈ M_{fr}(PPT/Cu). Significant difference only takes place for PPT/Zn and Zn admixtures; in this pair the antifriction properties of the PPT/Zn additive is much better.
3) The PPT/Me nanopowders can be shared in the two groups. The additives of the 1^{st} group (PPT/Ni, PPT/Co) reduce friction coefficient in 1.6 times in comparison with the basic grease (Litol-24). The additives of the 2^{nd} group (PPT/Zn, PPT/Mn, PPT/Cu, PPT/Cr) decrease this tribological characteristics in 2.1 times and allow obtaining a friction coefficient lower of this one recognized for the commercial grease of Megaplex XD3 trademark containing 3 wt.% of MoS_2 additive.

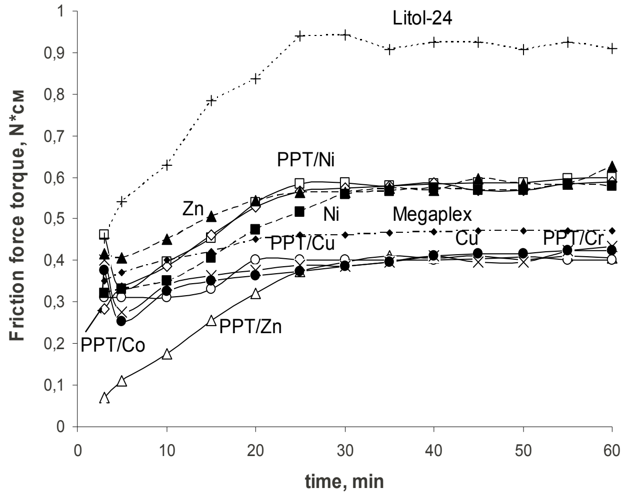

Fig.2. Kinetic covers of the friction force torque change during the tests realized with Litol-24 containing different antiftiction/antiwear additives (3 wt.%).

Table 2. Friction coefficient (μ), average wear scar diameter after 1h test realized with Litol-24 containing different antifriction/antiwear additives (3 wt.%), microhardness (H) and nonseizure load (PB).

Lubricant	μ	d, mm	H, GPa	PB, N
Litol-24	0.024	0.64	3.2	735
Litol-24/Zn	0.017	0.65	-	-
Litol-24-PPT/Zn	0.010	0.43	9.9	784
Litol-24-PT/Ni	0.011	0.55	-	-
Litol-24-PPT/Cu	0.011	0.51	-	929
Litol-24-PPT/Cr	0.012	0.45	6.2	-
Megaplex XD3	0.013	0.39	3.1	-

It is well known that tribilogical properties of rubbed surfaces, including microhardness and wear, depend on tribochemical processes taking place in the contact points in the conditions of high pressure and temperature accompanying with intensive elastic deformations [1, 17]. That is why the structure and chemical composition as well as microhardness of wear scar obtained on the ball surfaces lubricated with different nanoadditives, were investigated.

The microhardness was analized by Vickers method (diamond pyramid) using the PMT-3 equipment with 0.2N indentation load at 20 ^{o}C. The microhardness values were calculated from the following equation:

$$H_{\mu} = 1854{,}4 \cdot 10^{3} \cdot \frac{P}{d^{2}} ,$$

where: H_{μ} – microhradness (MPa), P – indentation load (g), d – length of the indentation, μm. The average microhardness were estimated taking into account 9 measurements in the scars of 9 balls (for each 3 bottom balls tested in 3 series of the same conditions.

It was recognized (table 2) that a use of PPT/Me additives in the composition of the basic grease promoted increased microhardness of the worn surfaces depending the type of additive. The maximal effect was obtained for the PPT/Zn additive which improved the microhardness of rubbing surfaces in 2.14 times in comparison with pure Litol-24.

Fig.4 shows the SEM micrographs of the worn surfaces of the balls obtained under various lubricating conditions.

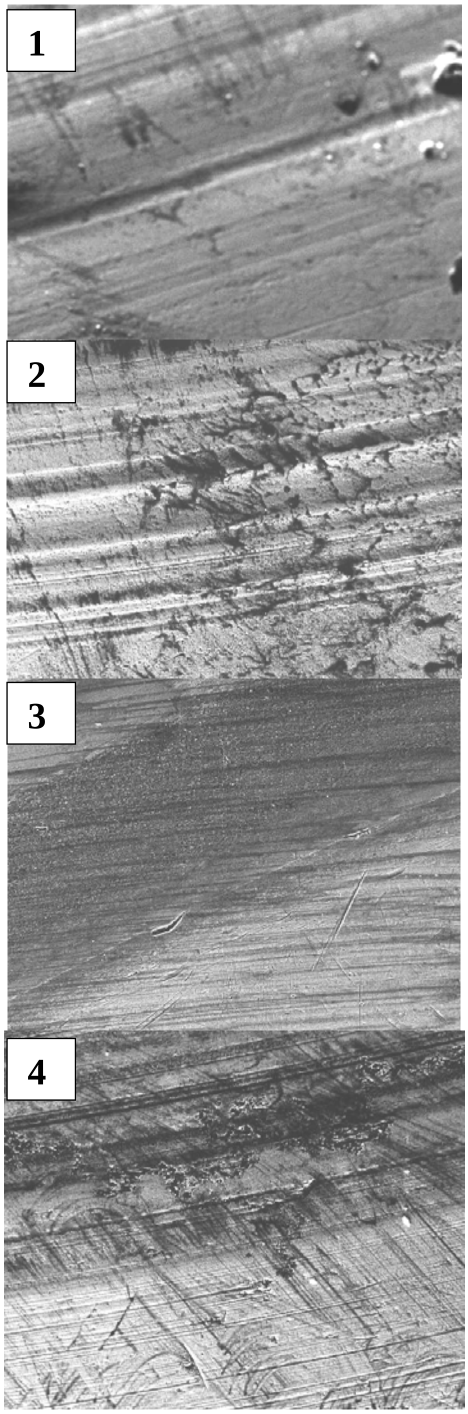

Fig.3. SEM images of the rubbed surface lubricated by Litol-24 (1), Litiol-24+3% PPT/Co (2), Litol-24+3% PPT/Zn (3) and Megaplex-XD3 (4). Magnification X200.

A number of small holes and deep grooves coupled with plastic deformation were found on the worn surface for the basic grease Litol-24, grease Megaplex XD3 and, especially, for the Litol-24/PPT/Co composition, indicating that severe scuffing happened. While for the Litol-24/PPT/Cu and, especially, Litol-24/PPT/Zn lubricating compositions the worn surfaces were relatively smooth.

To identify the mechanism of the processes promoting improved tribological characteristics, the EDS analysis of the rubbing surfaces was applied. The obtained results (table 3) indicated that a high antiwear effect of the PPT-based heterostructued additives could be explained by introduction of Ti and Me, presented in the composition of PPT/Me heterostructured particles, into the structure of the surface layer of balls. This modification of rubbing surfaces promotes increased microhardness, due to Ti atoms incorporation [18], while the Me, introduced into the surface layer of steel, supports increased plasticity and antiscuff properties, as well as increased corrosion resistance [1].

The heterostructured character of the PPT/Me nanoparticles promotes a combined influence of the additive. It is interesting that, in the case of the PPT/Zn composition, a synergetic effect takes place; an introduction of Zn in presence of Ti promotes more intensive effect in comparison with pure PPT and Zn additives.

Table 3. Chemical composition of the wear spot surfaces lubricated with different additives (greases).

Lubricating	Content, wt.%							
	C	O	Cr	Fe	Ti	Zn	S	Mo
Basic steel	7.4	-	1.5	91.2	-	-	-	-
Litol-24 (pure)	5,5	-	1.8	92.5	-	-	-	-
PPT/Zn	5.2	6.9	1.4	83.7	2.3	0.6	-	-
Megaplex XD3	7.3	-	1.6	89.4	-	-	0.3	1.5

Thus, the lubricating composition based on PPT/Zn heterostructured nanoparticles is a more promising to use in the composition of different universal and special greases as a new antifriction, antiwear and antiscuff additive (table 3), which is characterized by high tribology properties, better of the same obtained with the model greases based on Me nanoparticles and some commercial samples of greases based on MoS_2 powders. At the same time, the PPT/Zn powder has a cost in 3-4 times lower of the MoS_2 powders and in 15-20 times lower of the cost of Me-nanopowders.

In the case of the PPT/Zn powder application in the lubricating compositions, the surface layer of rubbing surfaces achieves improved tribological characteristics due to chemical modification supporting increased microhardness, corrosion resistance and antiscuff properties.

5. Conclusions

1. The nano-powders of complex chemical composition can be produced by intercalation of layered potassium polytitanate (PPT) particles with transition metal ions in the aqueous solutions of corresponding salts.
2. Due to the reduction properties of the PPT powders, the low temperature thermal treatment of their intercalated particles allows obtaining the heterostructured nanoparticles consisting of potassium polytitanate layers and Me nanoparticles located in the interlayer space and onto the surface of these particles.
3. The admixtures of the suspensions of heterostructured PPT/Me nanoparticles, obtained with special surfactants in the basic oils, can be easy dispersed in different greases, i.e. Litol-24, to obtain new effective lubrication compositions.
4. The tests realized using the four-balls machine in accordance with ASTM D2783 have shown that the model greases prepared in the system of Litol-24 - PPT/Me (3wt.%), Me=Zn,Cu,Cr are characterized with excellent antifriction properties, similar to the same obtained for the additives based on the corresponding Me nanoparticles. These lubricating compositions, especially the Litol-24/PPT/Cu, were also characterized with high values of nonseizure loads (antiscuff properties) and small values of wear spots, especially Litol-24/PPT/Zn, (antiwear properties).
5. The analysis of the chemical composition and morphology for the balls lubricated with different types of additives, based on PPT/Me nanopowders, has shown that these additives allowed obtaining the friction surfaces characterized with improved corrosion and wear resistance due to incorporation of Ti and Me into the structure of worn surfaces.
6. It was shown, in the control testing experiments with some standard bearings that a use of the PPT/Zn additives in the composition of the Litol-24 standard grease (3 wt.%) promoted reduced wear (in 3 times), increased time resource (in 3.2 times) and decreased friction force torque (in 1.45 times).

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