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Hydrothermal Synthesis of Copper Zirconium Phosphate Hydrate [$Cu(OH)_2Zr(HPO_4)_2·2H_2O$] and an Investigation of its Lubrication Properties in Grease

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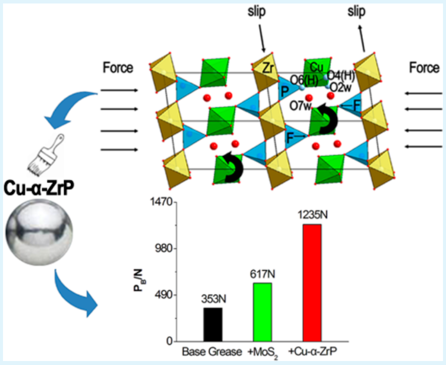
Supporting Information

ABSTRACT: Copper zirconium phosphate hydrate ($Cu(OH)_2Zr(HPO_4)_2·2H_2O$, hereafter referred to as Cu-α-ZrP) with high crystallinity was directly synthesized in a NaF-CuO-ZrO-P_2O_5-H_2O system under hydrothermal conditions. The copper ion was confirmed to be an exchangeable cation in the Cu-α-ZrP through elemental analysis and a proton ion exchange process. The crystal structure of the Cu-α-ZrP was determined ab initio by using X-ray powder diffraction data. In the structure, the CuO6 octahedron would be located in an exchangeable atom position. Moreover, Cu-α-ZrP was evaluated as an additive in grease in a four ball test. The maximum nonseizure load (P_B, representing the load-carrying capacity) of the base grease containing Cu-α-ZrP was increased from 353 to 1235 N. The excellent load-carrying capacity may be explained by the easier adherence of the material to the worn surface forming a tight protective film.



KEYWORDS: *lubrication, hydrothermal, layered materials, copper, zirconium phosphate*

INTRODUCTION

α-Zirconium phosphate ($Zr(HPO_4)_2·H_2O$, hereafter referred to as α-ZrP), is a typical artificial cationic layer compound. Each layer in the structure consists of planes of zirconium atoms bridged by phosphate groups which alternate above and below the metal atom planes.[1,2] To date, there has been research into various applications for α-ZrP, including catalysis,[3] fuel cell electrolytes,[4] self-assembled thin films,[5] chiral recognition,[6] carriers of cell membrane,[7] and so on. Our group has investigated the possibility of using α-ZrP as a solid lubrication additive,[8] replacing the materials of typical solid lubricant additives, such as MoS_2, graphite, and so on.[9−11] The experimental data showed that α-ZrP had a better performance, namely the increase in the maximum nonseizure load (P_B, representing the load-carrying capacity) of the base oil from 470 to 598N and the decrease in the wear scar diameter (WSD, representing the antiwear ability) of base oil from 0.58 to 0.33 mm.

As it is well-known that α-ZrP has the characteristic of ion exchange, the interlaminar hydrogen ion can be exchanged with various metal ions.[12−16] Some reports also implied that metal ion exchanged α-ZrP maintains its layer structure while the distance between layers expands.[13,17] Therefore, the cation exchange would be effective in changing the layer force and bond type, which may modify the lubricating ability. In this work, we tried to synthesize fully Cu^{2+}-exchanged α-ZrP [copper zirconium phosphate hydrate ($Cu(OH)_2Zr(HPO_4)_2·2H_2O$, hereafter referred to as Cu-α-ZrP)]. Until now, Cu-α-ZrP was synthesized only through the ion-exchange process in the literature. The reports regarding Cu^{2+} exchange of α-ZrP included: (1) α-ZrP that was low crystalline and semi-crystalline was conducive to the exchange of bivalent metal ions;[18−21] (2) At first, α-ZrP was exchanged by Na^+ to produce the $ZrNaH(PO_4)_2·5H_2O$, then it was exchanged by the bivalent metal salt;[22] (3) α-ZrP with high crystalline was fully exchanged by Cu^{2+} through the process of reflux.[14] Because the passage between the α-ZrP layers is narrow, whereas the radius of hydrated copper ion is large,[23] it is not easy to obtain Cu-α-ZrP from the ion exchange process. Meanwhile, for a two or more step reaction, the efficiency of the ion exchange process is quite low.

In this paper, it is reported that Cu-α-ZrP can be directly synthesized hydrothermally in the NaF-CuO-ZrO-P_2O_5-H_2O system. The crystal structure of Cu-α-ZrP was determined by X-ray powder diffraction. A point contact test was employed to measure its solid lubrication properties as a lubricant additive in grease. The data showed that Cu-α-ZrP as grease additive may increase the P_B value and decrease the WSD value greatly.

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EXPERIMENTAL SECTION

Materials and Instrumentation. *Materials.* Orthophosphoric acid (85% in water, Sinopharm), zirconium(IV) oxychloride octahydrate (AR, Sinopharm), zirconium(IV) nitrate pentahydrate (AR, Sinopharm), sodium fluoride (AR, Sinopharm), copper(II) acetate monohydrate (AR, Sinopharm), sodium acetate anhydrous (AR, Sinopharm), sodium hydroxide (AR, Aladdin), hydrogen chloride (AR, Aladdin), and molybdenum disulfide (SCM Industrial Chemical Co., Ltd.). All raw chemicals were used without further purification. Distilled water (H_2O) was prepared in our laboratory.

Instrumentation. XRD patterns were recorded with a X-ray diffractometer (Rigaku, MiniFlex II) using CuKα 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 worn surface (Hitachi, TM-3000). For the determination of the structure by powder XRD, the data were collected on an X'Pert MPD Philips diffractometer (CuKα X-radiation) with a curved graphite monochromator and a flat plate sample holder, in a Bragg–Brentano para-focusing optics configuration. Intensity data were collected by the step counting method (step 0.01°) in the 2θ range 7–115°. The lubrication properties of 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).

Experimental Details. *Synthesis of Cu-α-ZrP.* A typical hydrothermal process for the preparation of Cu-α-ZrP was as follows: $Zr(NO_3)_4 \cdot 5H_2O$ (3.0 g, 6.98 mmol), H_3PO_4 (2.017 g, 17.45 mmol), NaF (29.9 mg, 0.70 mmol) and H_2O (14.59 mL, 810.56 mmol) were mixed together with vigorous stirring until homogeneous. Then the mixture was transferred into a Teflon-lined stainless steel autoclave (30 mL total volume). The crystallization was then carried out at 180 °C for 72 h. After cooling the autoclave to room temperature, the solid products were separated by filtration and washed with distilled water.

Synthesis of Na-α-ZrP. On the basis of the method reported in the literature,[24] Na-α-ZrP was prepared by an ion-exchange method in the sealed Teflon-lined stainless steel autoclave (150 mL). Typical reaction conditions are as follows: α-ZrP (0.5 g, 1.66 mmol), CH_3COONa (2.05 g, 24.99 mmol), NaOH (0.1 g, 2.5 mmol), H_2O (100 mL, 5555.56 mmol); 100 °C; 24 h.

Synthesis of α-ZrP. On the basis of three typical methods, refluxing method,[12] precipitation method,[25] and sol–gel method,[26] we also prepared α-ZrP by hydrothermal process in the sealed Teflon-lined stainless steel autoclave (30 mL) in this paper. Typical reaction conditions are as follows: $ZrOCl_2 \cdot 8H_2O$ (4.5 g, 13.68 mmol), H_3PO_4 (3.2 g, 27.69 mmol), NaF (58.8 mg, 1.37 mmol), and H_2O (5 mL, 277.78 mmol); 180 °C; 36 h.

Ab Initio Structure Determination. An ab initio structure determination from laboratory powder diffraction data was carried out using FullProf,[27] EXPO2009.[28] and TOPAS[29] software packages. The details are in the Supporting Information. CSD 426001 contains the supplementary crystallographic data for this paper.

Simulation Calculation and Details. The bond energies (E, eV) in Cu-α-ZrP, Na-α-ZrP, and α-ZrP were calculated by the density-functional theory (DFT). All the DFT calculations were performed with the program Dmol^3 package in Materials Studio.[30,31] DFT was employed to perform all calculations using the general gradient approximation (GGA)[32] with the Perdew–Wang (PW91) exchange-correlation functional. The electronic structures were obtained by solving the Kohn–Sham (KS)[33] equation self-consistently in the condition of spin unrestricted. Double-numeric quality basis set with polarization functions (DNP) was used.[34]

Lubrication Test and Analytical Procedures. The lubrication properties of grease were determined by a point contact test (four-ball method). The balls (diameter 12.7 mm) used in the test were made of GCr15 bearing steel (SAE52100 steel) with an HRc of 59–61. Load carrying capacity (P_B values) were measured according to the China Petrochemical Standard SH/T 0202-92 (similar to ASTM D2596-97). The four-ball tester was also used to evaluate the anti-wear properties of GCr15 bearing steel self-mated frictional pairs under the lubrication of grease. Lubricating greases were brought to 75° ± 1.7 °C, the rotating speed was 1450 rpm and loads were set to 98, 196, 294, 392, 490, 588, 686, 784, and 882 N for test durations of 60, 300, 600, and 1800 s. After each test completion, the WSD values on the stationary balls were measured on an optical microscope with an accuracy of 0.01 mm in the directions parallel and perpendicular to the sliding motion. Three identical tests were performed for an average so as to minimize data scattering. SEM and EDS were employed to analyze the worn surface.

RESULTS AND DISCUSSION

Preparation and Characterization of Cu-α-ZrP. In experiments, the synthesis conditions of Cu-α-ZrP were investigated by changing the ratio of raw materials, reaction temperature and reaction time. Figure 1 shows the effect of copper (Cu) content on the synthesis of Cu-α-ZrP. When the molar ratio of Cu/Zr in the starting mixture was 1.5, Cu-α-ZrP was obtained after 72 h at 180 °C. If the molar ratio of Cu/Zr was 1.25, a mixture of Cu-α-ZrP and α-ZrP was obtained while the product was a mixture of Cu-α-ZrP and an unknown phase if the molar ratio of Cu/Zr was 1.75. Through changing the synthesis conditions, Cu-α-ZrP can be prepared in the range of feed ratio Cu/Zr = 1.5, P/Zr = 2.5-2.75, F/Zr = 0.1, H_2O/Zr = 125-150 and the time range 24-72 h under the temperature of 180 °C (see Figure S1 in the Supporting Information). The scanning electron microscope (SEM) image (see Figure S2 in the Supporting Information) shows that the typical Cu-α-ZrP samples consist of regular hexagon particles and exhibit a uniform size of about 600 nm, which is similar to that of the α-ZrP.

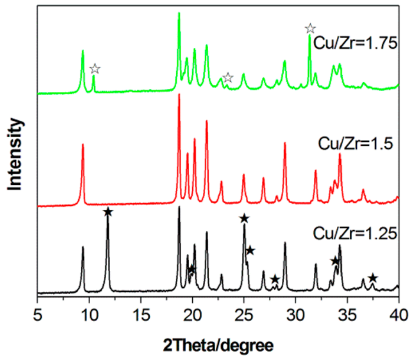

Figure 1. Effect of the Cu content on the synthesis of Cu-α-ZrP at 180 °C for 72 h (★, α-ZrP; ☆, unknown phase (2θ = 10.4, 23.4, and 31.4°)).

The elemental analysis and the proton ion exchange proved that the copper is exchangeable in the synthesized samples. According to the element analysis, the copper content of typical samples is about 14.97%, which is in good accordance with theoretical value, 15.35%, suggested by formula $Cu(OH)_2Zr(HPO_4)_2 \cdot 2H_2O$. In the proton ion exchange experiments, 0.5 g of Cu-α-ZrP samples were added into 25 mL of HCl solution with a typical molar ratio of Cu-α-ZrP to H^+ of 1:6 and the solution was stirred for 12 h at room temperature. After the ion exchange experiment, the material changed to α-ZrP (Figure 2). Clearly, the Cu^{2+} in the synthesized samples was exchangeable.

Structure of Cu-α-ZrP. To the best of our knowledge, the structural solution of Cu-α-ZrP has not been reported. Figure 3 shows the final Rietveld plot of the structure derived by ab

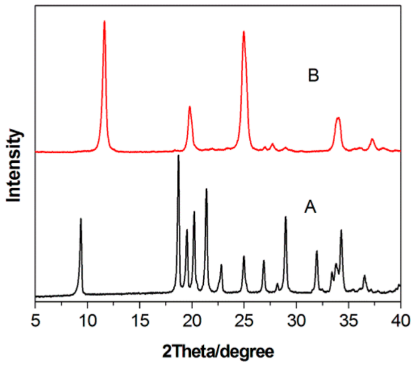

Figure 2. Proton ion exchange process of Cu-*α*-ZrP: (A) Cu-*α*-ZrP; (B) the proton ion exchanged sample (*α*-ZrP).

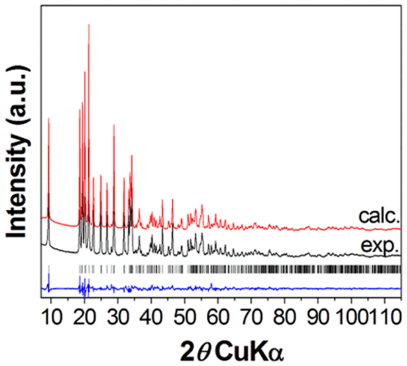

Figure 3. PXRD of typical Cu-*α*-ZrP.

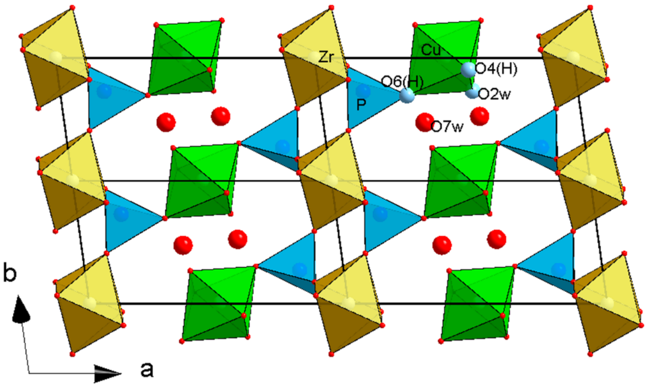

Figure 4. Crystal structure of typical Cu-*α*-ZrP.

initio methods. The obtained structural model is presented in Figure 4. Cu-*α*-ZrP has microporous, mixed-metal framework structure composed of S-shaped 8-ring channels running along the *b*- and *c*-axes (Figure 9). The rings are composed of four isolated PO4 tetrahedra alternating with two ZrO6 and two CuO6 octahedra. The asymmetric unit consists of one P, one Zr, one Cu and seven O sites. The isolated PO4 tetrahedron share three of its corners with regular ZrO6 octahedron and the fourth one is connected with distorted CuO6 octahedron. Within the PO4 tetrahedron the bond lengths pointing to the ZrO6 octhedron are shorter than the one linked to the CuO6 which suggests a possible protonation of O6(H) (see Table S3 in the Supporting Information). The Cu octahedron has four unshared oxygen with two disordered apexes (see Table S3 and Figure S4 in the Supporting Information). Considering the obtained bond distances (see Figure S5 in the Supporting Information) and required positive charge these terminal oxygen atoms are assigned to hydroxyl group and/or water molecule (O2w and O4(H)). The site of the second water molecule (O7w) was found within the space of the 8-ring channel (Figure 9).

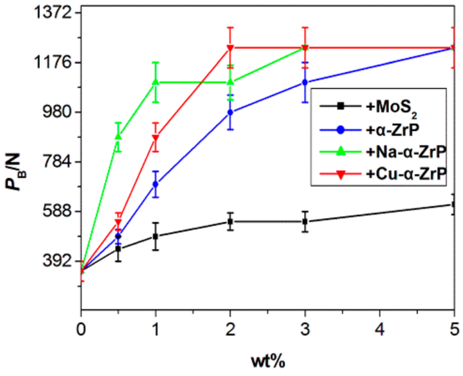

Figure 5. Load carrying capacity (P_B values) of grease with various additives.

Lubrication Properties of Cu-*α*-ZrP. According to the China petrochemical standard SH/T 0202-92, similar to ASTM D2596-97, the load-carrying capacity of Cu-*α*-ZrP as the grease additive was investigated by a point contact test (four-ball method). The P_B values of grease increased with the Cu-*α*-ZrP content (Figure 5) from 549 N (0.5%) to 1235 N (2.0%), and then was stable (2.0-5.0% of Cu-*α*-ZrP); the values are higher than the P_B value of the base lithium grease (353 N). So Cu-*α*-ZrP as an additive may increase the load-carrying capacity of base grease. As a comparison, the data of the Na$^+$-exchanged *α*-ZrP ($Zr(NaPO_4)_2 \cdot (H_2O)_3$, hereafter referred to as Na-*α*-ZrP[24]), *α*-ZrP, and MoS$_2$ are also given in Figure 5. The P_B values of the grease with 0.5−2.0% MoS$_2$ and *α*-ZrP are lower than those of Cu-*α*-ZrP, whereas Na-*α*-ZrP has a better load-carrying capacity than Cu-*α*-ZrP in the low content range. Adding 5.0% of the Cu-*α*-ZrP, Na-*α*-ZrP, *α*-ZrP, or MoS$_2$ to the grease resulted in the P_B values of 1235, 1235, 1235, and 617 N, respectively. So the three layered zirconium phosphates perform better in improving the load-carrying capacity of lithium grease than MoS$_2$.

Because the P_B test, according to the China petrochemical standard SH/T 0202-92, is a process with a short run time (10 s) and is intensive, a wear test under different loads for a long run time (1800 s) was used to evaluate the load-carrying capacity and anti-wear property of grease with Cu-*α*-ZrP as the additive. In the experiments, the load was increased from 98 to 882 N. Under this working conditions, the load-carrying capacity can reach up to 882 N using the lithium grease with 5.0% Cu-*α*-ZrP while the lithium grease with 5.0% Na-*α*-ZrP or *α*-ZrP may only work under loads below 686 N (Figure 6). Obviously, the load-carrying capacity under this working condition is less than its P_B value. On the other hand, the load-carrying capacity of the base lithium grease and the grease with 5.0% MoS$_2$ under this working condition only reach up to 294 N, otherwise, severe friction (friction coefficient exceeding 0.2) occurs. Figure 6 also shows that lithium grease with 5.0% Cu-*α*-ZrP had a better anti-wear property than lithium grease with 5.0% Na-*α*-ZrP and *α*-ZrP. When testing the lithium grease with 5.0% Cu-*α*-ZrP, the WSD was continuously, steadily, and slowly increasing from 0.29 mm (98 N) to 0.47

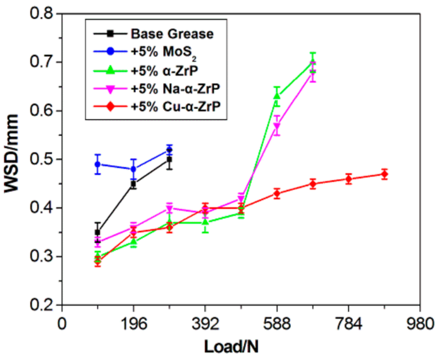

Figure 6. WSDs of lithium grease with 5.0% contents of different additives under various loads.

mm (882 N). For the test of the lithium grease with 5.0% Na-α-ZrP, the WSD was increased from 0.33 mm (98 N) to 0.37 mm (490 N) which was almost the same as the lithium grease with 5.0% Cu-α-ZrP. However, under the test loads greater than 490 N, the WSD increased sharply to 0.57 mm under 588 N and 0.68 mm under 686 N. Meanwhile the lithium grease with 5.0% α-ZrP performed almost the same as the lithium grease with 5.0% Na-α-ZrP with test loads in the range of 98-490 N; the WSD increased from 0.3 mm to 0.39 mm when the test load exceeded 490 N,and the WSD increased sharply to 0.63 mm under 588 N and 0.70 mm under 686 N. On the basis of the information above, Cu-α-ZrP has the best lubricating capacity for long running times.

To understand why there is higher load-carrying capacity of grease with the layered zirconium phosphates as an additive versus grease with MoS_2 as the additive, SEM and EDS were employed to characterize the worn surfaces of the friction pair (friction pair, as the term is understood in mechanics, is the contact objects in a frictional system, here it is the steel balls). Figure 7 shows the morphology and element composition of the worn surface of the friction pairs, which are the samples after a long duration wear test at the maximum load-carrying capacity of every grease (Cu-α-ZrP 882 N, Na-α-ZrP 490 N, α-ZrP 490 N, MoS_2 294 N, Base Grease 294 N).

Under a load of 294 N, the worn surface using the base grease was seriously damaged and a larger number of deep furrows were observed. Using the lithium grease with MoS_2 does not significantly improve the load-carrying capacity property. The EDS results show that there is no other element except those of the friction pair itself (C, Fe, Cr) on the worn surface of the friction pair lubricated by both the base grease and lithium grease with MoS_2. When using the grease with Cu-α-ZrP under the load of 882 N, smoother and shallower furrows exist on the worn surface of the friction pair. There are Cu, P, Zr, O on the worn surface besides Fe, Cr, C. When using Na-α-ZrP and α-ZrP as the additives, the morphology of the friction pairs is similar to that using Cu-α-ZrP; Na, P, Zr, O and P, Zr, O were found on the worn surfaces, respectively. So, the layered zirconium phosphates as the lubrication additives may form the protective films on the friction pairs, which increases the load-carrying capacity.

Also, the worn surfaces under different load and different test times were observed by SEM and analyzed by EDS (see Figures S6 and S7 in the Supporting Information). The protective films formed when using grease with Cu-α-ZrP, Na-α-ZrP, and α-ZrP, whereas no such layer was formed when using the base grease and the grease with MoS_2 (see Figure S6 in the Supporting Information). Under limited loads, Cu-α-ZrP, Na-α-ZrP and α-ZrP could form the protective film in a short time (less than 60 s) and the films may exist from 60 to 1800 s, whereas the base grease and the grease with MoS_2 could not form such layers (see Figure S7 in the Supporting Information). It is well-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 rate of friction pairs.[35] So these results indicate that Cu-α-ZrP, Na-α-ZrP, and α-ZrP have better lubricating properties than MoS_2 and they can more easily form protective films on the worn surface.

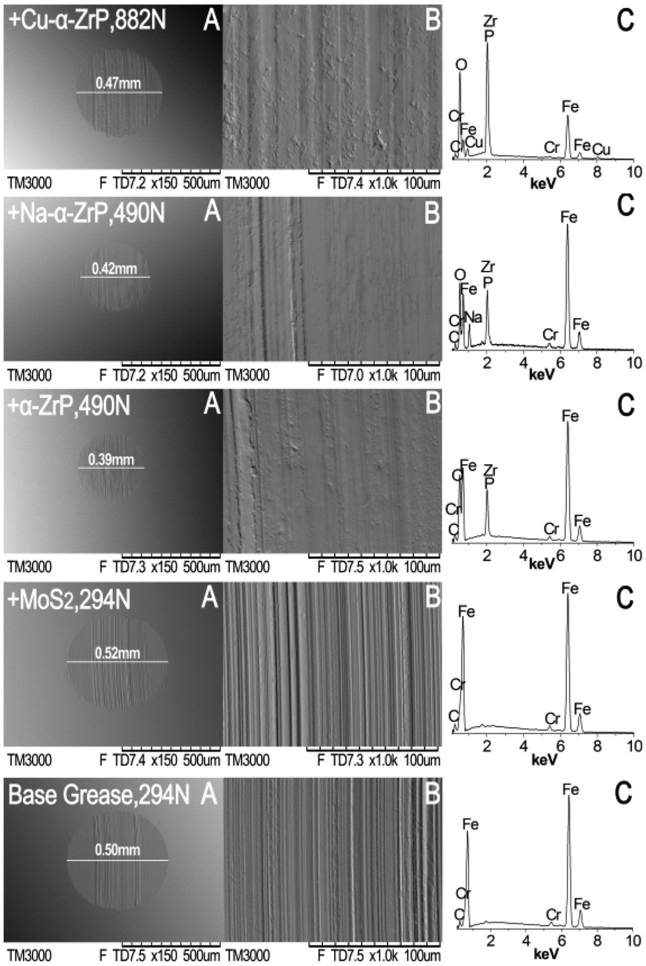

Figure 7. Surface morphologies and EDS of the worn surfaces under the maximum load-carrying capacity of each grease (Cu-α-ZrP 882 N, Na-α-ZrP 490 N, α-ZrP 490 N, MoS_2 294 N, Base Grease 294 N): (A) ×150; (B) ×1000; (C) the EDS results of the worn surfaces.

From the above, all the three kinds of layered zirconium phosphate materials have good lubricating properties, among which Cu-α-ZrP is the best. To explore the mechanism, the bond energies of PO-Zr, P-OZr, Cu(Na, H)O-P, and Cu(Na, H)-OP have been calculated (Table 1). After H is replaced by Cu, the bond energy of P-OZr significantly decreases (ΔE = −9.503 eV), whereas the same influence is found for the bond energy of PO-Zr (ΔE = −4.265 eV). This result indicates that the interaction between the ZrO and PO layer decreases, which will let the layers more easily slip in the horizontal direction. The bond energy of Cu-OP increases to about 3.585 eV for H-OP while little effect is also found for the bond energy of Cu(H)O-P (ΔE = 1.322 eV) after H is replaced by Cu. In

Table 1. Simulation Calculation Results of Bond Energy (*E*, eV) in Cu-*α*-ZrP, Na-*α*-ZrP, and *α*-ZrP

	$E_{PO\text{-}Zr}$	$E_{P\text{-}OZr}$	$E_{XO\text{-}P}$[a]	$E_{X\text{-}OP}$[a]
Cu-*α*-ZrP	16.147	5.515	5.144	8.628
Na-*α*-ZrP	21.706	18.417	13.762	6.556
α-ZrP	20.412	15.018	3.822	5.043

[a] X stands for Cu, Na, or H.

general, the binding force between layers of Cu-*α*-ZrP is weak, so this may indicate why Cu-*α*-ZrP is more flexible as it more easily forms the protective film on the surface of friction pair. On the other hand, when H is replaced by Na, the bond energy of P-OZr increases slightly ($\Delta E = 3.399$ eV) while little effect is found for the bond energy of PO-Zr ($\Delta E = 1.294$ eV). This result indicates that the interaction between the ZrO and PO layers increases slightly or is almost the same, so the shear force in the horizontal direction is almost the same. This may explain the similar results for Na-*α*-ZrP and *α*-ZrP in the long duration wear test. The bond energy of NaO-P significantly increases in HO-P ($\Delta E = 9.940$ eV), so the binding force in the vertical direction is stronger after H is replaced by Na. This may indicate a better resistance ability to high impact strength, which corresponds to the results of the P_B test.

From the structure point of view, all the three materials have similar zirconium phosphate layers but different cations exist between their layers (Figure 8), among which, the layers of *α*-ZrP are linked by various hydrogen bonding.[1,2] The short distance between the surface O(H) of adjacent sheets is 3.063 Å while the distance between surface O(H) of sheets and O of water is 2.770 and 3.137 Å, respectively. The distance between sheets is ca. 7.55 Å. On the other hand, the distances between sheets of Na-*α*-ZrP and Cu-*α*-ZrP are much longer, at ca. 9.88 and 9.52 Å, respectively.[24] It seems that the interaction between sheets of Na-*α*-ZrP should be similar to or weaker than that of Cu-*α*-ZrP, and they should have similar lubricating properties. However, their experimental results are quite different. Close inspection of both structures indicates the difference. The cation number between layers of Cu-*α*-ZrP is only half of that of Na-*α*-ZrP, and the Cu^{2+} ion in six-coordination (0.73 Å) is much smaller than the Na^+ ion (≥0.99 Å), which suggests that Cu-*α*-ZrP is more flexible. Furthermore, only two corners of the CuO_6 octahedron are connected to PO_4 tetrahedra, and CuO_6 may rotate when pressed against the zirconium phosphate layers (Figure 9). The proton ion exchange also suggests that the Cu^{2+} is only weakly bonded to the zirconium phosphate layers. On the whole, both the DFT calculation and structural characteristics indicate that Cu-*α*-ZrP is more flexible. Therefore, the friction experimental results may also be explained by the intrinsic cleavage mechanism.[11]

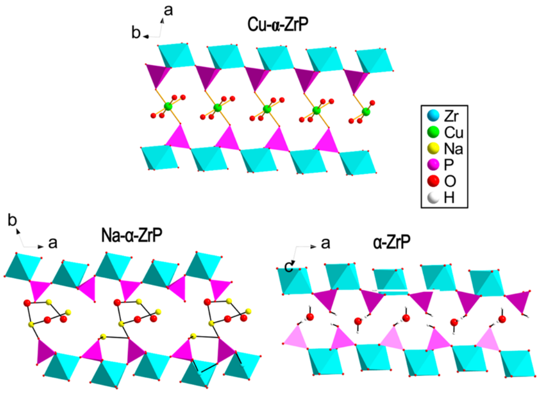

Figure 8. Layered structure of Cu-*α*-ZrP, Na-*α*-ZrP, and *α*-ZrP.

When comparing the strengths of protective films under different loads, the films with Cu-*α*-ZrP are stable from 490 to 882 N while the ones formed by grease with Na-*α*-ZrP and *α*-ZrP are almost completely damaged as the surfaces of the friction pairs were worn seriously at loads of 588 and 686 N, respectively (Figure 10 and Figure S6 in the Supporting Inforamtion). This implies that the films formed by Cu-*α*-ZrP are tighter than the ones formed by Na-*α*-ZrP and *α*-ZrP with respect to resistance to wear under heavy loads. This would explain the excellent lubricating property of Cu-*α*-ZrP compared to Na-*α*-ZrP and *α*-ZrP.

CONCLUSIONS

In summary, high-crystalline Cu-*α*-ZrP has been directly synthesized in the NaF-CuO-ZrO-P_2O_5-H_2O system under hydrothermal conditions. The copper ion was confirmed to be an exchangeable cation in the Cu-*α*-ZrP through elemental analysis and the proton ion exchange process. The crystal structure of the Cu-*α*-ZrP has been determined ab initio by using X-ray powder diffraction data. Moreover, as an additive in

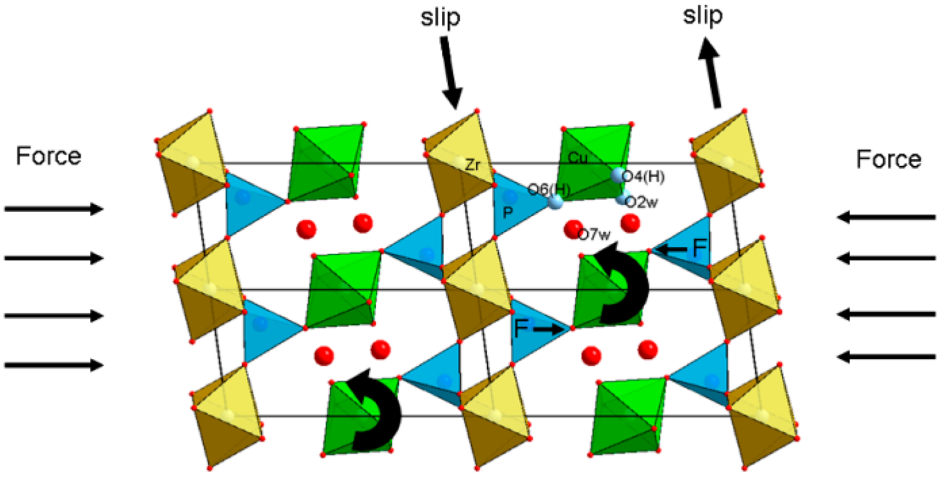

Figure 9. The scheme of the suggested mechanism for Cu-*α*-ZrP.

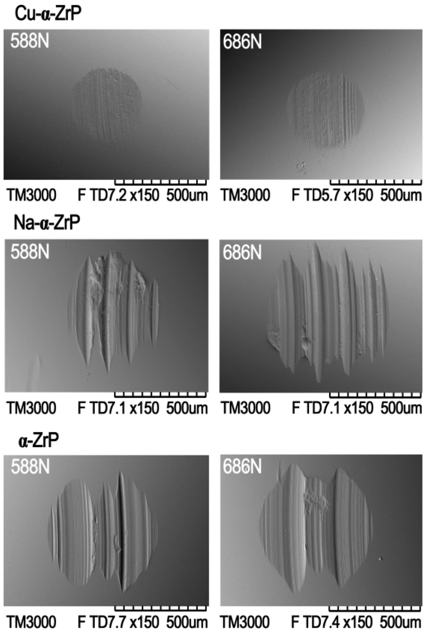

Figure 10. Comparison of the films on the worn surface of grease with different zirconium phosphates under heavy loads (588N, 686N).

grease, Cu-α-ZrP has excellent lubricating ability, and it easily adhered to the worn surface to form a tight protective film. We expect that such materials have potential industrial application as lubricant additives for wear resistance under the heavy loads.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

PXRD and SEM patterns of samples synthesized were provided as images. Crystallographic details from the Rietveld refinement, refined atomic coordinates and isotropic and displacement parameters and selected bond distances of the refinement were tabulated. A CIF file was obtained. The detailed results of antiwear properties of GCr15 bearing steel self-mated frictional pairs under the lubrication of grease are also shown in the figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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