Synthesis, structure and tribological properties of nanocomposite materials in the system of potassium polytitanate – layered double hydroxide – serpentinite

A Tsiganov, A Krivonogova, T Nikityuk, O Smirnova and A Gorokhovsky

Yuri Gagarin State Technical University of Saratov, 77 Polytekhniacheskaya str., Saratov, 410054, Russia

E-mail: tsyganov.a.93@mail.ru

Abstract. The synthesis of some nanocomposite materials in the ternary system of potassium polytitanate (PPT) -layered double hydroxide (LDH) -synthetic serpentinite (SS) is considered. The tribology behavior of some model greases obtained by introduction of different nanocomposite additives in the universal industrial grease of the Litol-24 trademark is investigated using standard testing procedures. The obtained results have shown that the synthesized nanopowders improve anti-friction and anti-wear properties of the standard lubricating composition. It is shown that the enhanced tribology performance is attributed to a complex layered structure of the produced nanocomposites and their chemical interaction with a worn surface of the metal.

1. Introduction

With the advancements in machine industry and energy consumption, conventional lubricant (MoS$_2$) has become inadequate for practical applications due to a sufficiently high cost and fast mechano-chemical degradation promoting increased corrosion and abrasion activity, i.e. an appearance of abrasive particles (molybdenum oxides, MoS$_2$) and H$_2$SO$_4$(in a presence of H$_2$O) during exploitation. In order to prolong the lifetime of machines and mechanisms, as well as reduce energy consumption, many efforts have been made to develop new types of antifriction additives. Nanoparticles are considered as an effective approach to upgrade the lubricants due to their small size and physico-chemical properties, which have been thoroughly investigated during the past decade. It is found that nanoparticles such as metal, oxides, sulfides, borate, carbonates, as well as carbon nanomaterials, and rare-earth compounds [1-3], can significantly improve the tribological properties of liquid lubricant.

Potassium polytitanate (PPT) characterized with the chemical composition of K$_2$O·nTiO$_2$·mH$_2$O has relatively low cost and represents a new promising type of lubricating additive. A layered lepidocrocite-like structure of the PPT particles is formed by polyanions constructed by double edge – shared TiO$_6$ octahedra; K$^+$ and H$_2$O$^+$ cations locate in the interlayer space and compensate negative electric charge of polyanions. Due to a large distance between the layers in the PPT particles varied in the range of 0.2-1.1 nm, they have quasi-amorphous character and low coefficient of friction [4].

The particles of layered double hydroxides (LDH) include positively charged brucite-like metal hydroxide layeres which are seperated by charge-balancing anions and H$_2$O molecules. The generaal formula of LDHs can be presented as [Me$_{2x}$$^{2+}$,M$_{y}$]$^{x^+}$[(OH)$_2$]$^{2-x^+}$A$^{x^+}$xH$_2$O. Part of divalent metal cations (Zn$^{2+}$, Mg$^{2+}$,Ni$^{2+}$, etc.) are substituted by trivalent metal cations (Al$^{3+}$, Cr$^{3+}$,Fe$^{3+}$, etc.), resulting surplus

Content from this work may be used under the terms of the CreativeCommons Attribution 3.0 licence. Any further distribution of this work must maintain attribution to the author(s) and the title of the work, journal citation and DOI.
positively charged on layers on which they are compensated by interlayer anion (CO$_3^{2-}$, SO$_4^{2-}$, NO$_3^{2-}$, Cl, etc.) [5]. Various groups of scientists have found that LDHs used as lubricant additives can significantly reduce the coefficient of friction and energy consumption [6, 7].

Serpentinites (Mg$_2$Si$_2$O$_7$(OH)$_4$) are also considered as promising antifriction materias due to their layered structure and soft abrasion action which promotes self-repairing properties of worn metal surfaces [8-10]. The lubricating mechanism of serpentine-like powders is caused by tribochemical reactions and filling of surface microcracks with nanoscale ceramic particles.

Each kind of the above mentioned materials has own preferences; however, their separate application does not allow obtaining the additives characterized with an optimal complex of all the tribology characteristics. That is why, the aim of this work is to study a possibility to synthesize some nanocomposite materials based on different combinations of structural fragments of these three types of sustances and investigate some tribology properties of the obtained products.

2. Materials and methods
The parent PPT powder (anatase, Aldrich, purity – 99 %, average diameter of particles - 7 µm) was treated in the molten mixture of KOH and KNO$_3$ at 500 °C for 2 h in the alumina crucible. The obtained product with the chemical composition corresponding to the molar ratio of TiO$_2$: K$_2$O = 4.2 was washed with distilled water (20 weight parts of H$_2$O for 1 weight part of the product) to dissolve water soluble components. After that 80 % of the obtained dispersion was selected for the following modification.

The LDHs particles were synthesized using the following procedures. Some aqueous solutions of salts were prepared in advance: Zn(NO$_3$)$_2$･6H$_2$O/Al(NO$_3$)$_3$･9H$_2$O, mixed solution of Zn(NO$_3$)$_2$･6H$_2$O and Cr(NO$_3$)$_3$･9H$_2$O (M$^{2+}$/M$^{3+}$=2:1, 1M) and mixed solution KOH and K$_2$CO$_3$ (6:1, 2.5M). According to the coprecipitation method [11], the mixtures of above mentioned solutions of the salts were introduced into the selected aqueous dispersion of PPT in an amount corresponding to the ratio of 1 g of PPT to 1 g ([M$^{2+}$]+ [M$^{3+}$]). At the same time, the mixed alkaline solution of KOH/K$_2$CO$_3$ was added dropwise to obtain the dispersion with pH = 10 homogenized by stirring for 1h. The resulting suspension was soaked for 5h at 90 °C for the final maturation. After that, the precipitate was washed several times with distilled water until pH reached 8.

The next stage was done to obtain the powders of nanocomposites based on the obtained suspensions of the potassium polytitanate modified by layered double hydroxides: PPT-LDH(Zn/Al), PPT-LDH(Zn/Cr), and synthetic serpentinite (SS). The synthesis was performed according to the procedure described in [12]. The following aqueous solutions were prepared: 500 g of Mg(NO$_3$)$_2$･6H$_2$O was dissolved in 593.52 ml distilled water, 593.52 g of 40 % sodium liquid glass (GOST 13078–81) was dissolved in distilled water (550 ml). To obtain 100 g of nanoscale SS (Mg$_2$Si$_2$O$_7$(OH)$_4$), an aqueous solution of liquid glass was added dropwise to 436.3 ml of Mg(NO$_3$)$_2$ based solution with intensive stirring. The obtained product was maturated without stirring for 24 h then washed with distilled water (20 weight parts of H$_2$O for 1 weight part of the product) centrifuged (3000 rpm), dried at 50 °C for 4 h and, finally, grinded in the ball mill (Al$_2$O$_3$ ceramic set).

To produce the samples of lubricating compositions, the synthesized powders were mechanically dispersed and joint milled in the industrial oil I-20A (Russian standard GOST 20799–88). The obtained 50 % dispersions were stabilized by ultrasonic treatment and used to produce model lubricating compositions on the base of the universal grease of the Litol-24 (Russian Standard GOST 21150-87) traditionally applied in different bearings. The model greases were prepared by mixing of Litol-24 with the samples of the 50 % oil dispersion in proportion, which allowed obtaining the compositions containing 3 wt.% of the corresponding powder (additive). This concentration was selected taking into account that a major part of commercial greases is characterized by this content of additives.

A four-ball tribotester SR-1A was used to assess the tribology characteristics of the investigated model greases. The tests were made in accordance with the Russian standard GOST-9490-75 (analog of the ASTM D 2266 standard), using the balls of 6.35 mm in diameter. The balls produced with steel SX-15 (Russian standard GOST 801-78) were cleaned with ethyl alcohol and petroleum ether in an
ultrasonic bath before the testing. A wear-scar diameter value ($d_{ws}$) obtained under a constant load of 196 N for 1h testing was selected as anti-wear characteristic. The friction coefficient was measured for a given time of 1 h with a step of 3 min and used to estimate an average value for each series taking into account the data obtained in three experimental series. Each test was done with a new portion of the corresponding lubricating compound and new balls. The four-ball test was conducted under rotating speed of 1200 rpm and load of 196N at room temperature. The morphology of worn surface under the lubrication and the wear scar diameter were determined using a scanning electron microscope (Aspex explorer) equipped with the EDS analyser.

3. Structure of the synthesized powders
The XRD patterns of the synthesized powders are shown in figure 1. All the products have a quasi-amorphous structure characterized with wide weak reflections typical for the parent PPT powder (destroyed lepidocrocite-like structure).

![Figure 1. XRD patterns of the nanocomposite powders. A - PPT-LDH(Zn/Al)-SS, B - PPT-LDH(Zn/Cr)-SS.](image)

![Figure 2. SEM images of different nanocomposite powders: A - PPT-LDH(Zn/Al)-SS, B - PPT-LDH(Zn/Cr)-SS.](image)
The morphology of the obtained nanocomposite particles is shown in figure 2. The particles are represented by agglomerated layered particles of the basic PPT decorated with nanoscale particles of the LDH and synthetic serpentinite.

4. Tribology properties
A friction coefficient dependence on time for different compositions of as-synthesized particles used as lubricating additives is shown in figure 3. The PPT-LDH(Zn/Al)-SS and PPT-LDH(Zn/Cr)-SS additives reduce a value of the average coefficient of friction for 28.1 % and 32.9 %, respectively. Furthermore, PPT-LDH(Zn/Cr)-SS has better antifriction properties than PPT-LDH(Zn/Al)-SS. A value of the wear scar diameter obtained with the greases containing PPT-LDH(Zn/Al)-SS and PPT-LDH(Zn/Cr)-SS additives decreased by 39 and 33 %, respectively, as compared with a use of pure Litol-24 grease (table 1). A welding point value for the greases containing investigated additives increased in comparison with pure Litol-24, for 64 % (PPT-LDH (Zn/Al) –SS additive) and 57 % (PPT-LDH (Zn / Cr) –SS additive). Thus, the LDH (Zn/Cr)-containing composition has more attractive antifriction properties, whereas the composition, containing LDH (Zn/Al), can be considered as preferable antiscaff lubricant.

![Figure 3](image-url)

**Figure 3.** Data on friction coefficient of Litol-24 and Litol-24 with different nanocomposite additives.

| Lubricating composition | Wear-scar diameter, (µm) | Weld point, (N) |
|-------------------------|--------------------------|-----------------|
| Litol-24                | 668                      | 1400            |
| Litol-24 +3% (PPT-LDH(Zn/Al)-SS) | 411              | 2300            |
| Litol-24 +3% (PPT-LDH(Zn/Cr)-SS) | 450              | 2200            |

A scanning electron microscope (SEM) equipped with the EDS analyzer (Aspex Explorer) was applied to analyze morphology and distribution of the chemical elements along worn balls surfaces. Figure 4 shows the micro-photographs of worn surfaces lubricated with the parent Litol-24 and Litol-24 containing 3 % admixtures of the investigated additives. It can be seen that when the parent grease was used as a lubricant, the scuffing of the worn surface is severe with many deep furrows and grooves coupled with small pits and plastic deformation thereon. At the same time, for the greases containing additives, worn surface is smooth and only contain slight signs of wear, suggesting that the scuffing of the worn surface is mild and a protective film has formed in the sliding process. Such trend of a worn
surface morphology is in good agreement with the obtained experimental data related to the friction and wear behavior of these greases.

Figure 4. SEM morphology of the worn metal surfaces lubricated with: (A) Litol-24, (B) Litol-24 containing 3 wt.% PPT-LDH(Zn/Al)-SS, (C) Litol-24 containing 3 wt.% PPT-LDH(Zn/Al)-SS.

Figure 5 presents the data on the chemical composition of the worn surfaces lubricated with the parent grease and grease containing 3 wt% of the investigated additives. The elemental analysis shows a presence of Ti, Fe, K, C and Si in the surface layer of rubbing surfaces. It is obvious that Si, Ti and K come from the solid additives suspended in grease, while Fe is from the steel worn surface. It is important to note that the content of Si and Ti is fairly high in the area of the micropores. This is due to the fact that the particles from the additive are introduced into the micro-appertures on the worn surface. The presence of Ti and Si evenly distributed on the surface can be observed in the area of the smooth surface. The results obtained indicate that the introduced solid additives react with the surface of the substrate of friction pairs, resulting in a protective film formed on the worn surface, on which the elements of the additive structure are adsorbed and introduced.

Figure 5. EDS analysis of the worn steel surfaces lubricated with Litol-24 containing 3 wt.% PPT-LDH(Zn/Al)-SS. 1 – typical surface with pure grease, 2 – zone A, 3 – zone B.

5. Conclusion
The results on tribology properties obtained for the lubricating compositions containing the LDH(Zn/Al)-SS and PPT-LDH(Zn/Cr)-SS nanocomposites particles as additives allow the following conclusions to be made:

1. The greases containing 3 wt. % of the synthesized and investigated nanocomposites exhibit excellent tribological characteristics, wherein the chemical composition of LDH influences the effect of
additives. In particular, Cr-containing additive reduces friction phenomena more effectively, whereas Al-containing additive increases welding load and reduces wear.

2. The impact of additive on tribology properties can be explained by the layered structure of the powders and formation of the protective films on the worn surface.

3. The formed tribochemical films contain structurally embedded chemical elements of the nanocomposite compounds as well as nanoparticles of the additives.

Acknowledgment
The reported study was supported by the Russian Ministry of Science and Higher Education (project 10.1434.2017/4.6).

References
[1] Spalvins T 1982 Morphological and frictional behavior of sputtered MoS2 films Thin Solid Films 96 17–24
[2] Dienwiebel M, Verhoeven G S, Pradeep N and Frenken J W M 2004 Superlubricity of graphite Phys. Rev. Lett. 92 126101
[3] Bull S J 1995 Tribology of carbon coating: DLC, diamond and beyond Diam. Relat. Mater. 4 827–836
[4] Sanches-Monjaras T, Gorokhovsky A and Escalante-Garcia J 2008 Molten salt synthesis and characterization of polytitanate ceramic precursors with varied J. Am. Ceram. Soc. 91(9) 3058-65
[5] Miyata S 1983 Anion–exchange properties of hydrotalcite–like compounds Clay. Clay Miner. 31(4) 305–311
[6] Bai Z M, Wang Z Y, Zhang T G, Fu F and Yang N 2012 Characterization and friction performances of Co-Al-layered double-metal hydroxides synthesized in the presence of dodecylsulfate Appl. Clay Sci. 59-60 36-41
[7] Li S and Bhushan B 2016 Lubrication performance and mechanisms of Mg/Al-, Zn/Al-, and Zn/Mg/Al-layered double hydroxide nanoparticles as lubricant additives Appl. Surf. Sci. 378 308-319
[8] Yuansheng J, Shenghua L, Zhengye Z, He Y and Feng W 2004 In situ mechanochemical reconditioning of worn ferrous surfaces Tribol. Int. 37 561–567
[9] Yu H L, Xu Y, Shi P J, Wang H M, Zhao Y, Xu B S and Bai Z M 2010 Dissipated energy and fretting damage in CoCrAlY-MoS2 coating Tribol. Int. 43 667–675
[10] Zhang B, Xu Y, Gao F, Shi P, Xu B and Wu Y 2011 Sliding friction and wear behaviors of surface-coated natural serpentine mineral powders as lubricant additive Appl. Surf. Sci. 257 2540–49
[11] Gastuehe M C, Brown G and Mortland M M 1967 Mixed magnesium-aluminium hydroxides Clay Miner. 7 177–192
[12] Gorokhovskiy A V, Smirnova O A, Azarov A S, Safonov V V, Tretyachenko E V, Goffman V G, Shindrov A A and Kolbasina T V 2012 Preparation of synthetic serpentine, optical and tribological characteristics of oleophylic dispersions Bulletin of the Saratov State Technical University [in Russian – Vestnik SGTU] 4(68) 85-90