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Abstract

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Article: Effect of Loading on the Friction and Interface Microstructure of Lubricated Steel Tribopairs

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Abstract

In this study, the tribological behavior and interfacial evolution of GCr15/Mild steel tribopairs lubricated by inorganic sodium metaphosphate was investigated under different applied loads at 800°C. The results show that sodium metaphosphate lubricates the contact effectively at the load ranging from 5 to 30 N, with higher loads causing increased friction and wear. A layer of glassy phosphate film formed between the contacts is responsible for the improved tribological

performance. FIB/TEM and XRD analysis reveals that the phosphate film was mainly composed of amorphous Na-Fe orthophosphate matrix filled up with fine oxide wear debris.

Keywords: Sodium metaphosphate; Phosphate tribofilm; Ball-on-disc; Na-Fe orthophosphate.

1 Introduction

Inorganic glass as hot metal working lubricant has attracted much attention because it can soften, spread and separate the sliding metallic surfaces by forming a thin film under highly stressed shearing and temperature conditions [1, 2]. Inorganic alkali glass lubricant also can prevent surface cracks from forming by reducing the deformation resistance, and reduce the oxidation of workpieces by providing a barrier which retards the oxygen atoms from infiltrating into the workpiece material [3]. It also provides an insulation to reduce the temperature drop of the workpiece when in direct contact with the tools [3-5]. Tribological investigations indicate that a low coefficient of friction between 0.03~0.25 can be obtained dependent on the applied load and method of lubrication [6-9]. Although the use of glass lubricant brings about so many benefits, their working mechanism was still continuously explored and not fully understood.

Laboratory-scale investigations of the tribological behavior of inorganic polymer glass as a lubricant at elevated temperature were widely performed. The tribological behavior of inorganic polymer glass is temperature-dependent during hot forming operations. A pronounced peak friction coefficient can be found at the temperature close to the softening point of phosphate, whereas friction decreases sharply if the temperature is above the softening point, due to the fluid film lubrication [10]. In reference [6], the coefficient of friction lubricated by alkali polyphosphate was found to decrease, whereas the wear rate increases with the rise of temperature. However, the rise of wear rate with temperature was severely restrained compared with an unlubricated tribopair. The chemical affinity between the solid surface and molten glass lubricant also affects the resultant friction and wear behaviour of the hot rubbing contacts. For example, glass lubricant can easily wet the solid surface sufficiently and thereby reduce the friction significantly [10]. In addition, the mode of lubricant supply substantially produces much

difference in the tribological performance. If aqueous alkali phosphate solution is continuously fed during operation, a multi-layered phosphate tribofilm with a thickness of around 100 nm accounts for a significant friction and wear reduction by 60% [6]. If the steel disc was pre-coated by alkali inorganic glass solution before sliding, after high temperature friction testing a thicker layer of glass lubricant (4.5~30 μm) was observed on the tribosurface [1]. Furugen *et al* [11] conducted hot tube extrusion tests, where a 40 μm thick silicate and borate glass lubricant was pre-coated on the workpieces before heating. Hot tube extrusion was found to operate in a hydrodynamic condition, with the coefficient of friction 0.02-0.14 being proportional to the logarithmic viscosity of glass lubricant; A residual 20~30 μm thick glass film was left on the workpiece after test.

The tribochemical interaction between inorganic alkali polymers and oxide scale has been investigated, but it remains controversial. Grunze [12] and Danchenko [13] proposed that the initial alkali polyphosphate lubricant will interact with oxide scale at elevated temperatures to transform into a substance with similar structures as the initial polymers and performs as well as the original lubricant. Sterry *et al* [14, 15] disputed that the oxides produced during metal forming dissolve into the polyphosphate glass and destroy its polymer structure and lubricity properties. In a previous publication [4], alkali polyphosphates with different chain-length, i.e. metaphosphate, pyrophosphate and orthophosphate, were studied as a lubricant at an elevated temperature. Metaphosphate obtains desirable performance in terms of friction reduction, wear inhibition and oxidation prevention, while short-chain orthophosphate displays a poor anti-oxidation property. Furthermore, XANES analysis of the worn surface shows metaphosphate has severely depolymerized into short-chain Na-Fe orthophosphates at high temperature [4]. This greatly differs from the structure of polyphosphate tribofilm derived from ZDDP at room and ambient temperatures, in which long-chain polyphosphate locates at the top surface [16]. Though inorganic phosphate glass serving as a hot forming lubricant attracted much attention, the effects of applied load on the tribological behaviour and interface evolution were still poorly understood.

This paper uses a ball-on-disc high temperature tribometer in which the disc surface is pre-coated with sodium metaphosphate before heating, this lubricant was found to have an excellent wettability with a steel surface at high temperature [6]. This layer of phosphate film can form a viscous tribofilm in the contacting zone and help to reduce the friction and wear [17, 18]. This paper comprehensively considers the effect of applied load on the tribological behaviour of sodium metaphosphate. Especially, the evolution of the microstructure and the mechanical properties of phosphate film on the ball are investigated due to loading effects, supported by SEM, FIB/TEM and nanoindentation.

2 Materials and experimental procedure

The preparation details of 20w.t% sodium metaphosphate lubricant, and the pre-coating procedures with a thickness of around 50 μm on the mild steel disc were introduced in ref [4]. The tribological behavior of GCr15 steel/ mild carbon steel tribopair lubricated by sodium metaphosphate was evaluated by a ball-on-disc high temperature tribometer. Test conditions were shown in Table 1. The frictional sliding test started when the temperature of the furnace was in a steady state at 800°C for 5 min. The applied load on the ball was changed with every test being performed at a constant load (5, 10, 20 and 30 N) for 900 s to test the effect of long term exposure of the lubricant under load. After tribological test, the GCr15 ball was lifted out of furnace to avoid the crystallization of phosphate, and the disc was cooled with the furnace.

Table 1 ball-on-disc test conditions

Ball	
Material	GCr15 steel: 0.98%C-1.48%Cr-0.27% Mn-0.35%Si
Diameter	6.35 mm
Disc	
Material	Mild steel: 0.20%C-0.40%Mn-0.50%Si
Size	$\Phi 50\text{ mm} \times 5\text{ mm}$
Sliding speed	0.094 m/s
Temperature	800°C

Load	5, 10, 20 and 30 N
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3 Characterization methods

3.1 Differential scanning calorimetry (DSC) and thermogravimetry (TG)

The thermal behavior of sodium metaphosphate lubricant was investigated using a NETZSCH STA 449C DSC equipment (Germany). The test was conducted in an alumina crucible under the following conditions: The tested temperature range is from 25~800°C with the protection of N₂, the increasing speed of temperature was 10°C /min.

3.2 Microscopy

The morphology and chemical composition of wear surfaces and cross sections are characterized with a JSM-6490LA Scanning Electron Microscope (SEM) (JEOL, Japan) at 15 kV and an integrated AZtechSynergy Software Suit.

3.3 Nanoindentation

The mechanical properties of the phosphate film on the ball and disc are measured with the ultra-micro-indentation system (UMIS) which is equipped with a Berkovich diamond indenter having a tip radius of 200 nm. A load of 10 mN was applied. For each sample, a matrix of indents was obtained with the distance between indents of 10 µm. The mechanical properties are acquired via the load-displacement curves using the initial slope of the unloading curves as proposed by ref [19]. After the nanoindentation tests, the indentations were observed by a JSM-6490LA SEM, which enabled all the interesting features to be captured.

3.4 Focused ion beam (FIB) and Transmission electron microscope (TEM)

The thin TEM specimens of phosphate film on the ball are prepared by FEI NovaNano lab 200 focused ion beam (FIB) miller. A JEOL JEM-ARM200F aberration-corrected scanning transmission electron microscope (STEM) working at a voltage of 200 kV, and which features a resolution of 0.08 nm, is used to analyze the FIB sample in a bright field (BF) and high-angle annular dark-field imaging (HADDF) mode. EDX-analysis is performed using a JEOL 100 mm² X-ray detector coupled to a Noran System Seven (NSS) analysis system.

4 Results

4.1 DSC&TG analysis

Figure 1 DSC&TG curves of sodium metaphosphate from 25-800°C

Figure 1 shows the DSC&TG curves of the commercial sodium metaphosphate glass. An endothermic peak was identified at 270°C. This was attributed to the glass transition temperature

(T_g) where the substance begins to behave as a viscous fluid. The exothermic peak at 364°C in the DSC curve was due to the crystallization of viscous sodium metaphosphate liquid glass, and the small endothermic peak at 412°C accompanied by small mass loss in the TGA curve was attributed to the condensed dehydration of –OH bond [20]. The large DSC endothermic peak at 623°C represented the transition of glass to the melt state with no accompanying mass loss.

4.2 Effect of phosphate coating on oxidation of steel

Figure 2 Geometric positions of sodium metaphosphate, Au and substrate layers (a) before and (b) after heating oxidation, (c) the EDX spectra of the circle position in (b).

For the purpose of investigating the effect of metaphosphate lubricant on the growth of oxide scale at elevated temperature, an experiment was designed with the polished steel surface coated by a 70 nm gold layer. After coating, the surface roughness (Ra) was measured to be 87 nm. The sample was sprayed by lubricant to form a layer of phosphate on top, as shown in Figure 2a. Then, the sample was put into the furnace heating up to 800°C for 900 s. After oxidation, the sample was taken out and quenched in air. Then the cross sections of samples were analyzed by SEM&EDX, shown in Figure 2b. The result shows oxide scale grows above the Au layer, while the metaphosphate locates below the Au layer. A layer of iron oxide forms above the phosphate

lubricant. This phenomenon indicates that the metaphosphate will firstly become soft and fluidic, when the temperature rose above 270°C as suggested by DSC curve in Figure 1. Then it penetrated below the gold layer to interact with the steel substrate. As a result, a large number of iron atoms were dissolved in the phosphate melt. When the iron-rich melt phosphate was placed in air at high temperature, an oxygen chemical potential gradient will exist in the melt [21]. The viscous melt containing Fe cations will experience chemical reactions and diffusive transport to the top surface in an attempt to come into equilibrium with the environment. This is consistent with a proposed model in which oxidation of mixed alkali-iron phosphate occurs by the outward diffusion of iron atoms to the top surface due to the thermodynamic and physicochemical driving force [21]. With the continuous dissolve of Fe atom from the steel substrate and transport of iron towards the surface, a thick layer of iron oxide will eventually form at the top surface, as shown in Figure 2b.

4.3 High temperature tribological tests

Figure 3 (a) Curves of friction coefficient as a function of sliding time for tribotests at different loads, in which the friction coefficient curves at 30 N is inserted. (b) Average friction coefficients as a function of load at both unlubricated and lubricated conditions.

Figure 3 shows the coefficients of friction at different applied loads with and without lubrication at 800°C, in which the D-10 and L-10 represent the unlubricated and lubricated conditions at 10 N, respectively. Clearly, the presence of polyphosphate significantly reduces friction and improves the rubbing stability compared to the same contacts in unlubricated sliding. With unlubricated sliding, the steel/steel contacts lead to higher coefficients of friction ranging from 0.17 to 0.44. Furthermore, the friction coefficient shows more fluctuation with the increase of load, whereas, the use of alkali polyphosphate lubricant can reduce the friction coefficient from 0.17 to 0.13 by 24% at 5 N and from 0.23 to 0.14 by 39% at 10 N. The friction curves at 5 N were shown as Figure S1 in the Supplementary Material. At 20 N, the friction is reduced from 0.41 to 0.21 by 49% shown in Figure 3b. Furthermore, the friction coefficient shows a more

stable value in the steady-state period. When the load increases to 30 N, the unlubricated GCr15/Mild steel pairs show the highest average friction coefficient of around 0.44. Furthermore, the curve of friction coefficient showed in Figure 3a exhibits an substantially unsteady and fluctuating trend. But after NaPO_3 lubricant was applied at 30 N, the friction coefficient curve becomes smoother, which gradually increases, and then stabilizes at 0.3. As the load increases, the average coefficient of friction increases regardless of the lubricated conditions, shown in Figure 3b.

Figure 4 Specific wear rates of (a) GCr15 ball and (b) mild steel disc at different loads at 800°C with a linear sliding speed of 0.094 m/s.

The specific wear rates of ball and disc sliding at different loads at 800°C have been measured and calculated shown in Figure 4, in which the disc always shows a higher wear rate than the ball under both cases with and without lubrication. Indeed for unlubricated tribopairs, the wear rate shows an increasing trend with the increase of applied load except at the load of 20 N, which presents a slightly lower wear rate than that at 10 N. This phenomenon has also been reported by

ref. [22]. The wear rate under lubricated condition is proportional to the applied load, which monotonously increases with load. A comparison of the wear rate between lubricated and unlubricated tribopairs shows that the polyphosphate lubricant can reduce ball and disc wear by approximately 65%~86% and 64%~90%, respectively.

4.4 SEM analysis

Figure 5 SEM micrographs of the worn surface of unlubricated ball and corresponding cross section at the constant load: (a) and (b) for D-10 N, (c) and (d) for D-20 N, (e) and (f) for D-30 N.

Figure 5 shows the SEM micrographs of the wear surfaces and corresponding cross section of the unlubricated ball scars at different constant loads. Figure 5a shows that at 10 N the worn and unlubricated surfaces of the ball having a diameter of 2200 μm are characterized by surface ploughing and deep grooves parallel to the direction of sliding. The corresponding cross-sectional image of the contact area shows the ‘glaze’ layer free of porosity and cracks has a thickness of 5 μm , this is determined by averaging the thickness values at 5 random locations. When the load increased to 20 N, a smaller wear scar with smooth and compacted worn surface was observed. However, spalling of the oxide glaze layer was also observed at some spots shown in Figure 5c, which is a reason for the slight fluctuation of friction in Figure 3a. The corresponding cross-sectional micrograph in Figure 5d shows that the oxide layer has a thickness of around 10 μm . The significant metallic transfer from mild steel to GCr15 steel ball occurs at 30 N. A large number of oxide lumps transferred from the opposite disc accumulated on the ball scar unevenly. Furthermore, a large number of cracks and fractures were observed within these oxide lumps, which were confirmed by the highly magnified SEM images in Figure S3 in the Supplementary Material.

Figure 6 SEM micrographs of the worn surface of ball and corresponding cross section at the constant load: (a) and (b) for L-10 N, (c) and (d) for L-20 N, (e) and (f) for L-30 N.

Figure 7 SEM/EDX elemental mappings of cross-section of ball track lubricated by NaPO_3 glass at the load of (a) 10 N and (b) 30 N at 800°C . The EDX mapping of cross-section of ball scar at the 20 N was shown as Fig. S4 in the Supplementary Material.

Figure 6 shows the SEM micrographs of ball scars lubricated by sodium metaphosphate at different loads. When alkali polyphosphate lubricant is applied at 10 N, a layer of distinct film was observed to cover the wear scar on the ball with a diameter of $1080\ \mu\text{m}$, which is around half that of unlubricated one. The cross section of the ball scar in Figure 6b shows that a distinct

film was located above the oxide scale with a thickness of 5 and 20 μm , respectively. The wear scars on the balls at 5 (Figure S2 in the Supplementary Material), 20 and 30 N were also observed to be covered by such a distinct film. The cross sections of ball scar shows that the thickness of the phosphate film under 20 and 30 N were 4.5 and 4 μm , respectively. The EDX mappings in Figure 7a and b confirm that this layer of film consists of Na, P, O and a small amount of Fe elements, which locates above the oxide layer. At 30 N, the initial phosphate tribofilm ruptures in the centre of the wear surface on the ball, as shown in Figure 7b. This indicates the phosphate tribofilm cannot continuously support the 30 N load for 900 s at 800°C.

4.5 Nanohardness

Figure 8 (a) Thickness of the oxide ‘glaze’ layers and phosphate tribofilm and (b) nanohardness of the oxide ‘glaze’ layers and phosphate tribofilms formed at different loads.

Figure 8a shows the thickness comparison of tribofilm of these tests: under unlubricated condition, the thickness of oxide glaze layer increases with the load from 5 μm at 10 N to 10 μm at 20 N, then decreases to 6 μm at 30 N. However, when sodium metaphosphate is used as a

lubricant, the phosphate tribofilm became thinner monotonously with increase of load. The reason is that the high pressure will squeeze the soft viscous phosphate fluid out of the wear track.

Figure 8b shows the nanohardness of the oxide ‘glaze’ layer and phosphate tribofilm formed on the unlubricated and lubricated ball, respectively. The tested indentations are shown in Figure 5 and Figure 6. The penetration depth of the indenter on the phosphate tribofilm and oxide glaze layer is around 0.33 and 0.25 μm , respectively. At 10 N, the oxide ‘glaze’ layer had a nanohardness of 8.5 and 6.5 GPa on the ball and disc, respectively, and this increased to a respective 18.8 and 11.1 GPa at 20 N, and to 10.8 and 12.4 GPa at 30 N. The glaze layer of the ball shows a higher hardness than that of the disc. This is related to the cooling process difference. Since the ball was lifted out of the furnace immediately after the finish of the test, and quickly cooled in air, while the disc stays in the furnace cooling slowly with furnace. As a result, the increase in hardness of disc due to deformation and compaction in sliding was alleviated by annealing behavior because of slow cooling. In comparison, the hardness of phosphate tribofilm on both the ball and disc shows a much smaller variation with applied load ranging from 4–5 GPa.

4.6 XRD characterization

Figure 9 XRD characterization of tribofilm scale collected in the wear track of disc.

Figure 9 shows the XRD spectra of the tribofilm which was scraped and collected in the wear track of the disc after the sliding test. This material has been characterized by XRD at a step size of 0.02° and scan speed of $1^\circ/\text{min}$. The crystallized compounds at room temperature can provide clues about the parent glass at high temperature. The XRD results show that the peaks of NaFePO_4 , $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$, and Na_3PO_4 predominate the spectra, which suggests that the long-chained sodium metaphosphate interacts with the oxide scale to form short-chained Na-Fe orthophosphate. The characterization of phosphate tribofilm by XRD shows that the chemical compounds of the tribofilm experienced little change for the load ranging from 10 to 30 N. Furthermore, the types of chemical compound in the tribofilm are also very close to that in the static thermal film.

4.7 FIB and TEM

In order to gain insightful information of the microstructure of the phosphate tribofilm on the ball, FIB equipment is used to cut out the region marked with a red dashed rectangle in Figure 6. The corresponding STEM bright field micrograph, high-angle annular dark-field imaging (HADDF), EDX mappings and the selected area diffraction (SAD) patterns were obtained and shown in the following figures.

Figure 10 TEM HADDF micrograph and corresponding EDX elemental mappings of the phosphate tribofilm formed at 10 N at 800°C.

Figure 11 (a) TEM bright field micrograph and (b, c) the selected area diffraction patterns of the phosphate tribofilm formed at 10 N at 800°C, in which the SAD patterns b and c represent the spot 1 and 2 in (a), respectively.

Figure 10 shows the HADDF micrograph and corresponding EDX elemental mappings of the cross-section of lubricated contact surface at 10 N, where there are a large number of nanoparticles with an average diameter of 360 nm within the matrix. The EDX mappings reveal that the matrix consists mainly of Na, P, Fe, Mn and O elements, while the nanoparticles dissolved in the matrix mainly consist of Fe and O elements, i.e. iron oxide. A thin layer of oxide particles appears to aggregate and accumulate on the top surface with a discontinuous thickness of around 200 nm shown in Figure 10b. The phosphate tribofilm is composed of soft phosphate phase and hard oxide particles further indicating that the integral hardness of tribofilm should be between those two phases, as shown in Figure 8b. The corresponding SAD patterns shown in Figure 11b and c indicate that the matrix is mainly amorphous, but it does have crystalline nanoparticles embedded within it. The SAD pattern of these nanoparticles indexed in Figure 11b indicates that the nanoparticles consist of both Fe_3O_4 and Fe_2O_3 .

Figure 12 TEM HADDF micrograph and corresponding EDX mappings of phosphate tribofilm at 20 N at 800°C.

Figure 13 TEM bright field micrograph (a) and the corresponding SAD pattern of position 1 (b) of the FIB milling cross section of ball scar lubricated by sodium metaphosphate at 20 N

Figure 12 shows the TEM micrograph and the corresponding EDX mapping of FIB milling cross section of ball scar lubricated by NaPO_3 at 20 N in nanoscale. It reveals the phosphate film in the wear track on the ball was composed of two layers. The top solid layer is evident with a thickness varying from 250-660 nm and the higher magnification micrograph in Figure 12b reveals that it was composed of nanoparticles with a mean diameter of 200 nm. The EDX mapping shows the top layer was mainly composed of Fe and O elements, i.e. iron oxide. The EDX mapping of the bottom layer shows that it was mainly composed of Na, P, Fe and O elements. There are also numerous particles distributing in the matrix, but less than that produced at 10N. The phosphate layer mainly presents an amorphous morphology with little observation of grain boundary. While there are several grains showing clear boundary with a mean grain diameter of around 1μm. The corresponding SAD pattern of this grain (position 1) in Figure 13 was obtained and indexed. This indicated that the crystalline grain was maricite (NaFePO_4),

which is consistent with the report that the short-chained oligomers are more easily to crystallize [23].

Figure 14 TEM HADDF micrographs and EDX elemental mappings of phosphate tribofilm at 30 N at 800°C.

Figure 14 shows the TEM&EDX analysis of the FIB milling cross-section of ball scar lubricated by sodium metaphosphate lubricant at the load of 30 N. Only one layer structure was identified in the tribofilm with an average thickness of 4.7 μm shown in Figure 14a, which was different from the microstructure of the tribofilm at 10 and 20 N. Oxide nanoparticles were also observed to being dissolved in the phosphate tribofilm shown in Figure 14b, but less than both of those at

10 and 20 N. The EDX mapping of Figure 14b shows that the tribofilm is rich in Na, P, Fe and O elements. The high content of iron elements in the phosphate film suggests the iron has massively diffused into the phosphate glass.

5 Discussions

The investigation of an unlubricated tribo-system of GCr15/Mild steel at 800°C show at a light load of 10 N, a 5 μm thick layer of protective oxide ‘glaze’ with a high nanohardness of 8.5 GPa was formed, but the very high wear rates of both ball and disc are still derived shown in Figure 4 due to the continuous oxidation and removal of the metal matrix. At 20 N, a shinier and smoother oxide ‘glaze’ layer can be seen with a smaller diameter and some partial superficial spalling. The abrasive wear and grooving caused by high asperity/adhered transfer particles were the main wear mechanism at the light load. At the heavier load of 30 N a massive metallic transfer occurs. The severe surface damage to the protective oxide ‘glaze’ layer, such as fractures and cracks shown in Figure 5e, which leads to a fresh metal-to-metal contact, is thought to be mainly responsible for the massive metallic transfer and highly fluctuating friction [24]. An examination of the cross-section of the wear surface shows that the applied load has a significant effect on the thickness and hardness of the oxide ‘glaze’ layer under unlubricated condition. The thickness of the oxide glaze layer firstly increases with load from 5 μm at 10 N to 10 μm at 20 N, then decreases to 6 μm at 30 N. The hardness of the glaze layer also shows a similar trend. The reason is that an increase in normal load is beneficial for the sintering and compaction of fine wear debris, and facilitates the formation of protective oxide ‘glaze’ layer [22]. Furthermore, a higher applied load had the effect of raising temperature, leading to a greater rate of oxidation [25]. These contribute to the increase of the glaze thickness and hardness from 10 to 20 N.

However, above a certain critical load, the superficial damage of the oxide 'glaze' layers including spallation and fracture occurs leading to thinning of oxide scale, which also engenders clean metal/metal contacts increasing the metallic transfer and fluctuating the friction [22, 24]. The higher hardness of oxide layer on the surface of ball scar at 20 N than that at 30 N attributed to the formation mechanism of the oxide 'glaze' layer. It was reported that the higher hardness values were derived with smoother areas of glaze, apparently free of cracks and porosity [26]. At 20 N, a smooth and compact mechanically mixed oxide layer was derived as shown in Figure 5c. However, when the load increases to 30 N in Figure 5e, this layer of oxide glaze was mainly transferred from the opposite disc, showing a loose and fragmented morphology, which resulted in a much lower hardness value. The different wear rates in Figure 4 between the ball and disc occur because the ball is in continuous contact with the mating disc surface, while the point on the surface of the disc only makes contact once per revolution, which is why the oxide wear debris preferentially accumulates and forms a 'glaze' layer on the surface of the ball [27]. Furthermore, the GCr15 steel has a higher concentration of alloy (1.48% Cr) than mild steel, which can improve the antiwear resistance of the GCr15 ball by the formation of hard Chromium carbide in the iron matrix [28]. This is also an important reason for the higher hardness of ball than that of disc, shown in Figure 8b. In summary, with extreme conditions of pressure and temperature, high wear of tool, unsteady friction and the massive metallic transfer will occur, which rapidly cause damage to both the tool and workpiece, thus the high temperature lubricant needs to be applied to prevent or at least reduce this problem.

When sodium metaphosphate is used as lubrication at 800°C, it was in a melting state determined by the DSC&TG curves in Figure 1. The tribological tests indicate that a lower and more stable

friction occurs. A substantial reduction of wear rates by 64~90% were also produced in the load range from 5 to 30 N. Comparing the tribological behaviors at different loads, the wear rate and friction coefficient lubricated by sodium metaphosphate was proportional to the load, both increasing with load. The thickness of phosphate tribofilm reduced monotonously with increase of load, while the hardness of phosphate tribofilm experienced little change reaching the value of 4.5 ± 0.5 GPa. This finding is different from the tribofilm formed by ZDDP anti-wear additive at low temperature, which experiences an increased hardness with increased applied load due to coordination transformations at high pressure and shear [29]. The consistency of phosphate film hardness with load at high temperature indicates that the impact of high pressure on the mechanical properties of viscous glass state, which is proved by the DSC curves in Figure 1, is not as evident as viscoelastic solid state at room temperature.

The chemical compounds in the phosphate film were very similar at the load ranging from 10 to 30 N, which is predominated by NaFePO_4 with a little existence of $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$ and Na_3PO_4 . This finding supports the view that the interaction between oxide scale and polyphosphate polymer destroys its polymer structure, and forms short-chained orthophosphate. However, this structural change exerts little negative influence on its tribological performance, which is proved by the tribological results. The similar types of chemical compound at different applied load can also explain the similar hardness performance at room temperature in Figure 8b. Furthermore, literature confirms that the replacement of a P-O-P bond by a Fe-O-P bond can dramatically increase the chemical durability due to the shortening of the average chain-length and the ability of Fe^{3+} to strengthen the phosphate chains [30, 31]. The formation of orthophosphate shows a lower chemical reactivity which makes them unable to stick or be largely insensitive to chemical

bonding. The use of Na^+ also has a multi-functional role in the tribofilm; it facilitates the breakup of P-O-P bonds and reduces the viscosity of the phosphate network [31, 32], while participating in the saturation of phosphate charges. In summary, smaller network-forming PO_4 tetrahedron groups, which are surrounded by Na^+ and joined by unidirectional ionic bonds, enables the structure to be more flexible, so the components of this glass structure can change their internal positions according to the frictional shear.

The microstructures of the tribofilm at different applied loads were studied by high resolution STEM. TEM micrographs of tribofilm reveal that fine oxide debris is retained at the interface and incorporated within the phosphate matrix. This functionality of phosphate glass is also reported to being applied to nuclear waste immobilization and ZDDP anti-wear additives [33-35]. The extensive wear debris reintroduced into the soft phosphate matrix can perform multiple contributions in the improvement of tribological performance: Firstly, the abrasive wear caused by hard Fe_2O_3 debris was alleviated [35, 36], which can be observed by comparison of SEM micrographs of wear scar in Figure 5, 6 and 7. Secondly, the digestion of oxide debris into the phosphate matrix can enhance the integral mechanical properties of tribofilm shown in Figure 8, in which the tribofilm shows a four times higher hardness than that of pure sodium metaphosphate. Furthermore, the presence of oxide nanoparticles also facilitates the formation of transfer film by strengthening the interaction between phosphate film and the counter-face [37], otherwise, the adhesive strength of the pure polyphosphate film on the ball at an elevated temperature is too weak to resist rubbing, and will be instantly removed. SAD characterization of the crystallized grain in the tribofilm at 20 N shows that the grain belongs to chemical compound NaFePO_4 . This is consistent with the XRD characterized results of tribofilm on the slow cooling

disc, in which the film was predominated by short-chained maricite (NaFePO_4). As suggested in the experimental section, the ball cools down more quickly than the disc. As a result, the phosphates on the disc will crystallize, while those on the ball kept the same structure as that at high temperature. Consequently, it can be concluded the thin tribofilm on the ball was mainly composed of amorphous short-chained NaFePO_4 . The microstructure of the tribofilm also evolves with the applied load. At 10 and 20 N, the tribofilm presents a structure with two distinct layers shown in Figure 11 and Figure 12: a thin oxide layer with the thickness of several hundred nanometers locates above the amorphous NaFePO_4 matrix. However, the thin iron oxide layer was not observed at the surface of phosphate film at 30 N. A possible mechanism was suggested in this study, which is related to two processes: one is the formation rate of oxide layer at the top surface through the migration of iron atom from oxide scale/substrate to the top surface of phosphate melt and/or from slow cooling in air straight after testing, which was proved by the static oxidation test shown in Figure 2. The other is the wear rate of this oxide layer due to the shear stress in the rubbing. At a lighter load of 10 and 20 N, the formation rate of oxide achieves a balance with the wear rate. However, when the load increases to 30 N, the wear rate of the ball increased sharply, which is around twice that at 20 N shown in Figure 4. This high wear rate significantly outstrips the formation rate of the top oxide scale layer. As a result, no oxide layer was observed at the top surface of phosphate lubricant.

6 Conclusions

The tribological tests at 800°C shows that the use of inorganic alkali polyphosphate lubricant can reduce the friction coefficient and wear rate significantly, by around 24~49% and 64~90%, respectively, where both of them show a monotonously increase trend with the increase of loading. Furthermore, the use of sodium metaphosphate lubricant also restrains the metallic transfer from the disc to the ball scar surface. This improvement of tribological performance is the result of a build-up of phosphate tribofilm in wear track, composed of short-chained amorphous NaFePO_4 and a little $\text{Na}_3\text{Fe}(\text{PO}_4)_2$. The thickness of phosphate tribofilm monotonously decreases with the increase of applied load, while the corresponding hardness shows little change. However, when the load increases to 30 N, the phosphate tribofilm severely deteriorated.

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