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Tribological Properties of Layered α-Zirconium Phosphate as Lithium Grease Additive

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Layered α-zirconium phosphate [α-Zr(HPO_4)$_2$·H_2O, hereafter referred to as α-ZrP] with high crystallinity, uniform diameter and regular morphological forms was synthesized in a mild NaF-ZrO-P_2O_5-H_2O system under hydrothermal conditions. The four-ball test results indicated that the anti-wear, load-carrying and friction reduction capacity of lithium grease were significantly improved with the addition of α-zirconium phosphate. It was also observed that α-zirconium phosphate displayed a better lubricating property than MoS_2. The SEM and EDS results indicated that a protective film that was composed of Zr, P, Fe, Cr, O and C formed on the rubbing surface.

Keywords: Layered α-zirconium phosphate, Tribolgical properties, Lithium grease, Hydrothermal synthesis.

INTRODUCTION

The reduction of friction has always been one of the central focuses of civil engineering whenever mobile parts have been involved in the design of transport means, mechanical tools, or machines. Friction produces loss of materials and mechanical energy, unwanted release of heat and noise pollution[1]. To reduce friction, lubricants have to be employed. Solid lubricants fill a special niche in reducing wear in situations where the use of liquid lubricants is either impractical or inadequate. A number of inorganic compounds, such as metal dichalcogenides MX_2 (where M, for instance is Mo or W and X is S or Se)[2-4], graphite[5,6] and serpentine[7,8], have been used as solid lubricants and many research groups have focused on their synthetic processes over the past decades. These materials are characterized by a layered structure with weak (van der Waals) inter-layer forces that allow easy, low-strength shearing[9].

Layered α-zirconium phosphate [Zr(HPO_4)$_2$·H_2O, abbreviated as α-ZrP] is a typical artificial cationic layer compound material. The structure is layered, with each layer consisting of planes of zirconium atoms bridged through phosphate groups which alternate above and below the metal atom planes[10,11]. α-Zirconium phosphate has properties useful for ion exchange, adsorption, catalysis, *etc.*[12]. α-Zirconium phosphate has both high thermal and chemical stability and these properties make α-ZrP a promising candidate material for many technological applications.

Recent studies indicate that the addition of α-ZrP to lubricating oil can increase the maximum non-seizure load (P_B) of the base oil from 470 to 598 N and decrease the wear scar diameter (WSD) of the base oil from 0.58 to 0.33 mm; also, this additive which is shown to have anti-wear capabilities superior to those of MoS_2 and graphite additives[13]. α-ZrP and α-$Na_2Si_2O_5$ exhibited synergistic behaviour as lubricant additives in mineral oil. The wear scar diameter and the friction coefficient of the combination (α-ZrP: α-$Na_2Si_2O_5$ mass ratio 1:3) can reach 0.27 mm and 0.110, respectively[14]. The lubricating properties of the combination are superior to α-ZrP and α-$Na_2Si_2O_5$ alone.

To the best of our knowledge, the effect of α-ZrP as an additive on the tribological behaviour of lubricating grease has not been reported in the scientific literature. Therefore, this study focuses on α-ZrP being used as an additive for grease.

In this paper, α-ZrP is synthesized through a simple and mild method. A four-ball machine is used to evaluate α-ZrP as an additive in lithium grease. The results obtained for various amounts of additive are compared with those obtained with the MoS_2 additive. The action mechanism is estimated through analysis of the worn surface with scanning electron microscopy (SEM) and energy dispersive spectra (EDS).

EXPERIMENTAL

The raw chemicals used were $ZrOCl_2$·8H_2O (AR reagent grade, Sinopharm), H_3PO_4 (85 %, Sinopharm) and NaF (AR reagent grade, Sinopharm). These were purchased from commercial sources and used in all syntheses without further purification. Distilled water was produced in our own laboratory.

Synthesis of α-ZrP: α-ZrP was prepared as follows. Firstly, H_3PO_4 was added to $ZrOCl_2$ aqueous solution forming the precursor solution, then a small quantity of NaF was added to the precursor solution. A white gelatinous precipitate was obtained as soon as the solution was mixed together and the solution was stirred until it was homogeneous. Precipitates were kept in their mother liquor, moved to a sealed Teflon vessel and heated in an oven. The resulting precipitate was then filtered, washed with distilled water until the pH = 7 and dried in ambient air. The typical synthesis conditions were 180 °C for 36 h, with the molar ratio of raw materials of $ZrOCl_2$:H_3PO_4:NaF:H_2O = 1:2:0.1:30.

Preparation of lithium grease, α-ZrP-lithium grease and MoS_2-lithium grease: Lithium grease was prepared as follows. Firstly, the predetermined amounts of PAO9, 12-hydroxystearic acid and stearic acid were added to a grease kettle and the mixture was stirred and heated to 85 °C until it became homogeneous. Secondly, a water slurry of lithium hydroxide initially heated to about 80 °C was slowly added into the above mixture, then it was heated to 120 °C and kept at this temperature for approximately 3 h until the lithium soap formed. Additional base oil was slowly added into the lithium soap at 90 °C and once again heated to 130 °C until the water was completely evaporated. The mixture was kept at 205 °C for 10 min, then cooled to room temperature and ground in a triple-roller mill three times to form the desired lithium grease.

To investigate the effect of α-ZrP and MoS_2 on the tribological behaviour of lithium grease, the two additives were added at concentrations of 0.5 to 5.0 wt. %. Each variation of lithium grease was mixed by mechanical stirring and ground three times in a triple-roller mill.

Friction and wear tests: The anti-wear property, friction reduction property and load-carrying capacity of the as-prepared lithium grease were evaluated on a four-ball tester (a point contact test). The friction and wear tests were conducted at 75 °C, with a rotating speed of 1450 rpm, loads of 196, 294, 392, 490, 588 and 686 N and a test duration of 0.5 h. The weld point and maximum non-seizure loads were determined according to the national standard method SH/T 0202-92 which is similar to ASTM D2596-1997. The balls (diameter 12.7 mm, HRc 59-61) were made of GCr15 bearing steel (AISI-52100). The wear scar diameters on the three lower balls were measured using an optical microscope to an accuracy of ± 0.01 mm and the friction coefficients were recorded automatically with a strain gauge. Three identical tests were performed to determine an average so as to minimize data scattering. SEM and EDS were employed to analyze the rubbing surface.

XRD patterns were recorded with a X-ray diffractometer (Rigaku, MiniFlex II) using CuK_α radiation (λ = 1.5418 Å), 30 kV, 15 mA. SEM micrographs were obtained with a scanning electron microscope for powder samples (JEOL, JSM-6700E) and for the rubbing surface (Hitachi, TM-3000). The lubrication properties of lithium grease were determined by a four-ball friction and wear tester (Tenkey, MS-10J). The chemical compositions of the surface on the friction pair were analyzed by energy dispersive X-ray spectrometry (EDS, Bruker, QUANTAX 70).

RESULTS AND DISCUSSION

Preparation and characterization of α-ZrP: Since α-ZrP exhibited a good lubricating property in previous literature[13,14], we synthesized the material in a mild NaF-ZrO-P_2O_5-H_2O system under hydrothermal conditions. By replacing hydrofluoric acid with sodium fluoride, we significantly reduced the toxicity of the previous α-ZrP synthesis reaction[15,16]. In our experiments, the synthesis conditions of α-ZrP were investigated by changing the ratio of raw materials, reaction temperature and reaction time. Fig. 1 shows the comparison of XRD patterns of α-ZrP prepared by adding different amounts of NaF under the following synthesis conditions: $ZrOCl_2$: H_3PO_4 : H_2O = 1 : 2 : 30, 180 °C, 36 h. It can be seen that adding a small quantity of NaF to the reaction system (F/Zr = 0.1) improved the crystallinity of the samples. If the molar ratio of F/Zr was 0.2, α-ZrP and an impurity phase (2θ = 14.1, 19.6 and 31.2°) were obtained. From above, the optimum synthesis conditions were as follows: 180 °C, 36 h, with molar ratios of raw materials of $ZrOCl_2$:H_3PO_4:NaF:H_2O = 1:2:0.1:30.

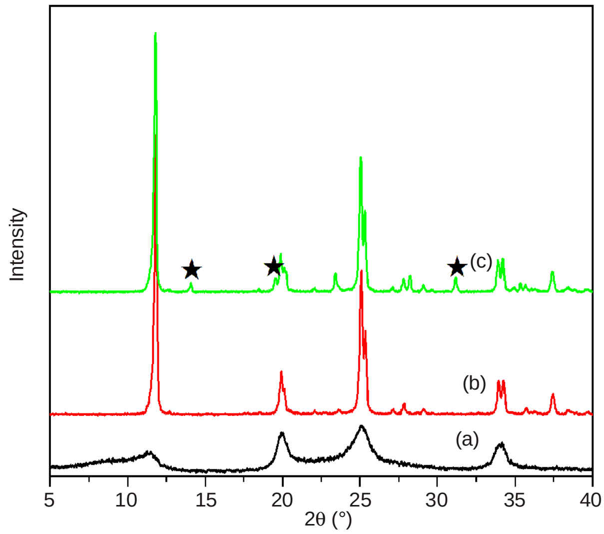

Fig. 1. XRD patterns of α-ZrP samples, synthesis conditions were $ZrOCl_2$: H_3PO_4 : H_2O = 1 : 2 : 30, 180 °C, 36 h with molar ratios of (a) F/Zr = 0; (b) F/Zr = 0.1; (c) F/Zr = 0.2 (★-Impurity phase (2θ = 14.1°, 19.6° and 31.2°))

For typical α-ZrP samples, seven intense peaks are found at 2θ = 11.7, 19.9, 20.5, 24.9, 25.2, 33.9, 34.1 and 37.4°; these are the characteristic peaks of α-ZrP, according to the literature[11]. Fig. 2 shows that the experimental powder XRD patterns of typical α-ZrP samples conform to the simulated powder XRD patterns. Also, the unit cell parameters of α-ZrP have been refined with PCW[17] from powder simulation and XRD pattern and the cell dimensions are: a = 9.0745 Å, b = 5.3020 Å, c = 15.4499 Å, β = 101.4535°. These values are very similar to those reported for α-ZrP, which were a = 9.060(2) Å, b = 5.297(1) Å, c = 15.414(3) Å, β = 101.71(2)°[11]. The simulated and experimental powder XRD patterns of α-ZrP are identical, indicating that they possess the same structure.

The SEM image (Fig. 3a) shows that the typical α-ZrP is a regular hexagonal shape with an average particle size of 600 nm. Comparing the morphology of α-ZrP prepared when adding NaF or not (Fig. 3a and 3b), the result shows that NaF has an effect on regulating and controlling the morphology of α-ZrP.

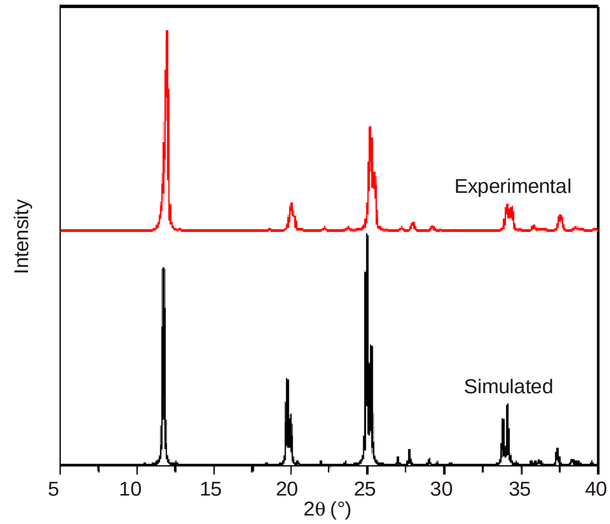

Fig. 2. Simulated and experimental powder XRD patterns of typical α-ZrP samples

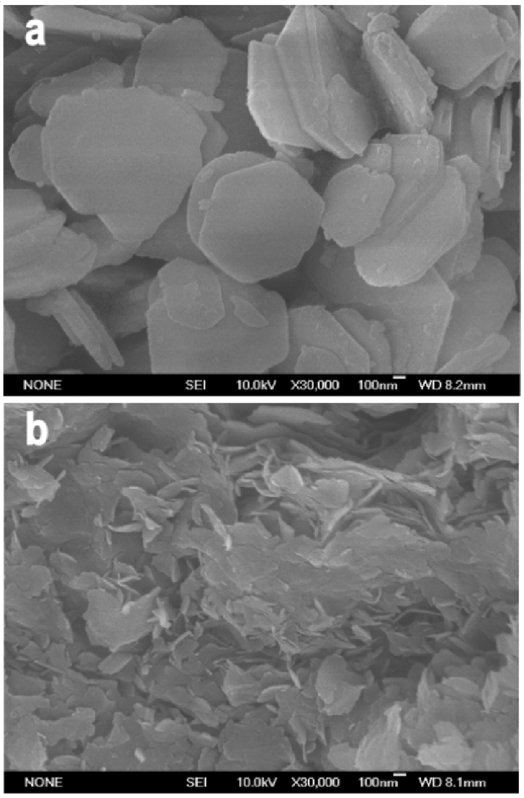

Fig. 3 SEM image of α-ZrP samples, synthesis conditions were $ZrOCl_2$:H_3PO_4:H_2O = 1:2:30, 180 °C, 36 h with molar ratios of (a) F/Zr = 0.1; (b) F/Zr = 0

Tribological properties of α-ZrP: The present study investigates the tribological properties of α-ZrP as grease additive and compares it with those of MoS_2. Fig. 4 displays the variation of the wear scar diameters with the concentration of additives under a load of 294 N and the variation of the P_B values with the concentration of additives. The wear scar diameters of the lithium grease containing α-ZrP are much lower than those containing of MoS_2 at all concentrations. The wear scar diameter of α-ZrP at first decreases from 0.50 mm (the wear scar diameter of the base lithium grease) to 0.30 mm quickly as the additive concentration increases from 0.5 to 3.0 wt. % and the wear scar

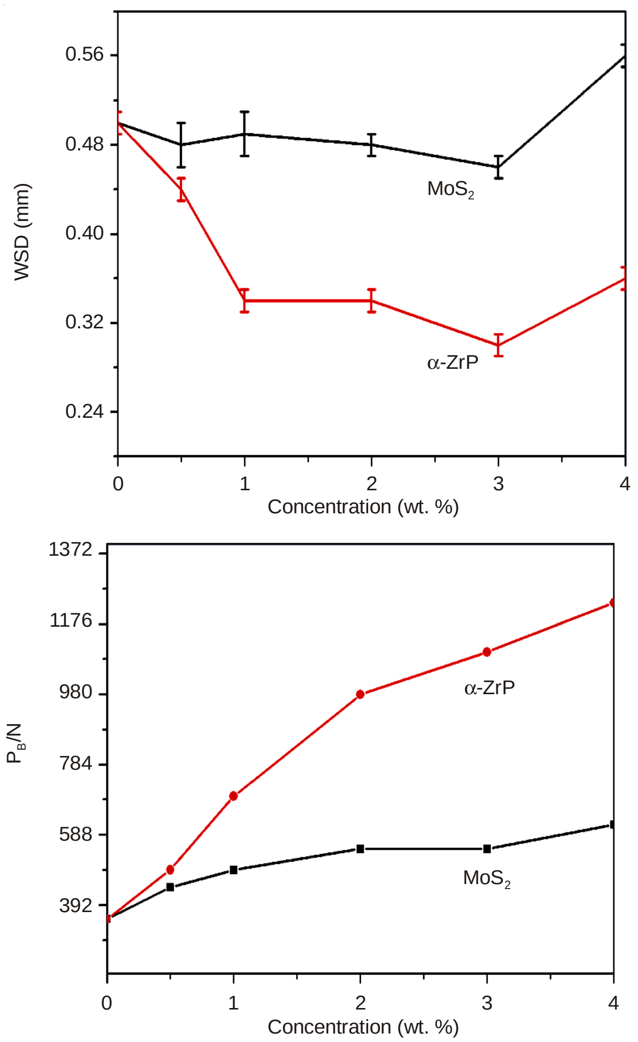

Fig. 4. Wear scar diameter and P_B as functions of additive concentration (wear scar diameter: 75 °C, 1450 rpm, 294 N, 0.5 h, P_B: 25 °C, 1770 rpm, 10 s)

diameter increases to 0.36 mm when the concentration increases to 4.0 wt. %. The wear scar diameter of MoS_2 decreases slowly from 0.50 to 0.46 mm when the additive concentration increases from 0.5 to 3.0 wt. % and then increases to 0.56 mm when the MoS_2 concentration reaches 4.0 wt. %. Compared to MoS_2, α-ZrP performs better with respect to anti-wear. Meanwhile, the P_B value of the lithium grease jumps from 353 to 1235 N when the additive concentration of α-ZrP jumps from 0 to 4.0 wt. %. The P_B values of the lithium grease go up slowly from 353 to 617 N when the additive concentration of MoS_2 increases from 0 to 4.0 wt. %, affording lower P_B values than those of α-ZrP. These results show that α-ZrP has excellent load-carrying capacity. According to the above (that is, minimum wear scar diameter values were obtained at additive concentration of 3.0 wt. % and P_B values increased slowly from 3.0 to 4.0 wt. %), the optimum concentration of the α-ZrP and MoS_2 as additives in lithium grease is around 3.0 wt. %.

Fig. 5 shows the relationship between the friction coefficient and the applied loads with the lubrication of lithium grease containing the two additives. As an additive, α-ZrP was found to considerably decrease the friction coefficient from 0.102 to 0.058 as the applied load increases from 98 to 686 N.

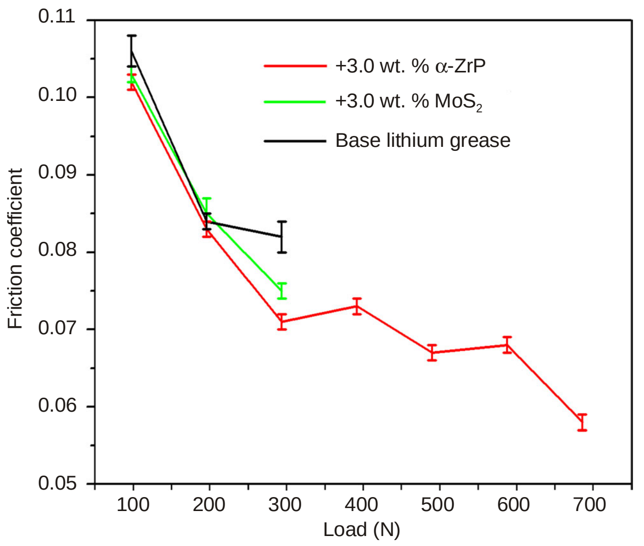

Fig. 5. Friction coefficient as a function of applied load with the lubrication of base lithium grease, containing 3.0 wt. % of a-ZrP and MoS_2 additives (75 °C, 1450 rpm, 0.5 h)

With regard to MoS_2, the friction coefficient decreases gradually with applied loads ranging from 98 to 294 N and then the wear test was interrupted when the applied load increased to 392 N. This is because the MS-10J four-ball tester has automatic protection settings when the friction coefficient reaches a value of 0.2 (severe wear). The friction coefficient trends of base lithium grease are similar to grease with MoS_2. The results of the friction coefficient demonstrate that α-ZrP is an effective additive in improving the friction-reduction properties of lithium grease.

From Fig. 6, it can be observed that wear scar diameter of α-ZrP at first gently undulates from 0.28 to 0.30 mm as the applied load increases from 98 to 294 N and the wear scar diameter values increase from 0.37 to 0.41 mm when the applied load rises from 392 to 686 N. For MoS_2, the wear scar diameter values fluctuate a little in the range of 0.43 to 0.46 mm as the applied load increases from 98 to 294 N. In contrast,

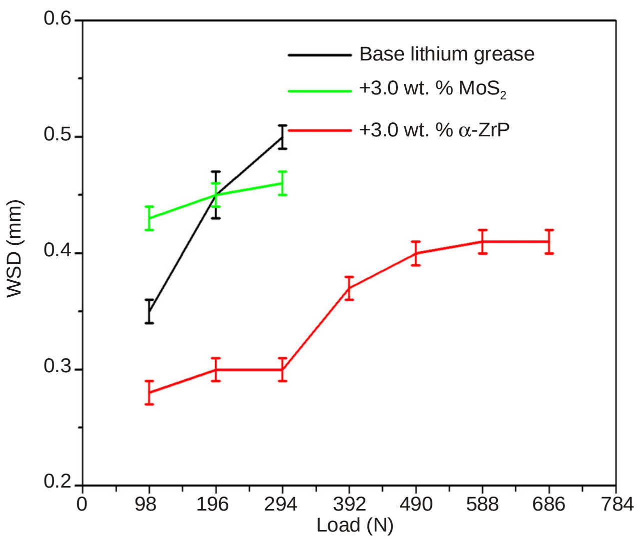

Fig. 6. Wear scar diameter (WSD) as a function of applied load with the lubrication of base lithium grease, containing 3.0 wt. % α-ZrP and MoS_2 additives (75 °C, 1450 rpm, 0.5 h)

the wear scar diameter of base lithium grease goes up almost linearly from 0.35 to 0.50 mm. Considering that the wear scar diameter values in the whole range of applied loads, as-prepared α-ZrP performs the best with respect to anti-wear. This also suggests that α-ZrP has a high load-carrying ability in the relative long-time run wear test.

Scanning electron microscope and energy dispersive spectra analysis of rubbing surfaces: Scanning electron microscope (SEM) and energy dispersive spectra (EDS) analysis were employed to observe the rubbing surface of the lower steel balls after testing with the base lithium grease, lithium grease with 3.0 wt. % MoS_2 and lithium grease with 3.0 wt. % α-ZrP and the results are presented in Fig. 7. Under a load of 294 N, the worn surface lubricated by the base lithium grease and 3.0 wt. % MoS_2 lithium grease were seriously damaged with deep furrows on the rubbing surface. On the other hand, steel balls lubricated by 3.0 wt. % α-ZrP grease exhibited a relatively shallow wear scar. This is consistent with previously measured wear scar diameter results in Fig. 4 and 6 (base lithium grease: 0.50 mm; lithium grease with 3.0 wt. % MoS_2: 0.46 mm; lithium grease with 3.0 wt. % α-ZrP: 0.30 mm). As the load increased to 686 N, the wear scar diameter of the 3.0 wt. % α-ZrP grease only reached about 0.41 mm with some deposits spread out on top of the wear surface.

The element composition of the rubbing surface lubricated by base lithium grease, lithium grease with 3.0 wt. % MoS_2 and lithium grease with 3.0 wt.% α-ZrP were analyzed by EDS and the results are showed in the left column of Fig. 7. It can be seen that there is no other element except those of the friction pair itself (C, Fe and Cr) on the rubbing surface of the friction pair lubricated by both the base lithium grease and the lithium grease with 3.0 wt. % MoS_2, while there are Zr, P and O on the rubbing surface besides Fe, Cr and C after using α-ZrP as an additive in lithium grease. It is known that the purpose of lubrication is to form films that have high load-carrying capacities and low shear strengths, so as to reduce the friction resistance and decrease the wear of the friction pair[18]. Obviously, α-ZrP grease can form a protective film and the solid protective film provides for further reduction of the friction and wear of the contacting pairs and thereby increases their load carrying capacity and anti-wear property compared to the base lithium grease and the lithium grease with MoS_2.

Conclusions

To summarize the present work, the following conclusions are drawn:

- α-ZrP with high crystallinity, uniform diameter and regular morphological forms was synthesized in a mild NaF-ZrO-P_2O_5-H_2O system under hydrothermal conditions.
- The tribological test showed that the anti-wear property of α-ZrP as an additive in lithium grease depends on the additive concentration.
- The optimal concentration of α-ZrP is 3.0 wt. %, which exhibits excellent anti-wear, load-carrying and friction-reducing properties. α-ZrP displayed a better lubricating property than MoS_2.
- SEM and EDS analysis indicate that α-ZrP may form a protective film composed of the elements (Zr, P, Fe, Cr, O, C) on the rubbing surface protecting the friction pairs from wear.

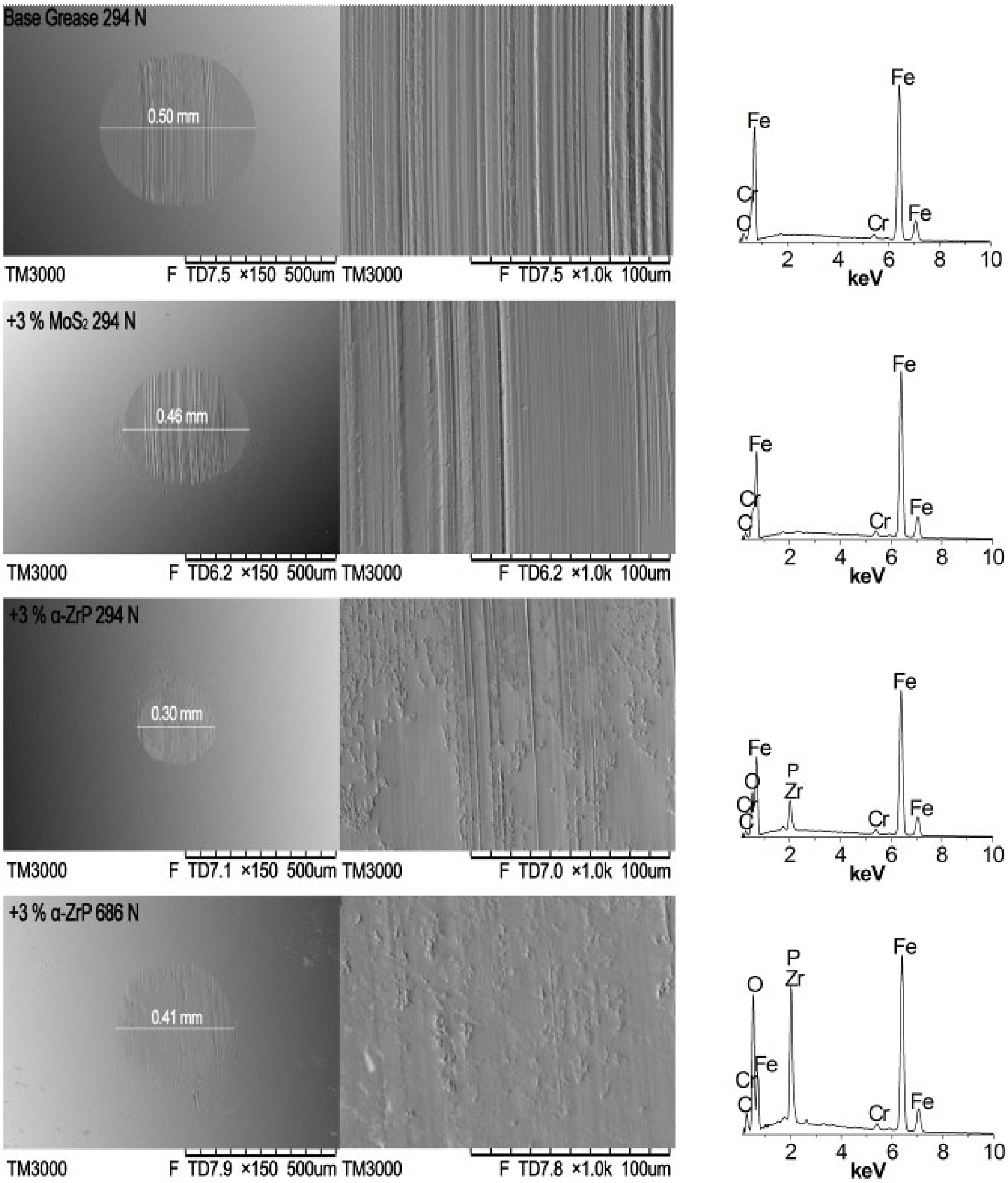

Fig. 7. SEM (left) and EDS (right) analysis of the rubbing surface (75 °C, 1450 rpm, 0.5 h); SEM magnification, on the left is 150× and on the right is 1000×

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