Lubrication mechanism investigation of alkali polyphosphate glass in hot rolling

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Lubrication mechanism investigation of alkali polyphosphate glass in hot rolling

A dissertation submitted for the award of the degree of

Doctor of Philosophy

From

University of Wollongong

By

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School of Mechanical, Materials, Mechatronic and Biomedical Engineering
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Jul, 2018
Declaration

I, Shaogang Cui, declare that this dissertation, submitted in partial fulfilment of the requirements for the award of Doctor of Philosophy, in the School of Mechanical, Materials, Mechatronic and Biomedical Engineering, University of Wollongong, Australia, is fully my own work unless otherwise referenced or acknowledged. No part of this thesis has ever been submitted to any other institution for any other degree or qualification.

Shaogang Cui
Jul, 2018
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Wollongong, Jul, 2018
List of Publication during the PhD course


3. **Shaogang Cui**, Hongtao Zhu, Shanhong Wan, Kiet Tieu, Investigation of different inorganic chemical compounds as hot metal forming lubricant by ball-on-disc and hot rolling, Tribology international, 2018,125:110-120.


Abstract

Increasing competition in steel industry facilitates high demands for high efficient, low cost and environmentally friendly lubricant in hot rolling so that better strip quality at the minimum cost can be manufactured. In this thesis, a type of inorganic alkali polyphosphate glass has been recommended as a lubricant in hot metal forming, with a particular attention being paid to hot rolling. Before hot rolling tests, laboratory-scale ball-on-disc tribometer was used to evaluate the tribological performance of alkali polyphosphate glass.

Firstly, the physical and chemical properties of the sodium polyphosphates aqueous solution were studied by SEM&EDX, TG&DSC, XRD as well as a high temperature laser microscope with a CCD camera. The result shows that some intermediate reactions such as hydrolysis and depolymerization in the aqueous solution have produced short-chained phosphates. However, once the polyphosphate solution is heated to 600°C, the dehydration and polymerization reaction causes these short-chained dihydrogen ortho- or pyro-phosphate to re-polymerize into desired long-chain polyphosphates. Therefore, the dissolution of alkali polyphosphate in the aqueous solution exerts little impact on the structure and properties of alkali polyphosphate glass at high temperatures.

A range of inorganic chemical compounds were tested as lubricant at high temperatures in Chapter 4, to explore their possible application in hot metal forming. Ball-on-disc and hot rolling apparatus were combined to conduct these tribological tests. The results indicate that sodium polyphosphate lubricant shows a superior performance than borax, commercial oil-in-water emulsion and layered solid lubricants in terms of lubricity,
antiwear and antiseizure ability. The excellent wettability and formation of viscous polyphosphate glass film on the tribo-surfaces are the main contributors to the excellent tribological performance. Furthermore, the anti-oxidation ability of glass lubricating film was also investigated by static oxidation tests. The result shows that the oxidation resistance functions of the protective glass film in hot rolling are not outstanding due to the formation of thin and discontinuous lubrication film when 20w.t.% sodium metaphosphate solution is applied. The low concentration of the lubricant was believed to be associated with the poor anti-oxidation behavior.

In Chapter 5, the tribological behaviors of three types of alkali phosphates (sodium ortho-, pyro- and meta-phosphate) with different chain-lengths are evaluated using the ball-on-disc tribometer at 800°C. The results show that compared to the unlubricated pair, a glassy film consisting of Na, Fe, P and O elements formed on the contacting area of disc reduces the friction coefficient by 45~65% and wear rate by 80~90% respectively. The tribochemistry at the interface investigated by XPS and XANES reveals that iron oxide scales react partially with the glassy polyphosphate film to form a tribo-boundary film being composed of mixed Na-Fe polyphosphate compound on the wear track, which leads to a severe depolymerization for sodium metaphosphate and a slight polymerization for sodium pyrophosphate. For Na₃PO₄, the main effect of tribological shear and stress at 800°C on sodium orthophosphate crystalline is the extensive irreversible amorphization with little polymerization.

In Chapter 6, the tribological behaviors and interfacial evolution of steel/steel tribopairs lubricated by inorganic sodium metaphosphate at 800°C under different loading conditions were studied. A series of high temperature ball-on-disc tribological tests have
indicated that the sodium metaphosphate lubricant produced a stable and significantly reduced friction, as well as a tool wear reduction of 65~90%. A tribo-induced adherent phosphate film with a thickness of 4.5~5 µm and nanohardness 4~5 GPa accounted for the remarkable wear resistance and friction reduction behaviors. XRD characterizations indicated that metaphosphate interacted with iron oxide to form a dominant NaFePO$_4$ and a small amount of Na$_3$Fe$_2$(PO$_4$)$_3$ and Na$_3$PO$_4$ in the tribofilm. FIB and TEM observations revealed that the submicron hard Fe$_2$O$_3$/Fe$_3$O$_4$ particles were incorporated in the transfer film, and the corresponding microstructure was load-dependent, where submicron oxide grains migrated gradually to the topmost layer with increasing load.

The abovementioned studies were mainly conducted in the lab-scale ball-on-disc tribometer. However, large quantities of publications pointed out some inconsistent results between the ball-on-disc and practical hot rolling, due to different operating conditions such as pressure, tool temperature distribution, contact time etc. Furthermore, the lubricating film characterization in Chapter 4 did not succeed due to the low concentration of lubricant. To further solve these problems, hot rolling tests were performed with a higher concentration of sodium metaphosphate (40w.t.%) and 20~60% rolling reductions. The results reveal that the lubricating ability of phosphate glass becomes weaker at lower reductions. Interfacial microstructures were studied in details to understand the role of the lubricating film in the contact. The lubricating function was provided by the glassy phosphate film with a calculated thickness 2.2~4.3 µm when subjected to 20%~60% rolling reductions. The thicker lubricating film formed at a high reduction also protects the hot rolled strip from oxidation more efficiently, resulting in a thinner oxide scale.
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1 Introduction

Many tribological interfaces of various moving assemblies are frequently exposed to elevated temperatures, e.g. aerospace industry, power generation and hot metal working processes, as shown in Figure 1-1. These relevant interfaces often involve high temperature tribology, which is an interesting but challenging field. Great changes in morphology, microstructure and mechanical properties take place at interfaces when exposed to high temperature and high pressure working conditions, as well as the unavoidable occurrence of oxidation and diffusion. The tribological behavior of materials is closely related to these changes at elevated temperatures.

Figure 1-1 High temperature tribology in aerospace [1], power generation and metalworking fields

Figure 1-2 Schematic diagram of (a) production line [2] and (b) the detailed schematic of lubricant and water cooling spraying in hot rolling mill [3].
This thesis mainly concentrates on the frictional interfaces in the hot metal forming process such as hot rolling, as shown in Figure 1-2. Hot rolling is a metal forming process that is usually conducted above the recrystallization temperature of metal. The large-sized and equiaxed grains experience severe plastic deformation into long bands. Then the deformed grains recrystallize into an equiaxed and fine microstructure. In the hot rolling production line in Figure 1-2a, the cast steel slabs are firstly soaked in a reheating furnace in a special atmosphere; as a result, a primary oxide scale with the thickness 3~5 millimeter is usually formed. When the thick primary scale is deformed, the scale will experience breakage, detachment and embedment into the steel substrate to cause a serious surface deterioration [4]. Therefore, the thick primary scale is normally descaled by high pressure water jet before entry to the rough rolling milling. However, a secondary scale will form immediately on the hot descaled surface in air atmosphere; therefore, steel strips are always hot rolled with the secondary scale.

Currently, hot rolling is normally performed with a high reduction to produce ultra-fine grained steels, so the tribological problems arising from the large high rolling force, severe material transfer, and friction pick up need to be investigated. All these pose considerable challenges for the steel production in hot rolling, which requires a selection of proper lubricants to alleviate these problems. In hot rolling, the lubricant is normally sprayed to the contact interface between the roll and strip, as shown in Figure 1-2b.

The thesis aims to find a highly efficient, low manufacturing cost and environmentally friendly compound material to work as hot rolling lubricant. Firstly, some potential candidates are being compared by laboratory ball/pin-on-disc simulation in terms of
friction coefficient, wear rate and antioxidation, and the working mechanism involving tribochemical reaction, impact of loading on tribology for the optimal candidate are studied in detail. Finally, the selected lubricant is tested by experimental hot rolling, and the lubrication behavior of the lubricant is elucidated.
2 Literature survey

2.1 High temperature tribology principles in dry conditions

Tribology at high temperature is a complex tribo-system involving complex and interactive mechanisms such as abrasive, oxidational or adhesive wear, thermal or mechanical fatigue, and plastic deformation, as shown in Figure 2-1. The interactions will become more complicated when a lubricant is applied to the system. Therefore, the high temperature tribology under dry condition should be clarified first, and the section is designed to summarize the unlubricated tribological studies at high temperature. Literature survey also shows that the published papers relating to dry tribology field far exceed those with lubricant at high temperature (>600°C).

In high temperature tribo-system, the rubbing surface is mostly subjected to high thermal and mechanical stresses. Attention is focused at the interface of tool-workpiece to understand the tribology in high temperature metal forming. These harsh working conditions usually damage the rubbing tribopairs, especially the tools, which are normally required to last as long as possible due to the high replacement cost. As a result, the selection of suitable material for a tool is fairly vital, which is dependent on the method of its wear or destruction. Normally, high speed steel is selected as the tool material in hot rolling, because of its superior wear capability in maintaining high hardness when subjected to high friction at elevated temperature [5].
Figure 2-1 Schematic diagram showing the influential factors in high temperature tribological processes [6].

2.1.1 Role of oxide scale in the high temperature tribological interface

Most metals in air interact with oxygen to form a layer of oxide film on the exposed surface. The high temperature of workpiece in hot metal forming facilitates the rapid formation of oxide scale on the surface of hot steel, which exerts a significant influence on friction and wear. The activation energy of FeO, Fe₃O₄ and Fe₂O₃ oxidation during rubbing was reported to be a quarter to half that in static condition [7]. Clearly, a rubbing surface is easier to be oxidized than a static one when exposed to the same oxidizing environment.

The growth mechanism of oxide scale was widely investigated, which is suggested that the positive metal cation ions firstly form at the oxide/metal interface, then diffuse through the previously formed oxide lattice until these metal ions arrive at the interface of scale/oxidizing atmosphere. Therefore, the oxide scale grows in an ‘inside out’ manner, i.e. the outer layers is formed later than the inner layers [8]. This formed oxide scale has a typical structure with three layers shown in Figure 2-2 [9]; the outermost layer is the thin hematite (Fe₂O₃), the columnar crystalline middle layer belongs to magnetite (Fe₃O₄) and
the inner most large-grained layer is wüstite (FeO). The oxide scale has an excellent oxidation resistance below 570°C which is attributed to the protection by a Fe₃O₄ layer beneath an outer Fe₂O₃ layer. However, above 570°C the oxidation rate increases substantially due to the establishment of a rapidly growing non-stoichiometric FeO layer at the oxide/metal interface [10]. Wüstite is reported to be only thermodynamically stable above the eutectoid temperature of 570°C and below which the Wüstite phase decomposes into magnetite and alpha-iron [11]. The formation of these layers provides a good protection of steel substrate against further oxidation by inhibiting inward diffusion of oxygen ions and outward diffusion of iron ions. As the oxide scale forms at the top surface of tribopairs, it plays a critical role in friction and wear control at the tool/workpiece interface at high temperature, such as prevention of direct metal-to-metal contact and adhesion, and provision of a protective antiwear film.

![Figure 2-2 Typical structure of oxide formed on a mild steel in air atmosphere at 900°C](image)

The existence of iron oxide layer on the steel substrate has been shown effective in minimizing direct metal-to-metal contact and reducing wear, and producing a transition from severe to mild wear [12-14]. Rosenberg and Jordan et al. [15] conducted a comparison of the tribological tests at two different atmospheres (hydrogen and air) by
using carbon steel under comparable conditions. The results reveal that the wear rate in hydrogen was 50 times that in air. The analysis of wear debris shows that they were Fe$_2$O$_3$ and Fe$_3$O$_4$ in air, and highly distorted iron in hydrogen. Minf et al. [16] investigated the friction behavior between X40CrMoV5 tool steel and Fe360B steel from room temperature to 800°C. At room temperature, the friction coefficient shows the characteristics of direct fresh metal-to-metal contact. From room temperature to 400°C the average friction coefficient varies little. However, beyond 400°C, the friction coefficient decreases drastically. This friction decrease is attributed to the formation of thin, smooth ‘glaze’ oxide layer. The research also changed the hardness of tool steel to observe its effect on friction; the result shows insignificant difference between these two friction behaviors. This study is in line with the work conducted by Tomala et al. [17], who points out that at room temperature very hard tool steel ploughs and cuts into the disc surface, resulting in a high friction, while at high temperature, the formation of glaze layer reduce the friction, abrasion and adhesion are the main type of wears. However, the undesired damage of the tool and changes in the geometry of deformed workpiece material are caused by formation oxide particles at high temperature [17]. This implies that the overall tribological process needs to be improved by an application of a lubricant on the tool steels. From a study of the effect of hardness on wear behavior [18], the softening temperature of steels differs from the temperature at which the abrupt wear decrease or severe material occurs. Consequently, it was concluded that the properties of the oxide formed at the rubbing interface were critical than the intrinsic hardness of the material. The oxide scale behavior in the rolling process was studied by Zhu et al [9]
through a pin-on-mild steel disc simulation at 900°C. Three distinct stages were observed in the evolution of friction coefficient with sliding time, as shown in Figure 2-3. The reduced friction in the first stage is due to the formation of thin oxide scale on the pin. The second stage, where the friction shows an upturn, is attributed to the re-growth of oxide scale. When the friction coefficient arrived at a stable level at the third stage, the thickness of the protective oxide scale reached a critical value where spallation occurred and wear debris were generated. The wear mechanism in the stable period is a mixture of adhesion, abrasion and oxidation. The researchers also claim that the oxide material transferred from the mild steel disc to High Speed Steel (HSS) pin facilitate the formation and subsequent growth of the oxide scale on the HSS pin surface. The frictional behavior of boron steel against tool steel as a function of temperature and load was studied by Hardell et al. using a high temperature ball-on-disc machine [6]. Generally, the friction coefficient will decline when the ambient temperature rises. However, the wear rate will increase with the increase of temperature. This is because the protective oxide glaze layer on the tool steel surface failed to be formed homogeneously. Furthermore, the thermal softening of tool steel also deteriorates with the rise of temperature, which is discussed in detail in section 2.1.2. Lastly, load itself has a pronounced effect on the morphology of glaze layer; the formation and growth of glaze oxide layer is benefited by an increase of load up to a critical value. Above this critical value, the glaze oxide layer experiences fracture and spalling, which leads to more direct metallic contacts and wear.
Tribo-surface and corresponding cross-sectional studies find that frictional and wear behaviors are governed by both surface and subsurface phenomena [6, 19]. Three characteristic material zones, as depicted in Figure 2-4, can be identified for test materials under various contact conditions [20].

Zone 1, the furthest zone from the contact surface, is composed of undisturbed substrate material. Zone 2 is an intermediate region, which is plastically deformed, is composed of only substrate material; the reorientation and disintegration of crystallites is commonly
observed in this zone with grain refinement in the microstructure. In contrast, zone 3 is the region where the high-resistance load-bearing layers are established. Such layers differ compositionally as well as morphologically from zone 1 and 2. Zone 3 possesses a homogeneous and fine structure, consisting of elements from both specimen and countersurface material, as well as of constituents from the operating environment. Tribo-induced surface composition changes are mainly caused by the material transfer from one surface to the countersurface and vice versa.

These literatures confirm that the oxide glaze layer usually forms at high temperature to protect the metal substrate from severe wear. The formation mechanism of the glaze layer was widely studied, and briefly summarized here. The load-bearing areas are formed from the agglomeration and compaction of wear debris which are subjected to plastic deformation, fragmentation, and breakdown into smaller sizes at high temperature and pressure. Then, these wear debris and particles are compacted and agglomerated by high pressure, forming condensed, smooth and hard protective layers on substrate surfaces. After the built-up of the oxide glaze protective layer, two dynamic processes competes during the rubbing; one is the breakdown of the layers leading to the generation of further wear debris particles, the other one is the strengthening of the debris layers by further sintering, welding and compaction of these particles. However, it should bear in mind that some oxide layers (Fe$_2$O$_3$ and Fe$_3$O$_4$) are hard and brittle; the detached wear debris can also cause increased third-body wear and are harmful to the system [21, 22]. The increase of temperature increases the rate of sintering and consolidation, also accelerates further the oxidation rate of these particles [23]. The formation of the load-bearing glaze
layers were widely reported when metals slide at high temperature without lubricant [6, 9, 23, 24]. The adhesion strength among these wear debris is a critical factor which governs the structure of the protective layers. A weak adhesion can lead to a break down or spalling of oxide layer into abrasive particles, while a strong adhesion can form smooth and hard protective layers. The increase of temperature can increase the kinetics of the wear debris oxidation and the surface chemical interaction among these particles. The fragmentation process of oxide scale includes the plastic deformation, dislocations generation, subgrains formation and increased refinement. The nano-structured oxide grains at the tribo-surface are created through the increasing refinement of oxide grains and disorientation. The formation of nano-structured grains in the glaze layer improves the wear resistance because of the absence of Hall-Patch softening and enhancement of fracture toughness and hardness of the surface. However, there are still some unclear questions around the formation mechanism of glaze layer. For instance, the roles of individual element and the rubbing parameters (temperature, speed, normal load) in the formation of glaze-forming process still remain unclear. Furthermore, whether the formation mechanism of the protective oxide glaze layer is material specific still needs to be investigated.

Besides the effect of oxide scale itself on friction and wear, surface parameters such as the surface features, chemical reactivity as a result of oxidation at high temperature are also an important consideration when investigating interactive contacts between two mating surfaces. A previous work [25] points out that the surface topography has a remarkable influence on material transfer, and the transferred materials adhered on one
surface in turn exert a significant influence on friction. Typically, excessive material transfer phenomenon is coupled to a high friction level and vice versa.

Material transfer is another challenge in hot metalworking, which affects the surface quality and tool life. The reasons behind this material transfer are explained as following [26, 27]; Under the load $F_N$, the contacting surface will touch only through discrete micro-asperities, and the sum of these contacting asperities forms the real contacting area $A_r$. These contacting asperities are subjected not only to an elastic deformation, but also to some plastic deformation. The molecular forces may act through the intimate contact and as a result, the interfacial bonding and adhesive junctions occur. A variety of molecular forces involving metallic, covalent, ionic and Van Der Waals forces can work synergistically at the interface to form interfacial adhesion. Under the action of pure normal contact and shear stress the material with a weak cohesion transfers to the one with a stronger cohesion. With relative tangential motion between the surfaces at high temperatures, interfacial materials transport becomes more complex with some influential factors such as plastic deformation, shear and high elemental diffusion etc., as shown in Figure 2-1.

2.1.2 Changes in mechanical properties of mild steel at high temperature

The properties of the load-bearing materials and any interposed substances can change when the temperature rises. In generally, a reduced resistance to deformation and abrasion can be expected at a higher temperature. The modulus of elasticity also changes as a function of temperature and that affects the elastic behavior of metals.
High temperature results in changes in mechanical properties due to microstructural changes and thermal softening. Young’s modulus shows a definite downward trend with increasing temperature. A relationship between Young’s modulus and the temperature has been studied in previous work [28]. The stress-strain relationship of steel can be described by Equation 2.1.

\[ Y = Y_0e^{-aT}(1 + B\varepsilon)^{n_1} \times (1 + D\dot{\varepsilon})^{n_2} \]  
Equation 2.1

Where \( Y_0 \), \( a \), \( B \), \( D \), \( n_1 \) and \( n_2 \) are constants. These constants (\( Y_0 \), \( a \), \( n_1 \) and \( n_2 \)) can be determined by multiple-regression, which was done by multiple-regressions through a large number of hot tensile tests [29]. The stress-strain relationship for mild steel at high temperature was proposed according to Equation 2.2.

\[ Y = 158.44 \times \exp(-0.002532T) \times (1 + 1000\varepsilon)^{0.3695} \times (1 + 1000\dot{\varepsilon})^{0.1097} \]  
Equation 2.2

Where \( T \) represents the temperature (°C), \( \varepsilon \) represents the strain, and \( \dot{\varepsilon} \) represents the strain rate. The relation between Young’s modulus and temperature provides a method to obtain the high temperature mechanical properties, which is useful to calculate the friction coefficient in hot rolling by an Alexander Model as described in the Appendix. In hot rolling, the strain rate was determined by Equation 2.3.

\[ \dot{\varepsilon} = \frac{V_r}{\sqrt{R\Delta h}} \ln \left( \frac{1}{1 - e} \right) \]  
Equation 2.3

\( v_r \) represents the rolling speed, and \( l_0 \) represents the initial length of steel strip. This proposed model agreed with other flow stress model. Equation 2.2 can be used to temperatures between 800-1100°C, strain rate from 0.5-10 s\(^{-1}\) and a strain below 0.7 and a constant \( C_{eq} \) equals 0.34 for mild steel.
2.2 High temperature tribology with lubricant

As described in section 2.1.1, oxide scale contributes to the reduction in friction and wear in high temperature rubbing, because it can form a protective glaze layer with a smooth surface with high hardness. However, the hot metal forming process usually produces a large plastic deformation at elevated temperature (600~1200°C), and as a result a high rolling pressure (0.1~1 GPa) is required. Those harsh conditions raise a number of tribological problems at the tool/workpiece rubbing surfaces, such as the spallation and flaking off of deformed oxide scale, abrasive wear, oxidation, thermal fatigue, material transfer etc. The interaction among those problems will cause a high friction in hot rolling and wear of work roll, which in turn cause a high maintenance cost and a poor production efficiency [33, 34]. Oxide glaze layer cannot cope with these problems alone.

Thus, appropriate lubricants are required to control friction, wear and oxidation in the tribo-system at elevated temperatures in hot metal working, and it is essential to have an in-depth understanding of their behaviors at the tool/workpiece interface. The high temperature and load as well as the complicated thermal stress in hot metal forming poses a significant challenge to select an appropriate lubricant as a large number of lubricants lose its lubricity behavior due to oxidation, decomposition, deterioration and even burn off at high temperature. For instance, conventional lubricants, such as mineral oils, fats, soaps and other organic lubricant, do not perform effectively when the temperature is over 200°C, because these organic liquid lubricants decompose and pyrolysis rapidly at high temperature [35-38]. The use of layered solid lubricant is also significantly limited at high temperature due to the deterioration of layered structure. For example, the
molybdenum disulfide (MoS$_2$) based composite lubricant, which is the most common ceramic lubricant used today, will be severely oxidized to form a hard abrasive molybdenum oxide MoO$_3$ above 400°C [39]. Graphite is most commonly used in hot metal working field now because of its low price and satisfactory lubricity. A report [40] recommends that graphite be added to liquid lubricant can improve their lubricity and antiseizure ability at high temperature. Furthermore, the graphite has the advantage of simple application. However, the use of graphite is also substantially discouraged due to its low adhesion on the hot steel surfaces and can be removed easily from the interfaces. Furthermore, lubricity of graphite is also affected by the adsorbed gases from atmosphere, which results in variation of performances [39]. Furthermore, there is also a growing concern about the penetration of graphite residue into the surface of workpiece, called carburization. This will affect the designed chemical composition of workpiece and strength. Environmental issue is another disadvantage by graphite lubricant due to pollution of the working environment, leakage to soil and groundwater or pipe corrosion due to their electric conductive properties [41]. Lastly, graphite lubricants can be changed into non-graphite materials in hot metalworking process and lose their lubricating ability [42].

Due to the abovementioned concerns, lubricant researchers are endeavoring to replace the graphite-based black lubricants with more environmental friendly ‘white’ lubricants such as liquid-glass and polymer-based lubricants.

Based on abovementioned problems, some basic requirements of high temperature lubricant in hot metal forming are listed:
• The cost of the lubricant should be as low as possible to reduce the cost of the products;
• The lubricant should have a strong adhesion and wettability with hot oxide scale; otherwise, the lubricant will be readily detached and contribute little to friction and wear reduction;
• The lubricant should be environmentally friendly, and should pose little threat to environment and operators;
• The lubricant should not promote corrosion of steel at high temperature.

Table 2-1 Comparison of different types of lubricants

<table>
<thead>
<tr>
<th>Lubricants</th>
<th>Examples</th>
<th>comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Organic</td>
<td>oils, greases, fats, soaps etc</td>
<td>• Pyrolysis over 300°C [38];</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Environmental and health problems [43, 44];</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Losing fluidity beyond a thickness [45];</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• No lubricating film formed at higher temperature [38].</td>
</tr>
<tr>
<td>Lamellar solids</td>
<td>MoS₂, WS₂ and Graphite</td>
<td>• Severe oxidation into a hard abrasive molybdenum oxide MoO₃ above 400°C;</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Carburization [37, 46].</td>
</tr>
<tr>
<td>Inorganic polymer (Molten glass)</td>
<td>Borate, Silicate and Phosphate</td>
<td>• Wide working temperature [47, 48];</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• High water solubility;</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Low manufacture cost;</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Environmentally friendly;</td>
</tr>
<tr>
<td>Solid lubricant</td>
<td>PbO, B₂O₃</td>
<td>• Higher friction;</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Difficult to be transported into roll bite and removed due to poor water solubility;</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Poor surface quality;</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Environmental issue [49].</td>
</tr>
</tbody>
</table>
Based on the above requirements, it has been accepted that white lubricants like polymer-based lubricants and liquid-glass-based lubricants have more prospect in hot metal forming [50, 51]. Compared with other commonly used lubricants, as shown in Table 2-1, the liquid-glass-based white lubricants have the following advantages; Firstly, inorganic glass as hot metal working lubricant has attracted much attention due to its viscous behaviour; the glass starts to soften at its softening point, and becomes increasingly fluidic with temperature. This allows the inorganic polymer to have a wide working temperature range. Furthermore, the glass polymer melt usually has an excellent wettability on the hot steel surface [52], it can soften, spread and separate the sliding metallic surfaces by forming a thin film under high shear and temperature conditions, as shown in Figure 2-5b [40, 53].

In seamless pipe making, relative slippage occurs between the inner surface of the hollow shell and outer surface of the mandrel bar. Consequently, good inner-surface quality and dimensional accuracy of the finished product can be obtained by applying a lubricant in the working interface to secure a low and stable friction coefficient and inhibit seizure between the hollow shell and the mandrel bar. Reference [54] suggests a powder lubricant with sodium borate pentahydrate as a main component and sodium carbonate and the like as a supplemental lubricant. When the lubricant is adhered to the inner surface of the hollow shell at 1000 to 1300°C, the lubricant melts down immediately and spread on the work surface while melting a generated scale existing thereon. However, in the cooling stage after rolling, the sodium borate crystallizes itself to become “white scale” adhering on the inner surface of the finished pipe product. In order to solve the “white scale”
problem, lamellar silicate and carbonate and/or alkali carbonate was added into the powdered borate lubricant [44]. Metal phosphate melt in the lubricant composition provides lubricity; metal carbonate helps the separation of the workpiece and to prevent the workpiece from “sticking” to the die, because it can form a gas cushion of CO₂. However, literature survey [43, 55] shows that sodium bicarbonate can only be worked as an insignificant ingredient of the lubricant rather than the main composition.

Hot extrusion of steel with molten glass lubrication represents another successful application of hydrodynamic and thick film lubrication in Figure 2-5b. In 1940s, the availability of high quality tool steel, economical extrusion was not possible due to the extremely short life and consequent expense [48]. The high friction generated caused rapid die wear and excessive defects in the extruded material. This could only be overcome by the application of an efficient lubricant. Sliney and Bisson [56] recommend that the potential lubricant should be applied as a solid, and it turns into a highly viscous fluid at the extrusion temperature. Such a lubricant can withstand the pressure and be extruded as a continuous, thin viscous film between the bars and die. Furugen et al. [57] conducted hot tube extrusion tests, where a 40 μm thick mixed silicate-borate glass lubricant was pre-coated on the workpieces before hot extrusion. The results show that hot tube extrusion operates in a hydrodynamic lubrication regime where the coefficient of friction stays in a range from 0.02~0.14, which was linearly proportional to the logarithmic viscosity of glass lubricant, shown as Figure 2-6; after test a residual 20~30 μm thick of glass film was left on the workpiece. However, the tribological conditions and configurations in the contact zone differ significantly among different hot metal
forming processes, the lubricant in hot extrusion was in a sealed environment shown in Figure 2-5. Hydrodynamic lubrication regime does not apply in hot rolling [45]. Furthermore, too low friction is not expected in hot rolling, as it would result in the work piece unable to enter the roll bite.

![Figure 2-5](image)

Figure 2-5 (a) Photo of molten glass liquid [58] and (b) schematic diagram of application of molten glass in hot extrusion process

<table>
<thead>
<tr>
<th>Mark</th>
<th>SiO$_2$</th>
<th>Al$_2$O$_3$</th>
<th>B$_2$O$_3$</th>
<th>Na$_2$O</th>
<th>K$_2$O</th>
<th>CaO</th>
<th>MgO</th>
</tr>
</thead>
<tbody>
<tr>
<td>G1</td>
<td>56</td>
<td>15</td>
<td>6</td>
<td>0.5</td>
<td>0.2</td>
<td>22</td>
<td>0.6</td>
</tr>
<tr>
<td>G2</td>
<td>72</td>
<td>2</td>
<td>-</td>
<td>13</td>
<td>1</td>
<td>8</td>
<td>1</td>
</tr>
<tr>
<td>G3</td>
<td>33</td>
<td>2</td>
<td>36</td>
<td>16</td>
<td>1</td>
<td>8</td>
<td>1</td>
</tr>
<tr>
<td>G5</td>
<td>67</td>
<td>-</td>
<td>33</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>G6</td>
<td>81</td>
<td>-</td>
<td>19</td>
<td>-</td>
<td>-</td>
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<td>-</td>
</tr>
</tbody>
</table>

![Figure 2-6](image)

Figure 2-6 Glass compositions used in the hot extrusion test and the obtained friction coefficient as a function of logarithmic viscosity of glass lubricants [57].

In Furugen’s work [57], two-valent cation chemical compounds were precoated on the workpiece surface. However in hot rolling, as the lubricant is normally delivered to the contact zone through nozzle spray, it requires a good solubility of the glass compounds, and the multiple valent cations should be avoided in the application due to low solubility in water, as listed in Table 2-2.
Furthermore, as inorganic glass with one-valence alkali metal has a high-water solubility, it can be applied as an aqueous solution or glass frit. After evaporation of water it would become a highly viscous liquid at high temperature, as shown in Figure 2-5a. Finally, inorganic alkali glass lubricant can prevent surface cracks and reduce the oxidation of workpieces by providing a barrier which retards the oxygen atoms from diffusing into the substrate [59]. It also provides an insulation to reduce the temperature of the workpiece when in direct contact with the tools [59, 60]. These features are needed in hot metal forming for energy saving and product quality improvement. Publications [61-64] suggest that a friction coefficient in the range of 0.03–0.25 can be obtained dependent on the tribological conditions and properties of lubricant. Although the use of glass lubricant brings about so many benefits, their working mechanism is still not fully understood.

Finally, these chemical compounds come from naturally abundant minerals, have a low manufacture, and pose no health hazards or environmental threats.

### 2.2.1 Antiwear mechanism of polyphosphate glass at low temperature

The literature survey reveals that very few papers were found to study the working mechanism of inorganic glass at high temperature, nor did detailed analysis was given. In contrary, a large volume of literature can be found relating to the application of organic polyphosphate glass as an antiwear additive in engine oil at low temperature. The most classic application of phosphate glass in the field of low temperature tribology is ZDDP additive, which is currently the most popular and classic phosphate compound in engine oil as an antiwear additive. Though the pathway of ZDDP tribofilm formation cannot be directly used at high temperature to explain the tribological behavior of polyphosphate
glass, information which has been acquired at low temperatures can still serve as a partial guide and research methods for the selection of lubricants at high temperature. Therefore, the acting mechanism of ZDDP additive will be summarized briefly here.

A number of published literatures have revealed that polyphosphate tribofilm derived from ZDDP can provide an effective protection of the rubbing surface from wear and friction at ambient temperatures [66-68]. There exist numerous possible mechanisms for the formation of ZDDP tribofilms: thermal degradation, surface adsorption, oxidation by hydro peroxide, radical reaction, hydrolysis, etc [69-72]. It is commonly accepted that the antiwear mechanism of ZDDP originates from the build-up of an amorphous interfacial material (anti-wear film) containing elements from the ZDDP molecules (P, S, Zn) and from the friction surfaces (Fe), as shown as Figure 2-7 [73-75]. Although the mechanism by which the film actually forms on the surface has not been proven by experiments, it is widely believed that ZDDP mainly undergoes thermal-oxidative decomposition at a high temperature is the main reason for its good tribological performance [21]. The corresponding reaction equation (Equation 2.4) can explain the formation of a tribofilm
on the metal surface. Extensive studies have demonstrated that ZDDP-derived tribofilm
contains phosphate compounds with different chain-length, including ortho-, pyro- and
meta-phosphates, they work together and thus deliver the desirable anti-wear and friction-
reducing capability in partnership [68, 76-79]. However, the contribution of individual
phosphate to the tribological efficiency of phosphate tribofilm still remains unclear.

\[
\text{Zn}[(\text{RO})_2\text{PS}_2]_2 + \text{O}_2(\text{ROOH}) \overset{T>100^\circ\text{C}}{\rightarrow} \text{Zn}_{n+2}[\text{P}_n\text{X}_{3n+1}]_2 + \text{sulphur}
\]

Equation 2.4

where X can be oxygen or sulfur. As a result, a solid poly(thio)phosphate film becomes
deposited on the surface. If the substrate is made of steel, the poly(thio)phosphate will
react with the iron oxide native films and the abrasive iron oxide particles to form zinc
oxide and shorter-chain-length mixed iron/zinc phosphates, based on the principle of hard
/soft acids and bases suggested by Martin [21] in Equation 2.5. The presence of such a
mixed iron/zinc phosphates at the base of the tribofilm could promote the film adhesion
to the surface, as shown in Figure 2-7b. Wear debris generated in sliding can exist in two
different forms; either they act as three-body abrasents that can move freely between the
contacting surfaces which will lead to abrasion damage to both surfaces, or the wear
debris embeds in one surface, then abrades the other contacting surface. Furthermore, the
abrasive damage caused by the oxide wear particles to the contacting surface during
sliding can be eliminated.

\[
5\text{Zn}(\text{PO}_3)_2 + \text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_2\text{Zn}_2\text{P}_{10}\text{O}_{31} + 2\text{ZnO}
\]

Equation 2.5
As reported in reference [80], the hardness of iron oxides including hematite, magnetite and wüstite are twice that of zinc oxide in Moh’s scale. The digestion of hard iron oxide debris through Equation 2.5 into the polyphosphate glass can relieve the abrasive wear significantly. In this circumstance, the polyphosphate glass acts as a reservoir for iron oxide, as the tribochemical reaction proceeds, the reservoir ability of the polyphosphate glass declines and the exchange reaction will be stopped at a certain degree of the digestion process. The dissolution of iron oxide into the polyphosphate is endothermic, thus it needs the initial energy produced by the friction process, such as high pressure/shear stress and frictional heating.

Triofilm consists of iron phosphate compounds are generally known for the excellent wear resistance ability [81]. Optimum antiwear protection is achieved when a film of iron phosphate and polymerized hydrocarbon are formed at high temperatures and pressures of frictional surface contacts, as shown in Figure 2-7 [82]. It has been acknowledged that this triofilm has a smart tribological characteristic when exposed to different conditions when the Fe-Zn polyphosphate undergoes interesting transformations under high pressure [68, 83, 84]: The structure of the material is transforming from tetrahedral coordination at low pressure to octahedral coordination of ions at high pressure. The transformation leads to the formation of new ionic structures, which improves substantially the material properties such as mechanical strength and elasticity as compared to the structure at low pressure.
2.2.2 Study of inorganic glass as high temperature lubricant

The tribofilm formation pathway of ZDDP antiwear additive discussed in section 2.2.1 provides some enlightenment to the research of polyphosphate glass at high temperature. The following part mainly discusses some literature investigation of glass lubrication at high temperature (above 600°C). In 1965, Grau et al. [85] proposes a form of high temperature inorganic glass to lubricate the hot metal working, which was composed of inorganic alkali, ammonium and potassium polyphosphates. The researchers suggest that inorganic glass lubricant containing insoluble glass, such as alumina glass should be avoid because it is extremely difficult to be removed from a metallic surface. These same disadvantages are also present when using silicate glasses or slags as high temperature lubricants. Such lubricants require a post treatment by sandblasting or pickling treatment with hydrofluoric acid. A polyphosphate mixture consists of sodium polyphosphate and potassium dihydrogen phosphate was used as a high temperature lubricant [61] and it was found that the coefficient of friction lubricated by alkali polyphosphate is reduced although the wear rate increases with temperature. However, the rise of wear rate with temperature was significantly modest compared with an unlubricated tribopair. An US patent [46] suggested that for hot forming of metals, a combined alkali and divalent or trivalent metal phosphate lubricant can improve lubricating properties and show little attack on the workpiece compared with other known high-temperature lubricants. However, divalent or trivalent metal phosphate normally has a low water solubility and high melting point, as shown in Table 2-2, thus, their dispersion and transportation to the working area can be a challenging issue. Kong [86] conducted hot rolling tests with the
lubrication of alkali polyphosphate at various temperatures from 600~800°C, and claimed that the rolling force can be reduced by 24.7%. The researcher proposes that the alkali polyphosphate melts into a uniform fluid covering the steel surface, and displays a liquid behavior in the valleys of the surface under contact. When the alkali polyphosphate digested oxide wear particles in the tribofilm, a mix film lubrication regime was produced. A lubrication film with a mean thickness of 50~100 nm was suggested to be responsible for this significant force reduction.

Table 2-2 Melting point and water solubility of phosphate compounds from reference [87]

<table>
<thead>
<tr>
<th>Phosphate</th>
<th>Temperature (°C)</th>
<th>Water solubility (weight of phosphate per 100g water)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg₃(PO₄)₂</td>
<td>1357</td>
<td>insoluble</td>
</tr>
<tr>
<td>Ca₃(PO₄)₂</td>
<td>1820</td>
<td>insoluble</td>
</tr>
<tr>
<td>Ba₃(PO₄)₂</td>
<td>1620</td>
<td>insoluble</td>
</tr>
<tr>
<td>Zn(PO₄)₂</td>
<td>1060</td>
<td>insoluble</td>
</tr>
<tr>
<td>AlPO₄</td>
<td>2000</td>
<td>insoluble</td>
</tr>
<tr>
<td>Pb₃(PO₄)₁₂</td>
<td>1014</td>
<td>insoluble</td>
</tr>
<tr>
<td>Na₃PO₄</td>
<td>1583</td>
<td>soluble</td>
</tr>
<tr>
<td>FePO₄</td>
<td>1000</td>
<td>low</td>
</tr>
<tr>
<td>CrPO₄</td>
<td>1850</td>
<td>Insoluble</td>
</tr>
<tr>
<td>Ca₂(PO₄)₃</td>
<td>/</td>
<td>insoluble</td>
</tr>
</tbody>
</table>

- Insoluble - less than 0.01g per 100g of distilled water;
- Low - low solubility represents 0.01-1g per 100g of water;

Table 2-2 lists the melting point and water solubility of different phosphate-based compounds. It indicates that phosphate compounds with a two- or three-valent cation tends to possess a high melting temperature in excess of 1000°C and a low water solubility less than 1 g per 100 g water. These shortcomings pose significant challenges
to their application to hot rolling, where the lubricant was normally transported to the roll bite through a spray nozzle, as shown in Figure 2-1b. Furthermore, these compounds are in a solid state when being transported into the roll bite due to their high melting point. Thus their lubricity and antiwear function will remain questionable. Based on the above-mentioned disadvantages, only one valence alkali phosphate is considered in this thesis.

The friction coefficient is affected significantly when inorganic glass was used as a high temperature lubricant. As mentioned above, these glass lubricants can operate in the viscous state at elevated temperatures, and shear easily within tribological contacts. A lubricated contact can be divided into three lubrication regimes based on the Stribeck curve, which was determined by the parameters of the operating condition (sliding speed and normal load) and lubricant (viscosity). The ratio of \((\text{sliding speed} \times \text{viscosity/normal load})\) was defined as \(U\). When the parameter \(U\) is at a low value, \(i.e.\) a low speed, low viscosity or a high load, the lubrication is in boundary lubrication (BL) regime where the load is predominantly carried by the asperities of contact surface and the friction is governed by tribo-boundary films formed on the asperities. With the further deterioration of normal load or sliding speed, the protective tribo-boundary film will collapse resulting in a sharp increase in friction on the rubbing solid surfaces, \(i.e.\) dry sliding. With the increase of the \(U\) parameter, a hydrodynamic pressure begins to build up in mixed lubrication region where a part of the load is also carried by the lubricant film. When the \(U\) parameter is further increased, the hydrodynamic lubrication film is then developed, and the load is carried entirely by the oil film.
Matsumoto et al. [40] investigated sodium silicate glass under a wide range of conditions (temperature, load and speed). The result indicates that the lubricity ability of the glass lubricant is strongly dependent on the state of glass, which is significantly influenced by temperature. The obtained friction coefficient shows a ‘V’ shape trend at 1000°C when the applied load is increased. The increase of friction at high load is attributed to the occurrence of seizure. When the temperature increases, sodium silicate melt film becomes thinner, and was completely removed at 900°C. Friction-temperature investigation of sodium silicate glass applying to the stainless steel surface reveals that it showed a peak friction coefficient near the softening point, then decrease above that temperature [52]. The peak friction is produced that when the lubricant becomes softer, the adhesion to each tribo-surface become stronger, and consequently the area that has to be sheared becomes larger leading to an increase in friction. However, the phenomenon disappears completely, when sodium silicate lubricant was introduced into a boron nitride interface. This suggests that there is a good correlation between frictional behavior and wettability; when the molten lubricating material shows poor wettability on the solid surface, the
friction curve shows no rises and fall. However, when the wettability improved, the friction curve shows both a peak and a drop.

Studies also show that the chemical durability can be drastically improved by properly adding small amounts of one or more oxides, such as Al\textsubscript{2}O\textsubscript{3}, B\textsubscript{2}O\textsubscript{3}, and Fe\textsubscript{2}O\textsubscript{3}, to the phosphate glasses [88-90]. To improve the antiseizure ability, it is recommended that iron oxide particles be added to silicate lubricant to improve its ability of anti-seizure. Sodium silicate containing 20~40\textit{w.t.}\% of iron oxide is proposed in the US Patent 8024953 [91] to lubricate a guide shoe in the production of seamless pipe. The combination of iron oxide and sodium silicate displays an excellent lubricity. Furthermore, sodium silicate also shows low corrosive attack on the workpiece and tool at high temperature. Patent JP04331292 [92] designed a glassy lubricant for hot tube rolling with a viscosity of 0.20~5 poises by dissolving or dispersing metal oxide powder, dispersant and/or thickener in sodium silicate aqueous solution to improve the anti-seizure property. It was proposed that sodium silicate is an essential component which can bring iron oxide into the friction interface due to its superior function of digesting particles of iron oxide. However, their relative ratio is strictly limited due to the consideration of viscosity and suppliability.

The lubricity performance of lead borate glass with different concentration of PbO was investigated [47], and the friction coefficients measured by virtue of a ball-on-disc machine at temperatures up to 700°C is shown in Figure 2-9. By varying the relative amount of PbO and B\textsubscript{2}O\textsubscript{3}, the glass transition and viscosity of the glass is varied. These frictional tests are performed below the corresponding melting point. For the glass
containing 88% PbO, a friction coefficient at 0.25 is obtained at 540°C. As the temperature cool down, the friction coefficient firstly decrease to a value of 0.14 at 480°C, then increase sharply to above 0.80 at 416°C. As the temperature continue to decrease, the friction coefficient decrease again, becoming approximately constant at 0.4-0.5. It is reported that the pronounced peak friction coefficient is at the temperature close to the softening point of glass, whereas friction decreases sharply if the temperature exceeds the softening point, due to the fluid film lubrication [52]. It is also observed the oxides debris generated in the sliding process is continuously dissolved into the glasses at its molten state, which increases significantly the viscosity of the melt. As a result, the friction coefficient is also affected by the sliding time. In Figure 2-9, the “initial” represents the friction coefficient at the beginning of the sliding, and the “final” denotes that at the end of the sliding. It can be seen that the initial friction coefficient is slightly lower than that at the final stage. The two curves in Figure 2-9 display similar shapes, but the turning points are at different temperatures. This suggests that the frictional behavior of glasses present a similar regularity with temperature, and the relative position was determined by the ratio between metal oxide and glass forming oxide. Lead element is now one of the principal environmental threats, and widespread lead poisoning is the chief environmental health issue [49]. Therefore, the use of lead element in lubricant should be avoided.
Another proposed lubricant for the working of low melting alloys was glasses containing alkali metal oxide and polyphosphate. Soluble potassium polyphosphate has the characteristic of rendering a solution viscous which can then be easily and uniformly applied to working surfaces. After the water has evaporated, the remaining residue melt will also be viscous but will have a different viscosity than the original solution, and will adhere readily to the surface. Such glasses are virtually insoluble in water when high valent metal oxide is added. Furthermore, it is quite difficult to remove high-valent metal glass lubricant from a metallic surface. These disadvantages are also present when using silicate glasses or slags as high temperature lubricants which require a post mechanical treatment by sandblasting or acid pickling. Further, the use of such enamels and glasses requires the prior descaling of the metal surface.

Tieu et al [61] adopts a continuous feeding of alkali polyphosphate lubricant into the tribo-interface of steel/steel at 600–800°C to achieve a boundary lubrication, where a substantial reduction in friction and wear by around 40% and 60%, respectively were
obtained. The FIB/STEM examination of the cross section of wear track on disc reveals a polyphosphate film thickness of 50-100 nanometers covering the tribo-surface.

The test conditions and the tribo-systems in the publications differ widely in the literature. The tribological performances and environmental friendliness of these glass lubricants are compared listed in Table 2-3, where ‘√’ represents ideal, ‘×’ represents non-ideal.

Table 2-3 Comparison of phosphate-, silicate- and borax based high temperature glass lubricant

<table>
<thead>
<tr>
<th></th>
<th>Borax</th>
<th>Silicate</th>
<th>Phosphate</th>
<th>o/w emulsion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Friction</td>
<td>√</td>
<td>√ [94]</td>
<td>√</td>
<td>√</td>
</tr>
<tr>
<td>Wear</td>
<td>√</td>
<td>√</td>
<td>√</td>
<td>unclear</td>
</tr>
<tr>
<td>Adherence</td>
<td>√</td>
<td>× [40, 94]</td>
<td>√</td>
<td>√</td>
</tr>
<tr>
<td>Antioxidation</td>
<td>√ [60]</td>
<td>√</td>
<td>√</td>
<td>Unclear</td>
</tr>
<tr>
<td>Toxicity</td>
<td>×</td>
<td>√</td>
<td>√</td>
<td>×</td>
</tr>
<tr>
<td>Economical</td>
<td>×</td>
<td>√</td>
<td>√</td>
<td>×</td>
</tr>
</tbody>
</table>

Based on the above summary regarding tribology for hot metalworking, and the lubricity of inorganic glass lubricants, some questions are still remained unanswered, which need to be studied further. For instance, in the area of high temperature tribology with the lubrication of inorganic glass, not much work has been done to explain the working mechanisms of glass lubricant in friction and wear reductions. In the literature survey, very little information was found to reveal the structure and component of the glass film.
2.2.3 Lubrication in hot rolling

2.2.3.1 Harsh tribological conditions at the contact zone

Hot rolling takes place above the recrystallization temperature of the metal in which metal plate is deformed through multi-pass hot rolling to reduce the thickness uniformly. In hot rolling, the hot strip mill is comprised of three independent components: the roll, the rolled strip and their contact interface. The most critical one is the interface which experiences harsh tribological conditions which are affected by material properties, process parameters and lubrication conditions. In the contact, the surface of work roll is rapidly heated up to around 650°C while in contact with hot steel strips within just 10\(^2\)~10\(^3\)s, and subsequently cooled by water to around 40°C during the same cycle [34]. The roll/strip interface are subjected to extremely high pressure (<1GPa), high temperature (600~1100°C) and high rolling speed (<10 m/s), the roll/strip interface inevitably experiences high friction and wear leading to severe surface degradation, even premature failure of the roll and an undesirable surface quality to the product [34, 91].

The primary scale formed in the reheating furnace undergoes descaling before entry to rough rolling; however, a secondary oxide scale develops promptly on the hot surface. The secondary oxide scale will fracture because its thermal conductivity is 10-15 times lower than that of the steel substrate [95], and the fractured oxide scale will cause undesired interfacial phenomena. The hot metal will be extruded through the cracked oxide scale under the high pressure to contact the cold roll surface and may cause adhesion problem as shown in Figure 2-10 [96] which illustrates the complexity and interdependence of the phenomena at the contact between a cold roll and a hot strip. As a
result, the conditions at the interface vary from location to location, thus affecting the coefficient of friction and heat transfer. These cracks formed in the oxide scale were due to the applied strain on the steel surface when the hot strip enters the roll gap [97].

![Schematic diagram of (a) friction forces along the arc and (b) the working interface between cold roll and hot steel strip during hot rolling of steels [96].](image)

The temperature of hot slabs/strips can be at between 800 and 1200°C as the heat between the rolling passes may be lost through different types of heat transfer such as convection, radiation, etc.. As a result, the surface of the work roll can be heated up by the heat transferred from the hotter strip to the work roll when they are in contact. The working temperature of hot rolls can easily exceed 600°C, although the flash temperature could rise above 800°C due to the heat generated by friction [98]. However, it is quite difficult for researchers to directly measure the surface temperature of the work rolls by means of contacted thermocouples or other measurements. The heat transferred from the strip to the work rolls provides the energy for the work roll surface to become oxidized, which in turn affects the surface profile of the work rolls [25]. For instance, investigations of surface topography of high speed steel roll after oxidation at different temperatures in both dry and moist air were conducted by Qiang et al. [99]. The results
show that the roughness of the surface increased significantly from an Ra of 100 nm at 550°C to 400 nm at 700°C, which suggests that the oxidation temperature has a significant influence on the oxidized surface topography of HSS roll.

The stresses within the layer of scale during a rolling pass, are complex. They include the compression normal to the surface by the roll pressure, the tension caused by the elongation of the strip in the direction of rolling, the interfacial shear stress between the roll / scale layer and the adhesion/bonding strength between the scale/ strip substrate. The deformation of oxide scale at the interface can affect the rolling process and product quality in significant ways, depending mostly on its mechanical attributes: its resistance to deformation, ductility, strain and strain rate sensitivity. Shaesby and Matsuno [100] suggested that the dominant appearance of wüstite in the oxide scale on the surface of steel strip contributes to the friction in hot rolling, because wüstite exhibits a considerable amount of plastic deformation before fracture when subjected to compression. Furthermore, sliding occurs easily in the soft wüstite layer that possesses a relatively lower melting point (1377°C) than hematite and magnetite layers (1566 and 1864°C respectively). Moreover, the wüstite also can interact with silicon oxide formed by the oxidation of Si element in the steel to form eutectic fayalite (2FeO.SiO$_2$) with a much lower melting point of around 1200°C. In addition, the formation of iron oxide layers on a steel surface can reduce the friction since the reactivity of the surface is reduced and it becomes less prone to form atomic junctions with mating surface. Although the properties and the deformation of oxide scale exert remarkable effect on the surface finish
qualities and the friction, the tribological behaviors of the scale or scale and lubricant are still not understood sufficiently.

2.2.3.2 Oil-in-water emulsion lubrication in hot rolling

Currently, the widely used water-based lubricant in hot rolling is oil-in-water (o/w) micro-emulsions, which is known to reduce the rolling force by around 5-8% [101, 102] and the tertiary scale thickness by around 51% [103]. A large number of researches have been carried out to elucidate its working mechanism, which were summarized and discussed in this section.

Figure 2-11 Schematic diagram of roll bite conditions with the lubrication of o/w emulsion in practical hot rolling

Figure 2-11 shows a schematic of the contacting interface condition in hot rolling with o/w emulsion. A temperature simulation shows that the thin oil film is expected to be in a boiling state, which can form a thin vapor film at the interface. The lubrication is consisted of a boundary and mixed lubrication regions, and the produced oxide debris can produce a three-body roll wear in hot rolling. Lenard et al. [104] has investigated the
influence of process and material’s parameters on the friction coefficient and rolling force for low carbon steel strips lubricated by o/w emulsion. The results show that the significant parameter is the thickness of the oxide scale layer between the rolled stock and the work roll. This is in agreement with the majority of observations: thicker scales produce a lower friction. It also reveals that the oxide scale experienced more strains than did the bulk rolled strip whose strength increased with reduced temperatures. Sun et al. [29] also investigated the effect of hot rolling parameters, including reduction, rolling speed and entry temperature on the friction coefficient under four lubrication conditions (dry, water, o/w emulsion and pure oil) by inverse calculation based on the experimental roll loads. The result shows that under all conditions the friction coefficient decreases as the rolling speed increases and the reduction decreases. However, under dry conditions the entry temperature has a diverse influence on the friction coefficient, which increases with a reduction of entry temperature. When o/w micro-emulsion was used, the influence of temperature on friction coefficient is not regular. Reference [29] also suggests that rolling speed displays an influence on the rolling force. Under most circumstances as the rolling speed increases, the roll forces decreases. When the rolling speed increases, the material’s resistance to plastic deformation also increases due to strain rate hardening. The shorter contact times decrease the heat flux from the strip to roll, which in turn keeps the hot strip at high temperature and a corresponding low strength. Under this case, the roll temperature is likely not rising as much as it did at slower speeds, which correspond to an increase in the strength of the rolled metal. Adding to these mechanisms is the availability of more lubricant, dragged in the roll bite by the moving surfaces at a higher
speed and causing a drop in the loads. Amnon et al. [105] conducted hot rolling experiments using low carbon steel strips, lubricated separately by water, \( \text{o/w} \) emulsions, neat oil and dry conditions. The results show that the rolling loads was reduced the most with the lubrication of the 1:1000 oil-to-water mixtures. Further increasing the oil volume did not create any further load reductions. This finding is aligned with the results obtained by Azushima et al. [106], who investigated the influence of the emulsion concentration on the friction coefficient in hot rolling. The results indicate that the friction coefficient decreases as the emulsion concentration increases up to 1%, but becomes unchanged when the emulsion concentration exceeds 1%. In this study [106] it is explained as that the friction coefficient in hot rolling decreases with a thicker oil film because the lubrication film is dominant in the contact, as shown in Figure 2-12b. However, when the oil film in the interface reaches a certain value, the friction coefficient becomes almost unchanged. In this case, the entire contact interface is covered by the lubrication film, as shown in Figure 2-12a.
Matsubara et al [45] suggests that the lubrication area in hot rolling consists of two areas; a direct dry contact of asperities of the work roll and the workpiece, and a boundary lubricated contact where the work roll contacts the workpiece through an oil film. The total friction coefficient can be expressed by the combination of these two areas, as shown in Equation 2.6.

\[ \mu = \alpha \mu_d + (1 - \alpha) \mu_b \]  

Equation 2.6

Where, \( \mu_d \) and \( \mu_b \) represent the friction coefficients generated in dry and boundary lubrication conditions, respectively. The parameter \( \alpha \) is the dry contact area percentage in the whole contact area, it declines with the rise of oil concentration in o/w emulsion.

The lubrication mechanisms of o/w emulsion in hot and cold rolling have been compared in reference [45]. The ratio of fluid lubrication becomes larger with an increase of the oil
film thickness in cold rolling. As a result, the friction coefficient will decrease and the oil-pits are formed.

However, a different circumstance was found in hot rolling where the friction coefficient declines substantially if even a thin oil film exists at the roll/strip interface to lubricate the direct sliding. However, the further decrease of friction coefficient will not occur even though the thickness of the lubricating oil film is increased. The oil-pits will also not be formed, either. This is because the extreme high temperature at the roll interface makes the viscosity of oil fluid film extremely low, and the oil film loses significantly its hydrodynamic behavior. In summary, the fluid lubrication regime can take place in cold rolling, but not feasible in hot rolling [45].

In spite of the extensive application of o/w micro-emulsions in hot rolling, several drawbacks were also attached, such as tendency to form phase segregation, significant disposal treatment cost and bio-instability. In addition, many forming oils are hazardous to the working environment. Therefore it is highly desirable to replace them with more environmentally friendly rolling lubricants, among which inorganic glass have attracted a lot of attention.

2.3 Main aims in this thesis

Based on the above literature summary, there are several questions that remain not sufficiently understood, and need further investigation. The principal objective of this thesis is to provide a novel and improved understanding of the working mechanism of inorganic glass lubricant at high temperature interface.
Chapter 3 is designed to compare frequently used lubricants using pin-on-disc and hot rolling to determine whether sodium polyphosphate glass has an advantage in friction and wear reduction over other lubricants. Chapter 4 compares the effect of chain length of sodium polyphosphate on the tribological performance and explains the tribo-chemical interactions at the tribo-interface. Chapter 5 studies the effect of load on the lubricative performance of sodium metaphosphate, which has been proven to be the optimal glass composition in chapter 3 and 4. The structural evolution of tribofilm with the load was also revealed in this chapter. In chapters 3, 4 and 5 tribological tests were conducted with ball-on-disc machine, however as discussed in section 2.1.3, the tests cannot fully simulate the practical hot metal forming process, thus, chapter 6 is designed to conduct hot rolling test, and detailed characterization of the tribofilm was performed to reveal the nature of lubricating film and interfacial structure.
Chapter 3-Experimental instruments and analytical methodology

This chapter introduces the experimental equipment used in this thesis, which can be categorized into high temperature tribological machine, and the following characterized instrument.

3.1 High temperature tribometer

3.1.1 Ball-on-disc

As introduced above, the practical hot metal forming experiment normally is highly expensive and it is very difficult to study the tribological problem *in-situ*. Some lab-simulation equipment is needed to conduct some pre-elementary test, under which the experimental parameters can be controlled more precisely. Numerous test configurations have been built to simulate the operating conditions in the roll bite, such as disc-on-disc, ball/ball-on-disc and ring compression configuration, in which one simulates the hot strip, the other one simulating the roll. It should be noted that the correlation between simulated test methods and practice does not appear to have been established. In this
thesis, A UMT high temperature ball-on-disc machine, whose schematic structure was shown in Figure 3-1, was used to carry out laboratory unidirectional sliding experiments. Generally, the disc is used to simulate the workpiece, and the pin/ball simulates the roll. The disc was mounted onto a sample holder, which was fixed on the rotating shaft. The disc specimen is heated by a wire-wound furnace and the temperature of the disc was measured by a thermocouple underneath. The friction force is measured using a strain gauge force transducer. This tribometer is equipped with a computerized data acquisition and control system to control and collect the various parameters.

3.1.2 Heating furnace and hot rolling mill

![Figure 3-2 Picture of MoSi₂ tube heating furnace with four heating zones and the protection of nitrogen gas](image)

Figure 3-2 Picture of MoSi₂ tube heating furnace with four heating zones and the protection of nitrogen gas
Chapter 3-Experimental instruments and analytical methodology

Figure 3-3 Photos of 2-high Hille 100 rolling mill (a) before and (b) after rolling with the lubrication of inorganic lubricant.

Figure 3-4 Schematic diagram of cooling facility in a N₂-filled box to reduce the oxidation in cooling stage.

The heat treatment of mild steel specimens was conducted in a MoSi₂ tube heating furnace, which is connected to a N₂ bottle by hose, as shown in Figure 3-2. The furnace is divided into four zones with their separate heating element. The furnace is calibrated and the temperature stable zone is measured. Sample is firstly put at one end of tube furnace for 5 min waiting for N₂ to fill up tube furnace, then is pushed by a steel rod to the center of tube furnace for required time to ensure a homogeneous temperature distribution and a uniform scale thickness.
The rolling experiments of mild carbon steel plate were performed on a 2-high Hille 100 rolling mill with rolls of 225 mm diameter and 254 mm roll body length as well as with a roll roughness (Ra) of 1.0 µm. The photos of the roll after being sprayed lubricant and after rolling were showed in Figure 3-3. The rolling mill was driven by a 56 kW motor, and the rolling forces were measured by load cells on the mill with a maximum load of 1500 kN and a torque of 12.7 kN·m. The rotation speed of roll can reach a maximum of 60 rpm, which correspond to a linear speed of 0.72 m/s. After hot rolling, the rolled samples were moved into a tank immediately, which was filled with inert N₂ to minimize the oxidation in the cooling stage. All experiments have been repeated to ensure repeatability. Representative samples have been selected for further study of the scale layers.

3.1.3 Comparison of hot rolling and ball-on-disc

Although high temperature ball-on-disc tribometer can simulate the hot rolling in some aspects, the conditions in practice bear little or no resemblance to those of the simulated sliding friction, such as:

- The contact pressure between ball and disc decreased continuously with sliding time, because the contact area increases with the wear of ball. This is not consistent with the rolling pressure in hot rolling, which almost is kept nearly constant during the hot rolling process.

- Temperature environment of the ball in high temperature ball-on-disc is different for the roll in hot rolling; in practical hot rolling, the roll was heated periodically
with a flash temperature of around 600-700°C. However, the ball has a stable temperature [9].

3.2 Analytical methodology

3.2.1 DSC-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 set to 10°C /min.

3.2.2 High temperature laser-confocal microscope

![Diagram of high temperature laser-confocal microscope](image)

Figure 3-5 Schematic illustration of high temperature laser-confocal microscope in a cross-sectional view [86].

High temperature laser scanning confocal microscopy (HTSCM) provides a powerful tool for *in-situ* observations of thermal behavior of glass and the corresponding reaction between glass and hot steel surface at high temperature. Figure 3-5 shows a cross-sectional schematic diagram of the microscope chamber and the position of specimen. Cube specimens with a dimension of 2.7×2.7×2 mm³ were cut from a mild steel strip.
One broad face of the cube specimen was polished and finished with 1 µm diamond paste. A minor amount of glass powder was then put on the polished mild steel, which was then placed into the chamber. These high temperature tests were conducted in natural air atmosphere for the purpose of closely simulating its real application. The morphology and glass state extracted from the real-time videos can provide important new information for the study of glass transformation at high temperature. One shortcoming with this equipment; highly rough surface was normally formed due to oxidation at high temperature, and the use of optical focus cannot provide a highly clear images. However, its impact on the observation is not vital.

### 3.2.3 Nanoindentation apparatus

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 range of ~100 mN with a designated distance between indents can be applied. The mechanical properties are acquired via the load-displacement curves using the initial slope of the unloading curves as proposed by reference [107]. After the nanoindentation tests, the indentations can be observed and imaged by an optical microscope and JSM-6490LA SEM, which enabled all the interesting features to be captured.
3.2.4 X-ray diffraction

![Diagram of X-ray diffraction principles and instrument](image)

Figure 3-6 (a) Principle of XRD phase identification (Bragg’s law) and (b) the GBC MMA XRD instrument used in this thesis

X-ray diffraction is a powerful method to identify the crystalline phases, even in multiple phases, by comparing the characteristic diffraction peak positions and intensities with standard crystalline phases. The principles for X-ray phase identification is based on Bragg’s law, shown in Figure 3-6a. The law suggests that the scattered waves in phase interfere in a constructive way and only produce diffracted beams in specific directions, which are determined by the characteristic parameter of the crystalline phase (interplanar distance $d$) and the X-ray wavelength ($\lambda$) produced by the XRD diffractometer. In other word, the relationship between wavelength of the X-rays and the interplanar distance of crystalline phase is built up through the Bragg’s law [108]. The crystalline distance is a characteristic of phase. As a result, the specific phase can be identified in a mixture.

The GBC MMA XRD equipment was used in this thesis to analyze the specimen, which was controlled by Visual XRD software. The measurement was conducted under a step size of 0.02°, and the X-ray wavelength is 1.54 nm.
3.2.5 Lv-6490LA SEM

The JEOL JSM-6490Lv SEM in Figure 3-7 located in Electron Microscope Center in University of Wollongong is a 30 kV conventional tungsten filament scanning electron microscope with variable pressure adjustment. The SEM is well designed for elementary surface morphology and structural imaging. The maximum resolution can reach 3.5 nm at 30 kV.

Quantitative micro-analysis and elemental mapping can be performed through the large area EDS detector. The signal of the EDX is collected by virtue of the Oxford instruments SDD energy dispersive detector. Integrated AZtecSynergy software suite is used for the post EDX analysis. In this thesis, this SEM is generally used to take images of wear scars and corresponding elemental analysis.
3.2.6 Scanning Transmission Electron Microscope (STEM)

STEM is substantially powerful in atomic resolution imaging and nanoscale characterization. Different from conventional transmission electron microscope, where the imaging is usually performed by electrons passing through a sufficiently thin specimen, approximately a hundred nanometers thick, the electron beam in STEM is focused to a well-defined probing spot, which is then scanned over the thin specimen through a raster \[109\]. The rastering of the beam scanning across the sample makes it suitable for analytical techniques such as bright field micrograph, which are imaged by collecting electrons scattered through small angles, high-angle annular dark-field image by collecting the large-angle scatter electrons, which can reveal the mass variations, spectroscopic mapping by energy dispersive X-ray (EDX) spectroscopy, or electron energy loss spectroscopy (EELS). These signals can be collected simultaneously, and are capable of direct correlation between images and spectroscopic information.

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 both bright field (BF) and high-angle annular dark-field imaging (HADDF) mode. The large area SDD EDS detector permits the STEM to conduct elemental mapping with an atomic resolution. The analysis of EDX data is performed using a JEOL 100 mm² X-ray detector coupled to a Noran System Seven (NSS) analysis system.
3.2.7 Focused Ion Beam (FIB)

Figure 3-8 Photo of FEI NovaNano lab 200 focused ion beam (FIB) miller

The thin TEM specimens of phosphate film on the ball are prepared by FEI NovaNano lab 200 focused ion beam (FIB) miller in Figure 3-8. The apparatus combined a high resolution focused ion beam (FIB) and a high resolution field emission scanning electron microscope (FESEM). The dual beam FIB has a built-in platinum gas injection system, which enables to form a thin layer of Pt deposition on the top of region of interest (ROI). It can be done slowly with the electron beam without any beam damage, or quickly with a wear ion beam with controllable damage on the top surface. A foil specimen with a size of around 6 (length) ×5 (width) ×<0.1µm (thickness) µm was milled in the thesis, which was then analyzed by high resolution STEM. The dual beam is also coupled with an Oxford Aztech EDS (X-ray) system. It is used to acquire X-ray emission spectra from the ROI, which enables elemental compositional and phase analysis.
3.2.8 X-ray Photoelectron Spectroscopy (XPS)

XPS, also known as Electron Spectroscopy for Chemical Analysis (ESCA), is a frequently used surface analysis technique due to its simplicity in data collection and interpretation. The schematic principle of XPS, i.e. Photoelectric effect, was shown in Figure 3-9. The sample is usually irradiated with a focused monochromatic X-rays activating photoelectrons to be emitted from the sample surface. Then electron energy analyzer was used to determine the kinetic energy of photo-emitted electrons, and then the binding energy can be calculated on the basis of Equation 3.1. From the binding energy, some chemical information can be obtained in the aspect of the elemental composition on the top surface (~ 5 nm usually), chemical or electronic state of each element in the surface, uniformity of elemental distribution across the surface etc.

\[ E_b = E_p - (E_k + \phi) \]

Equation 3.1
Where $E_b$ is the binding energy of the electron, $E_p$ represents the X-ray photon energy applied, $E_k$ denotes the kinetic energy of the electron. $\Phi$ is the work function relating to the spectrometer and the material.

In the 1970s, XPS was firstly used to analyze polyphosphate glass [66]. It was reported that that the O 1s signal can be deconvoluted into two components: one component is assigned to the bridging oxygen atom (BO), such as ($\alpha$) oxygen atom in Figure 3-10, the other component is designated as the non-bridging oxygen atom (NBO), i.e. $\beta$ oxygen atom in Figure 3-10, which includes two types of terminal oxygen atoms, P=O and P–O–M. The chemical shift between P=O and P–O–M signals is too small, and XPS spectrometer cannot distinguish the shift, consequently, a single peak labeled as NBO is usually used in XPS curve-fitting procedures to denote P=O and/or P–O–M. The signal intensity ratio of the BO/NBO can be used to distinguish the chain length in polyphosphate glasses, which was widely recommended in publications [111, 112].

![Figure 3-10 Bridging and non-bridging oxygen in polyphosphate glass [113]](image)
3.2.9 X-ray Absorption near Edge Structure spectroscopy (XANES)

XANES was routinely used to study the complex tribo-chemical interactions between ZDDP anti-wear additives in engine oil and metallic surfaces during the rubbing. The chemical and structural information of the formed tribofilms can be revealed by XANES in detail [79, 114-116]. XANES is a mature analysis technique to determine the chemical and structural information at different depth, which depends on the sensitivity of different signal on the depth. XANES analysis provides two modes of detection: total electron yield (TEY), which is a surface sensitive technique, has a depth sensitivity of ~5 nm, and fluorescence yield (FY) has a depth sensitivity of over 60 nm. Many publications studied the relation between the intensities ratio of peak a/c and the chain length of polyphosphate to reveal that a larger a:c ratio is an indication of a longer polyphosphate chain length [111, 117, 118], one of which was shown in Figure 3-11. The assignment of the transitions represented by these peaks is beyond the scope of the thesis, and has been discussed in other references [111, 119]. In this thesis, XANES is mainly used to characterize the chain-length of polyphosphate film inside and outside the wear track. XANES data was collected at the soft X-ray spectroscopy beamline of the Australian Synchrotron in Melbourne, which was described in detail in Chapter 5.
In this thesis, a synchrotron-based light source in Australian Synchrotron, Melbourne was used to conduct XPS and XANES analysis. Compared to lab-based X-ray sources, the most significant advantage of Synchrotron radiation is its brilliance, the brightness and angular spread of the beam, which is more than a billion times higher than a lab-based X-ray. Furthermore, synchrotron light also has a higher energy beam and small wavelengths, which permits a deeper penetration into sample and study of tiny features, such as molecules bonds, nanoscale target.
3.2.10 Comparison of analysis equipment

The advanced analysis equipment is compared in Table 3-1. The differences in information depth can provide a technical method to investigate the chemical information at different depth.

Table 3-1 A comparison of analyses instruments

<table>
<thead>
<tr>
<th>Equipment</th>
<th>Depth of information</th>
<th>Types of information</th>
<th>Surface or bulk</th>
<th>Detection limits</th>
</tr>
</thead>
<tbody>
<tr>
<td>XANES</td>
<td>Total Electron Yield: ~ 5nm</td>
<td>State of oxidation; Structure; Chain-length of polyphosphate glass;</td>
<td>TEY: Surface FY: Bulk</td>
<td>5%</td>
</tr>
<tr>
<td>XPS</td>
<td>~5 nm</td>
<td>State of oxidation; Chain-length of polyphosphate;</td>
<td>surface</td>
<td>0.1 atom%-1ppth</td>
</tr>
<tr>
<td>EDS</td>
<td>1000–3000 nm</td>
<td>Elemental distribution;</td>
<td>Bulk</td>
<td>0.1 atom%-1ppth</td>
</tr>
<tr>
<td>XRD</td>
<td>100-10000 nm</td>
<td>Crystalline structure; Phase identification;</td>
<td>Bulk</td>
<td>1%</td>
</tr>
<tr>
<td>FIB&amp; STEM</td>
<td>~7 µm</td>
<td>Morphology; Elemental distribution</td>
<td>Surface and Bulk</td>
<td></td>
</tr>
</tbody>
</table>
4 Investigation of inorganic chemical compounds as hot rolling lubricant

4.1 Introduction

Tribological research at tool/workpiece interface in hot metal forming has received a growing attention to reduce the energy consumption and prolong the service life of tool. In hot metal forming, the steel workpiece is normally heated to temperatures up to 1200°C in the austenite region and then subsequently deformed under a high pressure and shear stress when in contact with a colder tool. In hot metal forming, the high speed steel (HSS) tool has a microstructure composed of primary carbides (10-20 vol.%) distributed in a matrix of tempered Martensite and secondary carbides [120, 121], which allows the HSS tool to retain a high level of hardness at elevated temperature [122]. The tribology between the HSS tool and hot workpiece is critically important in determining the wear, surface quality and dimension tolerance of tool, which in turn determines the quality of workpiece. The literature on tribology at elevated temperature [6, 16, 17] shows that the formation of a glaze layer can reduce the friction and tool wear significantly. However, the undesirable damage to the tool and changes to the geometry of workpiece material caused by oxide layer and particles still occur at high temperature [17]. Furthermore, the fact that nascent surface generated from plastic deformation will be chemically active implies that the propensity for material transfer to the rolls is very strong. Currently, in order to manufacture fine-grained steel sheets, hot rolling with a large reduction is commonly conducted. As a result, tribological problems such as high
rolling force, increased roll wear, material transfer etc. will become worse. Thus, an application of appropriate process lubricants is essential to optimize the metal forming process. At present in the hot forming industry, water-based oil-in-water (o/w) micro-emulsion and graphite suspension are commonly used. These two lubricants possess acceptable lubricity. However, they have caused cleanliness and environmental concerns. For example, the decomposition of organic oil at high temperature can produce harmful smoke to the working environment [38, 44]. Therefore, there is a high demand to replace them with environmentally friendly inorganic lubricant, such as glass and layered solid lubricants.

Alkali inorganic polymer glass including alkali phosphate and borate etc. have been applied successfully in hot metal forming, e.g. hot drawing, hot extrusion [57] and hot forging [123]. These inorganic chemical compounds came from naturally abundant minerals, has a low manufacturing cost, little health or environmental issues. Furthermore, inorganic glass can also be applied as an aqueous solution, which at high working temperature transforms into a highly viscous fluid after the evaporation of water. Such a viscous melt can withstand the high pressure by forming a thin and easily sheared viscous film between the tool/workpiece interfaces. In addition, the glass lubricant can operate over a wide range of temperature because it can melt progressively and continuously [48]. However, information about their effective application is quite limited. Peterson et al. [47] studied the tribological performance of lead borate glass with different PbO/B₂O₃ ratio as a function of temperature by pin-on-disc. The result shows that the friction trends with temperature are similar but the changes in friction are affected by the ratio. Furthermore, it was also pointed out that the viscosity of molten
glass increases with time because these glasses dissolve the oxide from the surface. Tieu et al. [61] adopts a continuous feeding of alkali polyphosphate lubricant into the tribo-interface of steel/steel in the pin-on-disc tribotest at 600~800°C to achieve a boundary lubrication with a substantial reduction around 40% and 60%, respectively in friction and wear. The FIB/STEM examination of the wear track reveals a thin polyphosphate film in the nanoscale covering the tribo-surface. Matsumoto et al. [40] investigated sodium silicate glass with pin-on-disc under a wide range of conditions (temperature, load and speed) and found that the lubricant has its optimal working conditions with the temperature having the most significant influence on its lubricity performance. These papers investigated the glass lubricant under a wide variation of tribological parameters, including the modes of lubricant supply, temperatures, loads and speeds etc. However, its tribological performance in hot rolling is still not clear, as indicated in section 3.1.3 that the lab-scale tribometer can hardly simulate all the complex working conditions in hot rolling. Thus, a combination of laboratory simulation and hot rolling is needed to enhance the knowledge of tribological behavior of inorganic lubricant in rolling contact and provide an effective guidance for the hot rolling process in practice.

In hot metal forming, the steel workpiece is normally heated to temperatures between 600~1200°C in a protective atmosphere, where it was in the austenite region with a low hardness and excellent ductility. Subsequently, cold tool deforms the hot workpiece with a high pressure and shear stress. The tribology between the tool and hot workpiece is critically important in determining the wear, surface quality and dimension tolerance of tool, which in turn determines the quality of workpiece. The high temperature tribology occurred at the interface of tool/workpiece is very different from cold forming at low
temperature, and is much more complex with changes in mechanical properties and microstructure, surface oxidation of steel etc. All these changes will exert significant influence on its tribological performance. High temperature tribology research [16, 17] shows that the formation of glaze layer can greatly reduce the friction and tool wear. However, the undesired damage of the tool and wear of deformed workpiece material caused by formation of oxide particles still occurs at high temperature. Currently, in order to manufacture fine-grained steel sheets, hot rolling with a large reduction is commonly conducted. As a result, tribological problems such as high rolling force, increased roll wear, material transfer etc. will become worse. All of these indicate that the selection of appropriate process lubricants on tool steels is essential to optimize the metal forming process. At present, water-based oil-in-water (o/w) micro-emulsion and graphite suspension are widely used in practical hot forming industry, due to their acceptable lubricity. However, they have caused great cleanliness of workshop and environmental concerns. For example, the burn and decompose of organic oil at high temperature produce harmful smoke to the workers. Furthermore, whether the oil can form an effective lubrication film also remains doubtful, because a long residual time in the contact would burn the organic compounds and the redundant oil outside the interface also turn into pseudo-solid. Therefore, there is a high demand to replace them with environmentally friendly prospective inorganic lubricant, such as glass and layered solid lubricants.

This chapter investigated the tribological performances of different inorganic chemical compounds including sodium phosphate, borate as well as layered talc powder and oil-in-water emulsion as high temperature lubricant, for the purpose of exploring their possible
application in hot metal forming. Ball-on-disc and hot rolling apparatus were used to conduct these tribological tests, separately. Their performances in lubricity, antiwear ability, anti-oxidation versus temperature and their working mechanism were compared by both the ball-on-disc tribometer and an experimental hot rolling mill.

4.2 Experimental details

4.2.1 Materials

The selected oil purchased from Quaker Company is a specially designed for hot rolling process, which may comprise of base oil, emulsifier, sulfurized ester and also conventional additives such as free fatty acids like oleic acid, stearic acid, antioxidant containing amine, phenolic group, silicone containing antifoam. The oil was diluted with distilled water with the volume ratio of oil in water is 1:100 as suggested by Sun et al. [28]. Magnetic stir was used to facilitate the dissolution of 20g alkali inorganic chemical compounds in 80 ml distilled water forming the transparent solutions of 20w.t% concentration. The component was weighed on a balance that provided measurements accurate to ±0.001 g. As borax was found to be an excellent solid antiwear additive at low temperature [124, 125], therefore, its performance at high temperature is also investigated in this chapter. For the borax (Na₂B₄O₇·10H₂O), it can only be dissolved into distilled water to a maximum of 5%. This value is very close to the one reported in reference[126].

4.2.2 High temperature ball-on-disc tribotest
Table 4-1 Chemical composition of mild steel, (%)

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Cu</th>
<th>Ni</th>
<th>Cr</th>
<th>Mo</th>
<th>V</th>
<th>W</th>
</tr>
</thead>
<tbody>
<tr>
<td>MS</td>
<td>0.1356</td>
<td>0.1795</td>
<td>0.695</td>
<td>0.00875</td>
<td>0.0235</td>
<td>0.1807</td>
<td>0.0528</td>
<td>0.1444</td>
<td>/</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>HSS</td>
<td>1.96</td>
<td>0.99</td>
<td>1.26</td>
<td>0.028</td>
<td>0.034</td>
<td>/</td>
<td>0.78</td>
<td>4.85</td>
<td>4.47</td>
<td>4.00</td>
<td>3.40</td>
</tr>
</tbody>
</table>

Figure 4-1 Schematic diagram of (a) high temperature ball-on-disc test with the lubricant introducing onto the hot wear track and (b) hot rolling with lubricant sprayed overly on the cold roll.

The ball-on-disc high temperature tribometer was used to evaluate the tribological performance of different lubricants, with the High Speed Steel (HSS) ball simulating the tool, while the MS disc representing the workpiece, as shown in Figure 4-1a. The chemical compositions of HSS and MS are listed in Table 4-1. The hardness of HSS and MS were measured to be 9.2 and 4.1 GPa, respectively by nanoindentation at room temperature [122]. The frictional sliding test was started when the temperature of the
furnace was maintained at 900°C for 5 min. A 300s’ running in under dry sliding conditions was conducted before the lubricant was applied. The lubricant was continuously transported with a supply rate of 0.05 mL/s onto the ball contact area on the disc wear track under a pressure of 1.3 GPa and linear speed of 0.05 m/s, as shown in Figure 4-1a.

4.2.3 Hot rolling test

The hot rolling experiments of MS plate were performed on a 2-high Hille 100 rolling mill with rolls of 225 mm diameter × 254 mm length and a roughness (Rₐ) of 1.0 µm. Rolling forces were measured by load cells on the mill, and rolling speed can be set from 0.12 to 0.72 m/s. The rolling torque was obtained through strain gauges on the shaft. Commonly used mild steel (MS) plates were cut to specimens of 30 (W) ×20 (T) ×203 (L) mm and chamfered at the front end for the hot rolling experiments. The heat treatment of MS specimens was conducted at 1150°C for 30 min in a MoSi₂ tube heating furnace with the protection of N₂ at a flow rate of 10 L/min to ensure a homogeneous temperature distribution and a minimal uniform scale thickness. This results in an oxide scale thickness of 35 ±3.0 µm, as shown in Figure 4-2, and an average surface roughness of 8.3±0.9 µm. Measurements of both pre-rolled and rolled surfaces profile were made with a Bruker Contour GT-K 3D Optical Microscope profile. In this study, the hot rolling test was carried out with a reduction of 40% which corresponds to an average pressure of 132 MPa, and a linear speed of 0.5 m/s. A thick layer of aqueous inorganic polymer glass lubricant is sprayed on the rolls prior to strip entry into the roll bite, as shown in Figure 4-1b. As the length of rolled sample (203 mm) is appreciably shorter than the
circumference of the roll (706.5 mm), the rolled specimens can be fully lubricated during the whole rolling process. After rolling, the rolled samples were immediately quenched in the quench oil to avoid further oxidation in the cooling process, which was used to compare oxide scale thickness. Apart from the oil quenching, the cooling down in a sealed box purged with nitrogen gas was also carried out to eliminate the contamination of quenching oil to the lubrication film. All experiments have been repeated twice to ensure repeatability. Representative samples have been chosen for further analysis.

Figure 4-2 Optical microscope image of oxide scale formed in MoSi$_2$ tube furnace at 1150°C for 30 min with nitrogen protection at a flow rate of 10 L/min.

4.3 Results

4.3.1 Analysis of prepared lubricant

Talc aqueous solution

The provided talc powder suspension was further analyzed by SEM&EDX and XRD. The analyzed result in Figure 4-3 shows that the lubricant has a granular morphology
with a diameter of 13.6 μm, and was mainly composed of Mg, Si, O and a minor impurity containing Al and Ca element.

Figure 4-3 SEM&EDX analysis of talc powder

Figure 4-4 (a) XRD patterns and (b) DSC&TG curves of talc powder.

Figure 4-5 Molecular structure of talc mineral [127]
Figure 4-4a shows the XRD pattern of the talc powder after the evaporation of water at 100°C, which indicates the lubricant was predominantly composed of talc phase \((\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2)\) and a small part of clinochlore \(((\text{MgAl})_6(\text{SiAl})_4\text{O}_{10}(\text{OH})_8)\). Structurally, talc is composed of a sheet of brucite \((\text{Mg(OH})_2)\) sandwiched between \(\text{SiO}_2\) sheets [127]. Such a layered structure offers talc solid an inherent softness and lubricity, because these elementary sheets in Figure 4-5 are bonded by weak Van der Waals molecular forces. Figure 4-4b shows the DSC&TG curves of talc powder. The endothermic peak at 574°C is attributed to the dihydroxylation of the talc. It was reported that the release of water due to dehydration of talc will have some influences on the physical and chemical properties of materials. The endothermic peak at 845 and 915°C was attributed to the decomposition of talc, as shown in reference [128].

\[
\text{Mg}_3(\text{Si}_4\text{O}_{10})(\text{OH})_2 \rightarrow 3\text{MgSiO}_4 + \text{SiO}_2 + 4\text{H}_2\text{O} \quad \text{Equation 4.1}
\]

**Borax compound**

![Figure 4-6 DTG and DTA thermograms of the borax](image) [129]
DTG and DTA thermograms of borax were studied in reference [129], and was shown in Figure 4-6. The removal of hydrated water from the structure borax occurred at approximately 100-250°C. An exothermic peak at 565°C originates from the crystallization and internal rearrangement of the dehydrated borax. The melt of borax was observed at 736°C with an endothermic peak [130].

**High temperature thermal behavior of sodium phosphate**

![Diagram](image)

Figure 4-7 Relationships of condensed sodium metaphosphates [131].

Figure 4-7 shows the evolution of sodium metaphosphate with Na/P mole ratio at 1:1 under different conditions. The sodium dihydrogen pyrophosphate alone is formed when the NaH$_2$PO$_4$ is heated below 240°C with the removal of crystal water. With a further heating above 240°C the Na$_2$H$_2$P$_2$O$_7$ turns into a material with a long chain (Maddrell salt). The Grahams salt, a type of high-molecular-weight polyphosphate, can be obtained when the Maddrell salt is heated above 625°C. The Kurrol salt can be prepared by slow cooling of the metaphosphate. The obtained Kurrol salt has a form of long fibrous
needles; each contains long polyphosphate chains lying in the direction of the fiber axis. Both the Kurrol and Maddrell materials have the high molecular weight, having similar properties to the polymer [131].

Figure 4-7 shows that, when the temperature is above 600°C, the final product is melted sodium metaphosphate Graham glass, as long as the Na₂O/P₂O₅=1. When sodium metaphosphate was dissolved in water, it firstly experienced hydrolysis and decomposition into short-chained dihydrogen ortho- or pyrophosphate. However, once it was heated to above 600°C, water solvent evaporation, crystal water dehydration, polymerization reaction occurred subsequently to form the melted long-chained metaphosphate Graham salt again. Therefore, the hydrolysis of polyphosphate in water has a minor impact on its application at high temperature.

**Sodium metaphosphate glass**

![DSC&TG curves of sodium metaphosphate from 25-800°C and XRD patterns of sodium metaphosphate after calcination at 800°C](image)

Figure 4-8 (a) DSC&TG curves of sodium metaphosphate from 25-800°C and (b) XRD patterns of sodium metaphosphate after calcination at 800°C

Figure 4-8a shows the DSC&TG curves of the commercial sodium metaphosphate glass conducted by NETZSCH STA 449C DSC equipment (Germany). An endothermic peak
was identified at 270°C. This was attributed to the glass transition temperature (Tg) 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 \(-\text{OH}\) bond [132]. The large DSC endothermic peak at 623°C represented the transition of glass to the melt state with no accompanying mass loss.

Figure 4-8b shows the XRD patterns of sodium polyphosphate solution experiencing a natural drying and calcination at 800°C. The salt has an amorphous structure after natural drying confirming its glassy nature. After calcination, its XRD pattern has a fine crystallized characteristic, and these peaks all originated from sodium metaphosphate (NaPO_3) crystalline. The result combined with the theoretical analysis in Figure 4-7 dispels the doubt that long-chained alkali metaphosphate hydrated severely into short-chained hydrated ortho- or pyrophosphate in water solution and change its physical and chemical properties, as high temperature can subsequently polymerized them again.

**High temperature laser confocal microscope (HTLCM) observation**

The *in-situ* static thermal behaviours of NaPO_3 powder on the polished mild steel surface were examined using HTLCM in an air atmosphere with a heating rate of 1°C/s. The powder was observed to melt and wet the surface of the steel at 520°C, as shown in Figure 4-9b. The phosphate melt can interact with hot steel surface to form strongly chemisorbed layer and/or a physical glassy film, and the protection of steel surface from oxidation is mainly attributed to the physical barrier of phosphate glass between the
material surface and the oxidizing gas [133]. Consequently, the surface of the steel can be minimised from oxidising above 520°C with the protection of sodium metaphosphate. Otherwise, it will quickly become heavily oxidised above 570°C [10]. When the temperature increases to 650 and 800°C, a uniform adhesive phosphate film is formed and it completely covers the steel surface. This implies that once the polyphosphate molecules enter the contact zone, the high temperature can quickly melt the polyphosphate, and allows it to “plate-out” across the contact zone as an easily-sheared viscous glass lubricating film. Furthermore, viscous alkali phosphate chemically reacted with oxide scale on the strip to form a layer of soft phosphate reaction film on the top surface of strip.

Figure 4-9 Static In-situ HTLCM images of NaPO$_3$ powder on polished mild steel surface in air atmosphere at different temperature: (a) 25°C, (b) 520°C, (c) 650°C and (d) 800°C.
4.3.2 Ball-on-disc

Friction coefficient

Figure 4-10 (a) Average frictional curves of HSS ball against MS disc tribopairs and (b) mean friction coefficient with different lubrication at 900°C, 10 N and 0.05 m/s.

Figure 4-10 shows the average friction curves and the mean friction coefficient for different lubricants. It can be seen that the lowest friction of 0.23 was produced by sodium metaphosphate, followed by borax at 0.26. Distilled water lubricant exerts almost no influence on the lubrication at high temperature, producing a similar friction coefficient as that of dry sliding at 0.49. The commercial o/w emulsion produced a friction coefficient between that of dry sliding and glass lubricant at 0.31. The use of talc suspension increases the friction coefficient slightly; furthermore, the frictional curve exhibits a significant fluctuation as shown in Figure 4-10a. The mean friction coefficient was calculated by averaging the friction coefficient during the stable period, as shown in Figure 4-10b. The lubricants can be ranked on the basis of mean friction coefficient as: sodium metaphosphate < borax < oil-in-water < distilled water = dry < talc powder.
SEM analysis of wear surface

Figure 4-11 SEM micrographs of wear scars of HSS ball after exposure to high temperature sliding for 300 s with different lubricants: (a) dry, (c) o/w, (e) talc, (g) sodium metaphosphate and (i) borax.
Chapter 4-Investigation of inorganic chemical compounds as hot rolling lubricant

Figure 4-12 (a) the EDX spectrum of the red cross position in Figure 4-11 c and (b) EDX spectra of the white and grey areas in Figure 4-11 j.

SEM micrographs of wear scars of the HSS ball after exposure to high temperature sliding for 300 s with different lubricants are shown in Figure 4-11. Wear scars under dry, distilled water and talc condition present substantially similar morphologies with a significant material transfer from the MS disc to the HSS scar surface. This was confirmed by the EDX analysis on the ball scar showing that this protective layer was mainly composed of iron oxide from the mild steel without the detection of Mo, V and W alloys in Figure 4-12a. The material transfer from MS disc to tool surface roughened the tool surface, and in turn accelerated the tool wear. Material transfer occurred in ball-on-disc test implies a high chance of roll scoring in hot rolling. The o/w emulsion reduced the material transfer slightly and produced a smoother scar surface. However, this effect is not satisfactory because a large extent of material transfer still occurred in the sliding, as shown in
Figure 4-11b. These material transfers were noticeably suppressed when sodium metaphosphate and borax glass was applied, resulting in a uniform wear of HSS ball. Little transferred lumps were observed. The wear track lubricated by borax was composed of two areas; one is the grey area, and the other is the white area, as shown in Figure 4-11 (j). EDX analysis in Figure 4-12b shows that the grey area is rich in borax, while the white area contains very little borax. This indicates that borax fails to cover the whole wear track, probably due to low concentration of borax lubricant.

The measured statistical average surface roughness ($R_a$) of wear track on the HSS ball and MS disc by 3D surface profilemeter was given in Figure 4-13. The $R_a$ was obtained by measuring the square area 250×250 µm on the wear scar. Scar roughness result shows that a substantially rough surface of HSS ball was obtained under dry, water and talc conditions, which was the combined result of significant material transfer and deep grooves produced by severe abrasive wear. Sodium metaphosphate compound produced a
comparable scar roughness as that by o/w emulsion with an Ra at near 8 μm. The use of borax compound generates a smoother scar surface with an Ra below 3 μm.

**Wear rate study**

In hot rolling process, the roll wear is of vital importance due to the pronounced influence on surface quality of rolled workpiece and high manufacturing cost, which was reported to account for as high as 10% of the total process [134]. Therefore, the effect of different types of lubricants on the wear of roll and workpiece should be taken into consideration. Because of the difficulties to directly study the *in-situ* wear of the roll, the wear resistance of HSS material from the ball-on-disc tests has been studied.

![Figure 4-14](image.png)

Figure 4-14 (a) Wear scar sizes of HSS ball and (b) profile of wear track on MS disc at 900°C for 300 s with different lubricants.

Figure 4-14 shows the wear scar sizes of HSS ball and wear track profiles measured on MS disc, which were used to evaluate the high temperature wear experienced by the tribopair under different lubricants. The statistical scar sizes in Figure 4-14a shows that water and *o/w* emulsion show a high wear which is further exacerbated by around 25%.
when talc is used. In comparison, the use of borax produced the minimal scar size, followed by sodium metaphosphate producing approximately half the scar size of dry sliding. The comparison of wear track profiles in Figure 4-14b also suggests a similar trend, where the cross-sectional area of wear track ranks in the order of borax, sodium metaphosphate and o/w emulsion, talc, water, dry condition.

**XRD analysis**

![XRD patterns](image)

Figure 4-15 XRD patterns of wear debris collected in the wear track (a) for sodium metaphosphate, (b) for borax and (c) for talc.

Figure 4-15 shows the XRD analysis of wear debris collected in the wear track on MS disc. For sodium metaphosphate, the pattern peaks were predominated by maricite (NaFePO₄) with a little Fe₃O₄ and Na₃PO₄. This phenomenon indicates the high reactivity of phosphate with hot steel, which was responsible for the strong adherence on sodium metaphosphate glass on hot steel surface. For borax lubricant, it shows a low chemical reactivity; Even though a large amount of borax was used to lubricate the tribo-system at 900°C, the XRD patterns are still dominated by a large number of iron oxide peaks, which indicates that the weak reaction between iron oxide and borax. When talc was applied, little chemical reaction between talc and iron oxide occurs even at the ambient
temperature of 900°C, because no corresponding chemical product was detected as shown in Figure 4-15c. This case also implies a poor adhesion of talc on hot steel surface due to little formation of chemical bonds between these two materials.

4.3.3 **Static antioxidation ability comparison**

![Figure 4-16 Thickness of oxide scale as a function of inorganic compound film thickness](image1)

![Figure 4-17 SEM micrographs of cross section of coated mild steel after heating at 900°C for 6 min (a) talc powder, (b) sodium metaphosphate and (c) borax](image2)
An oxidation experiment was also conducted in a bid to compare the antioxidation ability of these inorganic chemical compounds. The finely ground and polished mild steel specimens were coated with different inorganic chemical compounds by spraying nozzle for the same spraying time, and then these specimens were oxidized in a muffle furnace at 900°C for 6 min in air atmosphere. After oxidation, specimens were immediately taken out from furnace to cool down in air. The cross sections of these steel specimens were analyzed by SEM&EDX to measure corresponding thickness of oxide scale and inorganic chemical compound film. The correlation between oxide scale thickness and the thickness of inorganic glass protective film were shown in Figure 4-16. The results indicate that these inorganic chemical compound coatings can protect the hot steel from oxidation to a certain degree depending on the coating thickness; a thicker protective coating generates a thinner oxide scale. The result in Figure 4-16 also reveals that phosphate- and borax-based glass have a minor influence on the prevention of oxidation at high temperature slightly when the coating thickness is below 10 μm, whereas the talc coating presents a better oxidation resistance than glass coating with a smaller oxide thickness. However, a substantially suppression of oxidation can be achieved by coating a thick layer of protective glass film.

Figure 4-17 shows the SEM images of the cross-section of oxidized specimens. Different interfacial structures were observed when different types of coatings were applied; talc can form a continuous solid film under which a thin oxide layer was formed. This solid film is not entirely compact with the appearance of a large number of cracks. Gaps between the solid talc film and oxide scale were observed which indicates a poor adhesion of talc on steel. When liquid-glass compounds such as sodium metaphosphate
and borax were applied as an antioxidation coating, the interfacial structure shows an opposite situation; an oxide scale locates layer formed above the glass film. Furthermore, a continuous glass layer containing small wüstite grains is obtained at the scale/steel interface. No gaps were observed at the interface between the oxide scale and the glass.

4.3.4 Hot rolling test results

Roll separating force and roll torques comparison

Figure 4-18a shows the rolling separating forces and torques at the contact surface, which compares the rolling forces for different lubricants under the same rolling conditions. For the un lubricated hot rolling, a high rolling force of 157 kN was obtained. The use of distilled water has little effect on the rolling force and produces a similar value as that of dry rolling. This result is in agreement with that in reference [134] where the distilled
water can reduce the rolling force fairly slightly only for the reduction below 30%, but once the reduction is above this critical value, little effect was found. Sodium metaphosphate solution (20%) yields the lowest rolling force among all the used lubricants with a reduction of rolling force by 11.5%, which were followed by the commercial o/w emulsion by 10.2%. Borax produces a slightly higher rolling force than the previous two lubricants, reducing the force by 8.6%. However, its low concentration in the aqueous lubricant reflected its high efficiency in lubrication. The highest rolling force among lubricated cases was obtained when the layered solid talc lubricant was applied, but it still can reduce the rolling force by 8.3%. This suggests that the alkali inorganic glass lubricant performs better in lubricity than the layered solid lubricants in a practical hot rolling process.

Figure 4-18b shows the average friction coefficients in hot rolling with different lubrication, and are also compared with their corresponding ball-on-disc results. These friction coefficients are calculated based on Alexander numerical model [135] by an inverse calculation, where the calculated rolling force was compared until its difference from the measured rolling force is less than 1% by varying the friction coefficient input. This program was based on Orowan’s rolling model [32]. The calculated friction coefficients were shown in Figure 4-18b, and follows the ranking sodium metaphosphate < oil-in-water < borax < talc powder < distilled water = dry. The hot rolling friction coefficient has the same trend as that of ball-on-disc, where sodium metaphosphate always shows the lowest friction coefficient, followed by borax salt. Talc compound shows a different lubrication behavior in these two equipment; it increases the friction coefficient with the ball-on-disc, while, when being tested by hot rolling, it reduces the
friction coefficient from 0.33 to 0.27. This disparity is related to the differences in tribological conditions caused by apparatus configurations, such as differences in lubricant exposure time, ball and roll temperature, thermal fatigues etc. Detailed interpretations of these factors will be given in the Discussion section.

**Surface roughness**

![Figure 4-19 3D-surface topography of (a) the pre-rolled oxide scale surface and (b) rolled surface lubricated by sodium metaphosphate.](image)

The surface finish of hot rolled strip is becoming an important concern. In many applications, a final bright and highly smooth surface is desired, and the hot rolled product is expected to be as smooth as possible. It was observed that the oxidized steel sample has a rough surface with an Ra of 8.9 μm. A large number of asperities can be seen in Figure 4-19a. After dry hot rolling, the surface roughness reduces appreciably to 1.4 μm. When the cold roll is in contact with the rough oxidized surface; the pressure compress the thick strip and shear these asperities to generate a smoother surface finish. The effect of different lubrication on the surface roughness (Rₐ) of hot rolled strip is shown in Figure 4-20. These rolled samples were immediately quenched in quench oil after hot rolling to avoid the further oxidation in the air. The results show that the samples
lubricated by water and sodium metaphosphate have the smoothest surface, followed by borax and talc lubricants. The rolled sample lubricated by o/w emulsion has the roughest surface among tested lubricants with an Ra of 2.1 μm.

![Figure 4-20 Average surface roughness (Ra) of rolled surface with a reduction of 40% and rolling speed of 0.5 m/s with the different lubricants](image)

**Antioxidation comparison**
Figure 4-21 Statistics of oxides scale thickness of hot rolled sample with the use of various lubricants.

Figure 4-21 shows the oxide scale thickness of hot rolled sample with various lubricants. The thickness of oxide scale was determined through SEM images of cross-section of hot rolled specimens by averaging the scale thickness at 10 different locations, which were 100 μm apart. The results show that the average oxide scale thickness of un lubricated sample is 22 ± 5 μm. Distilled water and o/w emulsion increase the oxide thickness slightly to approximately 25 μm. The oxide scale thickness is 24 and 26 μm respectively with sodium metaphosphate and borax.

**Impact on microstructure**
Lubrication film

Figure 4-22 Cross-sectional SEM/X-ray mapping of hot rolled strip lubricated by sodium metaphosphate with different concentrations (a) 20 % and (b) 40%. These rolled specimen were cooled in nitrogen purged box to avoid the contamination of quench oil.

Figure 4-22 shows the typical EDX mapping analysis of the cross section of rolled mild steel plate lubricated by sodium metaphosphate. This rolled sample was cooled in a nitrogen purge box instead of quenching in oil to avoid the oil contamination. The result
shows that when 20\text{w.t.\%} sodium metaphosphate was applied, elements Na and P were not detected in the cross section, and a continuous phosphate lubrication film was not observed, as shown in Figure 4-22a. This circumstance was also found for talc and borax lubricants, as shown in Figure A-1 and Figure A-2 in the Appendix. A higher concentration of sodium metaphosphate (40\text{w.t.\%}) was also tested, and the analysis result of the corresponding cross section was shown in Figure 4-22b. A layer of sodium and phosphorus element was detected sparsely and discontinuously. It is unexpected that the layer of phosphate film locates in the middle of oxide scale, and the oxide scale can be divided into three layers: Layer 1 with a thickness of 15 \( \mu \text{m} \) represents the newly grown oxide layer formed in the cooling process. Layer 2 is the phosphate lubrication film with an average thickness of around 5 \( \mu \text{m} \), consisting of Na, P, Fe and O elements. The oxide scale is shown in layer 3, which undergoes a severe deformation in hot rolling. Noted that the morphology of layer 1 is different from that of layer 3, which shows a solid and compact morphology without cracks as well as porosities. It was also observed that a part of lubricant in layer 2 moved to the interface between oxide and steel substrate to form this layer during rolling process. The porous and cracked secondary oxide scale provides the passageway for the liquid lubricant to enter the interface, which also left traces in the deformed oxide scale in layer 3.

This is related to the method to apply the lubricant. In this test, sodium metaphosphate solution was firstly sprayed on the cold roll, and it was observed that the majority of lubricant solution flows down the smooth roll. A layer of solution film was left and adhered on the roll surface, which lubricates the hot contact between cold roll and hot MS steel. It should be noted that after hot rolling the temperature of the strip was estimated to
be above 800°C. The mild steel has a weak antioxidation ability, hence the oxidation of mild steel in the cooling stage is very difficult to be completely suppressed, even though the cooling box is purged with nitrogen gas. Consequently, the hot rolled MS specimen still undergoes a degree of oxidation in the cooling process, where the diffusion of iron and oxygen occurs. This lubrication film is too thin to suppress the migration of iron and oxygen. At high temperature, this layer of phosphate film was expected to be continuous, and located at the top surface.

4.4 Discussions

The performance of different types of inorganic lubricants at high temperature has been examined. Tribotests conducted by ball-on-disc and hot rolling confirm phosphate- and borate-based glass have promising potential to replace commercial o/w emulsion in terms of lubricity, antiwear and prevention of material transfer. The use of borax produces a much smoother HSS tool surface than that of sodium metaphosphate. In comparison, talc powder presents a noticeably different lubricity behavior in these two apparatus. It shows an acceptable lubricity in hot rolling. However, when ball-on-disc was used to test the lubricant, it has a slightly negative effect on friction and wear reduction. The difference can be attributed to the tribological condition differences in these two apparatuses, which needs to be discussed in detail separately.

4.4.1 Ball-on-Disc tribotest

Ball-on-disc experiments show that unlubricated HSS/MS tribo-system experiences high friction and wear at 900°C. In most hot metal forming operations, a high friction coefficient and tool wear is not desirable because of the consequent high-energy input
and expensive tool replacement due to short service life. The wear mechanism on the HSS ball is complicated, involving oxidation, adhesion and abrasion. Furthermore, large, thick and uneven lumps were observed to build up on HSS scar due to the severe material transfer from MS disc. These transferred materials will become hardened in the subsequent oxidation, work hardening and grain refinement during the scratching of the soft disc material. The hardness difference as described in the Experimental section between the ball and disc was the main cause of the material transfer [9, 122]. This difference was further contributed by the temperature difference, as reported in a previous paper from our laboratory [9], when the disc temperature reaches 900°C, the temperature of HSS ball is around 660°C. At the high pressure of 1.3 GPa, the contact between HSS ball and MS disc is supported by discrete micro-asperities. These contacting asperities are not only subjected to an elastic deformation in the sliding, but also to some plastic deformation. Consequently, intimate contact between the tribo-pairs occurs such that molecular surface forces act through the interface, which leads to ‘interfacial bonding’ and the generation of adhesive ‘junctions’. Various kinds of surface forces such as metallic, covalent and ionic and van der Waals bonds can act synergistically within the interface of two contacting surfaces to form interfacial adhesion. Under the action of pure normal and shear stress, the MS material will transfer to the surface of HSS ball, as shown in Figure 4-13b.

When distilled water was fed onto the wear track, the water drop immediately rolls out of wear track due to combined effect from convection boiling and centrifugal force. This indicates that pure water has a poor adhesion with the hot steel surface. Consequently, the use of pure water will not exert much influence on lubrication in high temperature
tribology. This is also reflected by a similar tribological performance with dry sliding in friction and wear, as shown in Figure 4-10 and Figure 4-14. When the o/w emulsion was supplied onto the wear track on disc at 900°C, some smoke was firstly observed due to the burning of organic oil. However, a mild reduction of friction and wear is still obtained, as shown in Figure 4-10 and Figure 4-14, implying that some of the lubricating oil survives this harsh condition. Although the material transfer on HSS ball surface is reduced slightly compared to that of dry sliding shown in Figure 4-20 a and c, this performance is still not satisfactory. The reason is that the viscosity of lubricating oil drops sharply at high temperature, and the fluid lubrication may not occur [45]. The lubricating film was composed of two regions; the boundary lubricating film and the with direct metal-to-metal contact [45]. Under this circumstance, the contact between hard ball and nascent disc surface could not be eliminated completely; and as a result, a mild material transfer will occur.

When talc was introduced into the sliding interface, unexpectedly, the friction coefficient increases sharply. The MS disc was also flooded with talc powder in the ball-on-disc test, however, the dried talc film quickly detached once the sliding begins. These two cases indicate that talc powder has a poor adhesion on hot steel surface, as shown by the XRD analysis in Figure 4-15c, no chemical bonds were detected between talc and steel due to the chemical inertness of talc. As pointed out by Peterson [47], the bond of lubricant to the working surface must be stronger than the force necessary to shear the lubricant compound. If the bond is strong, the friction coefficient will be reflected by the shear strength of the lubrication film; otherwise, the lubricant will be instantly removed from the surface. An adverse effect is that talc decomposes at near 900°C to form MgSiO₄ and
SiO$_2$ shown in Equation 4.2 [128]. The MgSiO$_4$ and SiO$_2$ have a melting point as high as 1890 and 1710°C, respectively. Furthermore, these ceramic phases possess significantly high hardness at high temperature [136]. Analysis of tribo-surface reveals that these compounds enter into the tribo-interface, promote the third-body abrasive wear, and increases both the friction and wear as shown in Figure 4-10 and Figure 4-14. These two shortcomings, poor adhesion and decomposition, implies that the talc at high temperature loses its layered structure and therefore not suitable as an effective high temperature lubricant.

\[
\text{Mg}_3(\text{Si}_4\text{O}_{10})(\text{OH})_2 \rightarrow 3\text{MgSiO}_4 + \text{SiO}_2 + 4\text{H}_2\text{O}
\]  

Equation 4.2

When the sodium metaphosphate solution drops onto the hot wear track, it was observed that liquid drop quickly plates out, the water subsequently evaporates leaving a black-colored film on the hot wear track. When the ball slides through the phosphate glass covered track, the friction coefficient decreases immediately. This phenomenon indicates that phosphate-based glass has a strong adherence, wettability and effective lubrication on hot steel surface. In addition, the surface adhesion energy of both MS disc and HSS ball is greatly reduced due to the adsorption of molten glass on the fresh surface. Furthermore, polyphosphate can work as a digestion reservoir for iron oxide and react to produce a mixed Na-Fe phosphate as shown in Equation 4.3. As the reaction progresses, the reservoir of polyphosphate decreases, and the dissolution reaction slow down to a stop at a certain degree of the digestion process. The incorporation of abrasive oxide modifies significantly the rheological properties of the glass at high temperature by increasing the viscosity as suggested by Peterson [47]. It is important to note that as the
reaction proceeds, the chain-length of the phosphate decreases and a depolymerization process takes place.

\[
\text{FeO} + \text{NaPO}_3 \rightarrow \text{NaFePO}_4 \quad \text{Equation 4.3}
\]

When borax was applied, a similar phenomenon as sodium metaphosphate was observed. The borax was observed to melt immediately, spread across the wear track and adhere onto the hot disc. Borax has a similar physical properties as that of sodium metaphosphate; it is in a molten state at 900°C, and has a viscosity value close to that of metaphosphate [137, 138]. The similarity of physical properties between phosphate and borax enables them to show a similar frictional performance at high temperature, as shown in Figure 4-10. However, a large difference in antiwear and tool surface roughness was obtained, where borax was believed to have a better wear resistance and a smoother scar surface. These are more dependent on the chemical properties of the test lubricants. Sodium metaphosphate is more chemical reactive with hot steel oxide than borax, as shown in Figure 4-15, as a result, the strong chemical reaction between metaphosphate and oxide shown in Equation 4.3 on the rough oxide scale may produce a rougher tool surface.

4.4.2 Antioxidation mechanism

Inorganic glass compounds were reported as excellent antioxidation agent to prevent the formation of oxide scale, and the antioxidation function of these chemical compounds was mainly attributed to a continuous protective film isolating the hot material from interacting with oxygen in the atmosphere [139, 140]. The static oxidation experiment
results in Figure 4-16 also confirm this point. Therefore, the thickness, physical and chemical properties as well as the morphology of this protective film at high temperature are of vital importance in determining the antioxidation efficiency.

When the steel specimen covered with glass compound was heated to 900°C, the glass subsequently experienced softening and melting after the glass transition. Simultaneously, the diffusion of iron atom into the glass occurs to form mixed Na-Fe phosphate glass, as shown in the schematic diagram in Figure 4-23. The viscous state of the glass film made the penetration of oxygen into glass/substrate difficult. The Fe atom located at the top surface of Na-Fe phosphate glass will be oxidized with priority. As a result, an iron and oxygen concentration gradient was built up within the viscous glass, which drives the diffusion of iron atom to the surface. The diffusion of iron to the external oxidizing atmosphere through viscous glass was reported in a publication [141], where iron atom was found to migrate through the molten fayalite leading to oxide scale...
growth. The thickness of the glass film determines the length of diffusion path of iron atoms and exerts a remarkable barrier influence on the number of iron atoms migrating to the top surface in a given time; the thicker the glass films is, the longer time the migration will take. Thus, a smaller number of iron atoms migrate to the surface forming a thinner oxide scale. Because little oxidation scale was observed at the interface between the substrate and the glass film, it is suggested that oxygen molecule failed to diffuse into the interface due to the viscous state of the glass lubricant.

4.4.3 Hot rolling lubrication

The hot rolling tests reveal that all the tested lubricants can lubricate the hot rolling process, among which sodium metaphosphate solution has the best lubrication performance, borax and talc powder produce a slightly higher rolling force than traditional oil-in-water emulsion. It is noted that talc lubricant presents a different lubricity behavior when tested by ball-on-disc and hot rolling; it increases the friction coefficient in ball-on-disc, whereas decreases friction coefficient slightly in practical hot rolling, as shown in Figure 4-18b.

This disparity is caused mainly by the differences in configuration and working conditions between laboratory ball-on-disc simulation and hot rolling apparatus, as described in the introduction section. Firstly, the speed of hot rolling (0.5 m/s) is around 10 times higher than that of ball-on-disc (0.05 m/s). This means that the lubricant will reside in the hot MS track 10 times longer than that in hot rolling. The roll bite angle in hot rolling was calculated through Alexander program and the flow stress model [28] to be 0.266 radians, and the contact length is around 0.03m. Therefore, the strip needs only
0.06s to pass through the roll gap. Secondly, the temperature environment difference is also an important factor. The lubricant was directly introduced onto hot wear track in ball-on-disc, therefore, it was heated immediately, and the water was evaporated instantly. A totally different circumstance was found in hot rolling test, whereby the aqueous solution was sprayed on the cold roll. The lubricant solution and the cold roll were only heated in the extremely short contact with hot strip which takes a longer time to heat the roll, evaporate the water and decompose talc. Based on the friction coefficient produced by talc in Figure 4-18b, it can be said that layered talc lubricant can lubricate hot rolling effectively, where it has not sufficient time to decompose completely. This claim also gains support from publications [142, 143], which reported that lubricants containing graphite, MoS₂, fatty oil sulfide, can still lubricate hot rolling process, even though these chemicals undergo severe oxidation, pyrolysis or even burn off at high temperature. However, as the lubricity of talc is more related with the contact time in the contact, its lubricity control at high temperature will become difficult and complicated.

The function of inorganic chemical compounds in protecting the deformed hot strip from oxidation was also studied, as shown in Figure 4-21. Talc lubricant presents the best antioxidation performance as it reduces the oxide scale thickness among the tested lubricants. A comparison of oxide scale thickness shows that the use of sodium metaphosphate and borax glass compound has a minor effect on the prevention of oxidation of hot strip, exhibiting a similar thickness of oxide scale to that of dry rolling. This ineffectiveness is related to the thickness and morphology of the glassy lubrication film formed in hot rolling. As shown in Figure 4-22a, the lubricating film formed by the 20w.t.% sodium metaphosphate failed to be detected. This substantial thinness of the film
implies that it plays little role in isolating the hot mild steel from air. When the concentration of sodium metaphosphate was increased to 40% a clear lubricating film with a thickness of around 5 μm was observed. It still contributes little in oxidation prevention, and a thick oxide layer with a thickness of 15 μm is still formed above this lubrication film due to outward growth of oxide. This result agrees with the static oxidation result in Figure 4-16, which indicates that a thin glassy film exerts a minor influence on the oxidation of hot steel, and under this condition talc is more effective than glass in oxidation resistance. In summary, a large thickness of inorganic protective film is required to reach an effective reduction in oxidation, which can be achieved by spraying the glass lubricant directly onto hot workpiece instead of roll or improving the concentration of glass compound in water. In the rough rolling stage, the rolled secondary scale will be descaled by a hydraulic descaling operation before entry into the tandem finishing mill [37]. As shown by the EDX mapping in Figure 4-22, the lubricant exists predominantly in the oxide scale. Therefore, the lubricant will be removed by descaling before finishing mill. Furthermore, after finishing mill, the strip will be pickled by hydrochloric acid which is expected to remove the lubricant along with the scale [38].

4.5 Conclusions

High temperature ball-on-disc and hot rolling tests were combined to evaluate the tribological performances of different inorganic lubricants. At high temperature, the use of water has little effect on the lubrication and wear reduction of HSS/MS tribo-system. Although the o/w emulsion can lower the friction, it fails to provide a satisfactory performance in wear reduction and material transfer prevention at high temperature. The
layered talc lubricant shows a different lubrication performance in ball-on-disk and hot rolling configurations, the long exposure time in ball-on-disc causes the decomposition of talc resulting in increased friction and wear. However, an acceptable performance of talc was obtained in hot rolling due to the extremely short contact time. Sodium polyphosphate and borax exhibit the most desirable performances in lubrication, antiwear and material prevention among all the tested lubricants, although sodium polyphosphate has a slightly better performance.

When the protective film thickness is less than 10 μm, the protection of hot steel from oxidation is weak. The relative position of protective film and oxide scale are also different depending on the types of inorganic compounds used. The dissolution of iron atom into molten glass and its migration towards the top surface due to concentration gradient are the working mechanisms. The thickness of glassy film determines the diffusion length; as a result, it strongly affects the oxide thickness formed. In hot rolling, the lubrication film fails to protect the hot steel from oxidation due to its thin thinness and broken layer.
5 Tribochemical behavior of phosphate compounds at an elevated-temperature

5.1 Introduction

At low temperature, much work has been carried out to elucidate the correlation between chain-length of phosphate within the tribofilm and the corresponding antiwear efficiency [21, 78, 83, 144, 145]. Martin [21] proposed that the long-chain-length polyphosphates could limit wear by “digesting” the abrasive iron oxide particles, forming softer zinc oxide and mixed shorter-chain-length iron/zinc phosphates, which is energetically favorable on the basis of the principle of hard and soft acids and bases (HSAB). This viewpoint is further supported by Wan, et al, [144] who attributes the poor antiwear efficiency of the combined ZDDP plus detergent derived-tribofilm, to the absence of the long-chain polyphosphate film. However, these suggestions have been disputed by others.

The correlation of mechanical properties with the degree of phosphate depolymerization was investigated by Nicholls et al [145] who suggested the center of the antiwear pads, which is subjected to higher pressure and more severe depolymerization, is stiffer than the edges. Heuberger [83] also found that, in tribo-stressed area under higher contact pressures, a tough wear resistant surface is generated with a thicker film of shorter chain length polyphosphate. The work conducted by Spencer et al [78] also indicates that short-chain-length polyphosphates shows a lower coefficient of friction and wear than the long chain-length ones. The depolymerization reaction is taking place only with the long-chain length polyphosphates. In the non-contact areas, the thermal film remains as a long-chain
polyphosphate. Previous investigations mostly evaluate lubricant/additives at room and ambient temperatures. Since hot metal forming process particularly requires the lubricants to work effectively over a wide temperature range of 600~1200°C, it is questionable whether the tribological performance correlates with different chain-length phosphates precursors, thus their structure-performance relationship at elevated temperature need to be evaluated.

Since hot metal forming process requires the lubricants to work effectively over a wide temperature range of 600~1200°C, it is questionable whether the tribological performance correlates with different chain-length phosphates precursors, thus their structure-performance relationship at elevated temperature needs to be investigated. The previous work in reference [61, 146] included a combination of long-chain sodium polyphosphate (NaPO$_3$) and short-chain KH$_2$PO$_4$ as one lubricant, the corresponding friction and wear performance was evaluated at the temperature ranging from 600°C~800°C, and it reveals that the friction coefficient and wear rate can be reduced as much as 60% and 59%, respectively. But the effects of different chain length phosphates on reducing friction and wear were not considered.

In the chapter, the effect of polyphosphate chain-length on its tribological performances. In this chapter, ortho- (Na$_3$PO$_4$), pyro- (Na$_4$P$_2$O$_7$) and metaphosphate ((NaPO$_3$)$_6$) with different chain-length were selected as the principal component of aqueous lubricants. A Ball-on-Disc tribometer was used to compare the friction and wear performance of the steel/steel pairs lubricated by different phosphate lubricants at 800°C. The phosphate structure and depolymerization/polymerization in the wear track were characterized by
X-ray photoelectron spectroscopy (XPS) and the structure and bonding details of the tribofilm by X-ray absorption near-edge structure (XANES) analysis. These characterizations will extend our knowledge of tribofilm beyond that described in previous work [61], such as more detailed information of the chemical species and fine structure of the tribo-induced layer.

5.2 Experimental details

5.2.1 Materials preparation

Three different sodium phosphate lubricants with different chain-lengths, i.e. sodium ortho- (Na$_3$PO$_4$), pyro- (Na$_4$P$_2$O$_7$) and meta-phosphate ((NaPO$_3$)$_n$), were prepared. The ((NaPO$_3$)$_6$ is abbreviated to “NaPO$_3$” in the entire thesis. The chemical structures of the three sodium phosphates are shown in Figure 5-1. The chemicals were purchased from Sigma-Aldrich Corporation. The lubricant was made by dissolving sodium phosphate compounds (20 g) into deionized water (80 ml) to obtain aqueous solutions with 20 wt % concentration.

A 6.35 mm diameter chromium steel (GCr15) ball (Chemical position: 0.98%C-1.48%Cr-0.27% Mn-0.35%Si) with a hardness of 596 HV was fixed as the upper stationary ball. Mild carbon steel (0.20%C-0.40%Mn-0.50%Si, 3 mm thick, and with a hardness of 403 HV) was used as rotating discs: carbon steel was chosen due to its major percentage of hot rolled steel products.
5.2.2 Coating preparation

The discs were ultrasonically cleaned with alcohol and acetone for 10 min to remove any contaminants, and then, a solution of sodium phosphate was sprayed by the spray nozzle evenly over the disc and dried at 100°C for 10 min to produce a lubricant coating. The coating thickness was controlled to 50±5 μm by adjusting the spraying times, then a stylus profilemeter (Hommel Etamic W10, JENOPTIK Industrial Metrology Germany GmbH) was applied to measure the film thickness in a contact fashion, the thickness of deposit was coming from the step between the film and the substrate. One example of the profile measurements was shown in Figure 5-2. The $R_a$ roughness of the phosphate layer after baking was 2.5 μm.
5.2.3 Tribological Testing

A CETR UMT tribometer was used to carry out ball-on-disc tribological tests to study the tribological behavior of phosphate lubricants for a steel/steel contact pair. The disc was then mounted into a sample holder in a furnace where the heating wires were distributed around the furnace to ensure a uniform temperature distribution. The ball was then situated 5 mm above the disc. The entire chamber with the mounted samples and balls was heated to 750°C at 37°C/min, from 750 to 800°C at 5°C/min and then stabilized at 800°C for 5 min. Afterwards, the desired normal load (10 N) was applied, and the disc started to move with a rotation speed of 60 r/min (tangential speed 0.094 m·s⁻¹). These friction tests were carried out at 800°C for 15 min in an environment of 15-20% relative humidity (measured at room temperature). The Rₐ roughness of phosphate-coated disc heating at 800°C after 5 min was 2 µm, after sliding the Ra roughness of wear track changed to around 1 µm.
Chapter 5-Tribochemical behavior of phosphate compounds at an elevated-temperature

5.2.4 Characterization

The morphology and chemical elemental analysis of worn surfaces were determined by JSM-6490LA scanning electron microscope (SEM) with an accelerating voltage of 15 kV and 45 µm beam, and Energy Dispersive Spectroscopy (EDS) with 60 µm beam, respectively.

The data of X-ray Absorption Near-edge Structure (XANES) were obtained at the soft X-ray spectroscopy beamline of the Australian Synchrotron in Melbourne. The vacuum in the chamber was maintained at 5×10⁻⁷ Torr for XANES analysis. This beamline was equipped with a plane grating monochromator that can provide 10¹¹~10¹² photons/s at 200 mA at the K-edge of the required element with a resolving power better than 10⁴. The photon energy for XANES was calibrated using photoemissions of gold 4f⁷/2 peaking at 83.96 eV that was obtained from a reference foil available on the standard manipulator. The monochromator beamline covering an energy range of 90-2500 eV with a photon resolution ≤ 0.2 eV was used, and the area analyzed was 1×1mm. The photoabsorption spectra for the model compounds and samples were recorded in the total electron yield (TEY) mode for surface sensitivity. The XANES results were calibrated with respect to the peak in the reference foil spectra, normalized and peak fitted using Gaussian function [111]. As the XANES can provide detailed chemical and structural information on the resultant tribofilm formed on metallic surfaces, the XANES analysis has been routinely used to study the complex chemical interactions between lubricant and metallic surfaces under high-temperature and loaded sliding conditions [114].
X-ray photoelectron spectroscopy (XPS) was conducted at the same facility as XANES with a photon energy of 1200 eV and a step size of 0.5 eV. An area of 1×1 mm in the wear track of the discs was analyzed. This surface sensitive technique can analyze the very top layer of the surface (~5 nm depth) and provides the information about the chemical species in the worn area, and the intensity ratio of oxygen (O 1s) between the bridging oxygen (P-O-P) and the non-bridging oxygen (P=O/P-O-M, M represents metal element) via the fitting process, which helps to estimate the polyphosphate chain-length at the worn surface [78, 147]. The XPS spectra were analyzed using CasaXPS software (Casa Software Ltd), and were fitted with Gaussian-Lorentzian shape after a shirley background subtraction and normalization. The Full Width at Half Maximum (FWHM) value for O 1s and P 2p were set to 1.5~1.7 and 1.6~1.8 eV, respectively [78]. The position of C 1s peak (284.5eV) was considered as the reference for charge calibration [61].

5.3 Results

5.3.1 Lubricant analysis

Sodium orthophosphate

Sodium orthophosphate (Na₃PO₄) is a white, granular and crystalline solid, highly soluble in water, producing an alkaline solution. The item of commence is often partially hydrated and may range from anhydrous Na₃PO₄ to the dodecahydrate Na₃PO₄·12H₂O. Sodium orthophosphate has a melting point as high as 1583°C.
High temperature laser confocal microscopy

Figure 5-3 Static *In-situ* HTLCM images of Na₃PO₄ powder on polished mild steel surface in air atmosphere at different temperatures.

Figure 5-3 exhibits the morphology of sodium orthophosphate on polished mild steel surface at different temperatures from room temperature to 1000°C. It is in a liquid state from 100~200°C during which the hydrate orthophosphate melt. Then it dehydrates into anhydrous orthophosphate, which shows a granular morphology up to 1000°C. This agrees well with the reported melting point in Table 2-2, where the sodium orthophosphate has a melting point of 1538°C.
5.3.2 For sodium pyrophosphate

**DSC&TG**

![TGA and DSC analysis of sodium pyrophosphate decahydrate](image)

Figure 5-4 TGA and DSC analysis of sodium pyrophosphate decahydrate [148]

Figure 5-4 shows the TGA and DSC analysis of sodium pyrophosphate decahydrate. This analysis was conducted in a Mettler Toledo TGA/DSC thermal analyzer by Harris et al. [148]. Sodium pyrophosphate decahydrate has a melting point at 79.5°C (decahydrate). The large mass loss ranging from approximately 100°C to over 200°C is the weight loss associated with the loss of the waters of hydration. The large endothermic peak occurring at the same temperature as your water loss is the enthalpy of vaporization for the waters of hydration. Endothermic peaks at temperatures above the temperature of water loss, and not accompanied by mass loss, will be for phase transitions of the anhydrous salt. A sharp endothermic peak will indicate the melting point, which is at around 988°C. It is noted that there is no phase changes between the dehydration and melting.
Chapter 5-Tribochemical behavior of phosphate compounds at an elevated-temperature

HTLCM observation

Figure 5-5 Static in-situ HTLCM images of Na₄P₂O₇ powder on polished mild steel surface in air atmosphere at different temperature.

Figure 5-5 presents the HTLCM images of thermal behaviors of Na₄P₂O₇ powder on polished mild steel surface. At low temperature at 130°C, the Na₄P₂O₇ remains solid powder morphology; it experienced little changes until 505°C, at which it started to melt, and liquid material was captured. The liquid was gradually solidified by the mild steel surface, which indicates certain chemical reaction occurred causing some changes in its morphology. At 800°C, mixture of liquid and solid white materials were observed, and it turned into white materials completely at 1000°C.
5.3.3 Friction and wear

The frictional and wear behavior of different sodium phosphates was evaluated with respect to an unlubricated steel/steel response in comparable experimental conditions. The dry sliding curve in Figure 5-6a shows a continuous decrease of the friction coefficient and stabilizes at around 0.28. The progressive reduction in friction is attributed to the gradual build-up of the “lubricious” oxide glaze layer [33]. The lubricated friction curves in Figure 5-6a show that the addition of sodium phosphate lubricants all can substantially reduce the coefficients of friction to less than 0.2. However, the friction of pyrophosphate fluctuates significantly around a mean value of 0.16. Figure 5-6b shows that the average friction coefficient of steel/steel pairs lubricated by NaPO₃, Na₄P₂O₇ and Na₃PO₄ shows values of 0.14, 0.16 and 0.09, respectively. In metal forming processes, the importance may not always be attached to the minimization of friction but its control at an appropriate level. This means that all three tested lubricants fulfilled this role, and can therefore, be potential candidates for hot sheet metal forming, however, the friction fluctuates more with pyrophosphate than the other two.
Figure 5-6. (a) Coefficient of friction as a function of time and (b) average coefficient of friction in steady-state lubrication for the steel/steel pairs at 800°C, the error bars represent the fluctuation of friction curves in steady-state region. (Load 10 N; Tangential speed 0.094 m/s, Sliding distance: 85 m).

Figure 5-6 shows the wear rate produced by the unlubricated and three lubricated steel/steel pairs, the wear rate of ball and disc were calculated based on the wear scar diameter of ball and the height profile measurement of wear track of disc as described in reference [149]. The direct contact made by the steel/steel pair without lubricant produced severe wear: $1.3 \times 10^{-2}$ mm$^3$·N$^{-1}$·m$^{-1}$ for steel disc and $2.0 \times 10^{-4}$ mm$^3$·N$^{-1}$·m$^{-1}$ for the steel ball. With NaPO$_3$ lubricant, the wear rates of ball and disc both dropped by approximately 80%. The wear is reduced by around 82% compared to dry sliding for steel/steel pairs lubricated by Na$_4$P$_2$O$_7$, a figure close to the wear rate of NaPO$_3$. Note that shortest-chained sodium orthophosphate reduced wear by 90%, which has the best antiwear performance of the three lubricants.
5.3.4 Morphology of wear surface

The worn surfaces for steel/steel pairs at 800°C observed by SEM are shown in Figure 5-8. For the unlubricated steel/steel pair, the worn surface of the disc is heterogeneously covered by wear debris (Figure 5-8a and b), and a substantial amount of debris piled up in the contact area during sliding. The governing wear mode is the abrasive action of oxidized wear debris accompanied by adhesion for the unlubricated steel disc. The wear scar with a diameter of 2200 µm on the ball is characterized by scratches and deep grooves resulting from the abrasive action of hard oxidized wear particles that further aggravate wear.
When phosphate lubricants are applied, the wear tracks of all the discs became more compact and shallower (Figure 5-8c, e and g), meanwhile the size of the wear scars on all the balls decreased significantly (Figure 5-8d, f and h). As for the steel/steel pair lubricated by NaPO$_3$, there are no visible fragmentations and cracks on the worn surface of the disc, apart from the deformed plateau, and the wear track became smooth, as shown in Figure 5-8c. The ball shows some slight wear in Figure 5-8d, with ~1200 µm
diameter scar, and a continuous compact film covers the scar on the steel ball. With the steel/steel pair lubricated by Na₄P₂O₇, a relatively compact film adheres to the worn surface as shown in Figure 5-8e and 5f, with very little wear debris being found. It is noted that, the lubricating film breaks in some part, which possibly leads to the fluctuation in friction. The ball scar is ~1150 µm in diameter. When sodium orthophosphate (Na₃PO₄) was used to lubricate the steel/steel pair, although the wear on the disc is not as evident as those lubricated by the other two lubricants, some thin flake debris are scattered along the wear track, and no continuous film can be seen in the magnified image shown in Figure 5-8g. However, Figure 5-8h shows the wear on the ball differs significantly from the ball lubricated by NaPO₃ and Na₄P₂O₇, where there are no grooves or cracks on the central area of the ball. However, microcracks and microspalling occurs in the surrounding area of the wear scar, which is featured as adhesive wear in Figure 5-8h. The EDX mappings of the steel/steel surfaces lubricated with NaPO₃, Na₄P₂O₇ and Na₃PO₄ were shown in Figure A- 3, Figure A- 4 and Figure A- 5 in the Appendix, which reveal a layer of phosphate film composed of Na, Fe, P and O exists on the worn surface when subjected to high pressure and shearing stress at 800°C.

5.3.5 XPS analysis of the worn disc and thermal film

The chain length of polyphosphate at the top layer of tribo-surface (~5 nm) can be determined by XPS through an intensity ratio of bridging oxygen (BO) to non-bridging oxygen (NBO) ratio [78, 113]. Detailed spectra of O 1s together with P 2p, Fe 2p and Na 1s on the tribo-stressed wear track (WT) and outside wear track (OT), i.e. static thermal
film, were collected and analyzed to help in understanding the specific structure of tribofilm from different lubricants.

Figure 5-9a shows the XPS signal of oxygen (O 1s), including three centered peaks at 529.0 eV, 530.5 eV, 533.0 eV. The peaks at 529.0 eV and 530.5 eV are assigned to iron oxides (MO, M represents metal element) and non-bridging oxygen in phosphate, e.g. –P=O, -P-O-Fe, P-O-Na, respectively [61]. The higher peak at ~533.0 eV originates from the bridging oxygen in phosphates, which corresponds to P-O-P bonds. The fitted results are shown in Figure 5-9a and Table 5-1. For Na₃PO₄ lubricant, only MO and NBO peaks are observed in both WT and OT area, thus implying that little polymerization of orthophosphate reaction has taken place. A comparison with the O 1s peak at 531.0 eV in OT area shows that in the WT area it decreased slightly to 530.1 eV, due to the loss of order in the crystalline orthophosphate under extreme stress [76, 150]. In the worn surfaces lubricated by NaPO₃ and Na₄P₂O₇, both BO and NBO peaks are present. A comparison with thermal film of NaPO₃, the binding energy of the O 1s in the WT areas increased by 1.5 eV due to a significant increase of concentration in non-bridging oxygen from 30% to 50%, which suggests that the reaction between iron oxide and bridging oxygen (P-O-P) is facilitated in WT area rather than OT area due to the energy caused by friction [78]. This is further confirmed by the BO/NBO relative intensity ratios dropping from 0.30 in OT to 0.25 in WT in Table 5-1. For the steel/steel pairs lubricated by Na₄P₂O₇, the binding energy of O 1s in the WT areas is very close to the OT area implying a similar degree of polymerization. The intensity ratio of BO/NBO shows a similar trend, where the original Na₄P₂O₇ powder has a ratio of 0.20, which then rises to 0.31 in the OT area and 0.28 in the worn surface. Therefore, Figure 5-9a shows that not
only the tribofilm but also thermal film depolymerizes using NaPO₃, whereas, Na₄P₂O₇ experiences a certain degree polymerization in the static thermal and tribo-stressed films.

The similar trend of depolymerization was also reflected by P 2p XPS spectra, which are shown in Figure A-6 in the Appendix. Figure 5-9b shows the high resolution Fe 2p spectra in the analyzed wear track (WT) and the uncontacted area (OT). The iron signal contains two main peaks: Fe 2p3/2 at ~711.2eV and of Fe 2p 1/2 at ~724.5eV, due to the spin-orbit splitting [151]. The typical binding energy for the Fe 2p 3/2 peak is 709.3-710.3 in Fe(II)O and 710.3-711.5 in Fe(III)2O₃. The absence of shoulder peak at ~709 eV and the appearance of the broad satellite at 718 eV in the lubricated WT by Na₄P₂O₇ and NaPO₃ indicate a higher concentration of Fe³⁺ ions in the wear track than that of the thermal film (OT), which is due to the activation energy for tribo-oxidation occurring during sliding being typically half of that of static oxidation [152]. It is also noted that the Fe 2p3/2 peak for WT NaPO₃ broadens wider than that of the static thermal film (OT NaPO₃) which implies a lower iron concentration in the tribofilm [153]. This phenomenon is not evident for Na₄P₂O₇. As for Na₃PO₄, the Fe 2p3/2 spectrum has the binding energy of ~711.2 eV with a satellite peak at ~719 eV in the WT and OT areas, this confirms the dominant appearance of Fe³⁺ in the tribofilm and static thermal film surface lubricated by Na₃PO₄ [153].

Figure 5-9c shows the Na 1s spectra. The peak located at 1070.8eV for the thermal film of NaPO₃, but when it is subjected to shearing stress, the Na 1s shifts towards a higher binding energy of 1071.6 eV. A similar tendency can be found for Na₄P₂O₇. This result is explained by the increasing number of non-bridging oxygen atoms bonding to sodium.
that will transfer more electron density to sodium from NaPO$_3$ to Na$_4$P$_2$O$_7$. The results are in line with the depolymerization process that occurs at the tribo-stressed interface for NaPO$_3$ and Na$_4$P$_2$O$_7$. With orthophosphate, the binding energy shifts from 1070.2 to 1070.8 eV when the thermal film is subjected to shearing stress. This shift towards a positive binding energy is mainly attributed to tribo-induced bond compression (Na-O bond) due to the amorphization of crystalline orthophosphate.

![Diagram](image)

Figure 5-9 XPS analysis recorded within the wear track (WT) and outside the wear track (OT) lubricated by NaPO$_3$, Na$_4$P$_2$O$_7$ and Na$_3$PO$_4$ at 800°C: (a) O 1s, (b) Fe 2p, (c) Na 1s.
Table 5-1 XPS analysis of the steel discs lubricated by three phosphates: NaPO₃, Na₄P₂O₇ and Na₃PO₄.

<table>
<thead>
<tr>
<th></th>
<th>O 1s</th>
<th>Fe 2p 3/2</th>
<th>Fe 2p 1/2</th>
<th>Na 1s</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1s</td>
<td>BO/NBO</td>
<td>/</td>
<td></td>
</tr>
<tr>
<td>Na₃PO₄ a)</td>
<td>530.5</td>
<td>0</td>
<td>/</td>
<td>1071.5</td>
</tr>
<tr>
<td>Na₄P₂O₇ a)</td>
<td>531.3</td>
<td>0.20</td>
<td>/</td>
<td>1071.8</td>
</tr>
<tr>
<td>NaPO₃ a)</td>
<td>531.7</td>
<td>0.51</td>
<td>/</td>
<td>1072.0</td>
</tr>
<tr>
<td>WT Na₃PO₄</td>
<td>531.0</td>
<td>0</td>
<td>711</td>
<td>724.5</td>
</tr>
<tr>
<td>OT Na₃PO₄</td>
<td>530.1</td>
<td>0</td>
<td>710.5</td>
<td>724</td>
</tr>
<tr>
<td>WT Na₄P₂O₇</td>
<td>528.8</td>
<td>0.28</td>
<td>709.4</td>
<td>722.8</td>
</tr>
<tr>
<td>OT Na₄P₂O₇</td>
<td>529.2</td>
<td>0.31</td>
<td>710</td>
<td>723.4</td>
</tr>
<tr>
<td>WT NaPO₃ b)</td>
<td>529.8</td>
<td>0.25</td>
<td>709.5</td>
<td>722.8</td>
</tr>
<tr>
<td>OT NaPO₃ c)</td>
<td>529.1</td>
<td>0.30</td>
<td>709.7</td>
<td>723.2</td>
</tr>
</tbody>
</table>

a) Na₃PO₄, Na₄P₂O₇ and NaPO₃ represent the original chemical powders, obtained from reference [113];
b) WT NaPO₃ represents the wear track lubricated by NaPO₃;
c) OT NaPO₃ represents the outside track area formed by NaPO₃, i.e. static thermal film.

5.3.6 XANES analysis of the wear track

Compared to XPS, XANES spectroscopy cannot only reveal the polyphosphate chain-length as the peak intensity ratio (a/c) of the P L-edge changes, but also shed light on the fine structure of tribofilm. The P L-edge, probing electron transitions from the 2p orbitals to unoccupied higher levels and d orbitals, provides detailed information regarding the oxidation and local chemistry of the P species due to the narrow lines and high photon resolution at the L-edge [115].

Figure 5-10 shows the P L-edge XANES spectra of the worn surface of steel discs lubricated by three sodium phosphates, where some model compounds are also shown for
comparison. The shape of P L-edge XANES spectra lines in the wear track lubricated by three sodium phosphates are similar. The c peaks become wider and the energy of peak c shifts up slightly compared to the corresponding original powder, which relates to different local distributions of metal cations on the oxygen atoms surrounding phosphorus that cause, variations in the formal charge of phosphorus and a superposition of multiple signals [154]. The peaks were fitted based on the conditions: the peak width of peak a equals that of peak b (the spin-orbit doublet), all peaks heights and positions were allowed to vary except for the peaks a and b [111]. One example of the peak fitting using Gaussian lines for the WT NaPO$_3$ XANES spectra was shown in in Figure 5-10b. The intensity of peak a or b relative to peak c is normalized and calculated as shown in Table 5-2, and were used to indicate the length of the phosphate chain [111, 115]. After the friction test at 800°C, the a/c ratios decreased significantly in WT lubricated by NaPO$_3$ from 0.75 to 0.27. This indicates severe depolymerization within the phosphate film. The WT lubricated by NaP$_2$O$_7$ lubricant experiences a slight increase in the a/c ratio from 0.23 to 0.25. This result is in agreement with the XPS result and implies that a modest degree of polymerization occurs. The a/c intensity ratio for WT lubricated by Na$_3$PO$_4$, remain unchanged (0.13) compared to the original Na$_3$PO$_4$ powder. Compared to reference compounds, the main peaks c of P L-edge obtained in the lubricated WT are all in accordance with shorter-chain polyphosphates.
Figure 5-10 (a) P L-edge XANES spectra in TEY model recorded within the wear track (WT) lubricated by NaPO$_3$, Na$_4$P$_2$O$_7$ and Na$_3$PO$_4$, and corresponding model compounds, and (b) one example of the peak fitting using Gaussian lines for the WT NaPO$_3$ XANES spectra. * represents the original lubricant powder.

Table 5-2 XANES analysis of the P L-edge spectra obtained from model compounds and tribofilms

<table>
<thead>
<tr>
<th>Samples</th>
<th>Peak positions (eV)</th>
<th>Relative intensities ratio (peak a/c)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>a</td>
<td>b</td>
</tr>
<tr>
<td>Fe$_6$(P$_2$O$_7$)$_3$*</td>
<td>135.3</td>
<td>136.3</td>
</tr>
<tr>
<td>FePO$_4$*</td>
<td>135.7</td>
<td>136.6</td>
</tr>
<tr>
<td>Na$_3$PO$_4$*</td>
<td>134.6</td>
<td>135.4</td>
</tr>
<tr>
<td>Na$_4$P$_2$O$_7$*</td>
<td>134.9</td>
<td>135.8</td>
</tr>
<tr>
<td>NaPO$_3$*</td>
<td>135.5</td>
<td>136.4</td>
</tr>
<tr>
<td>WT NaPO$_3$</td>
<td>135.8</td>
<td>136.4</td>
</tr>
<tr>
<td>WT NaP$_2$O$_7$</td>
<td>135.6</td>
<td>136.3</td>
</tr>
<tr>
<td>WT Na$_3$PO$_4$</td>
<td>134.6</td>
<td>135.6</td>
</tr>
</tbody>
</table>

*These chemicals are the original chemical compounds obtained from reference [115].

Figure 5-11 shows the O K-edge XANES spectra of the worn surfaces. These O K-edge XANES spectra help to distinguish the cation of phosphate within the tribofilm and determine the presence of iron in the tribofilm [155]. The main peak c of the tribo-surface...
lubricated by NaPO₃ and Na₄P₂O₇ is located between Na₄P₂O₇ and FePO₄, which implies the formation of mixed Na/Fe polyphosphate, while that of WT Na₃PO₄ is not in this region. After the rubbing tests, some iron oxide will substitute the role of Na₂O, and be digested into phosphate matrix. For the tribo-surfaces lubricated by Na₄P₂O₇ and NaPO₃, as the O1s and 2p states of oxygen are hybridized with the partially filled Fe 3d orbitals that are separated by the ligand field splitting, transition from the O1s to 2p states will produce the pre-edge split peak (peak a) in Figure 5-11. This also provides the information of iron oxides locating near the top surface. The peaks ‘c’ and ‘d’ are also associated with the O 1s to O 2p transition that are hybridized with either the 4s or 4p of Fe or Na [156]. These results indicate that phosphate compounds containing sodium and iron elements appear on the top layer of the worn surface. The peak d, which was reported to be related to the bridging oxygen (P-O-P) [115], in WT lubricated by NaPO₃ and Na₄P₂O₇ also shows a strong signal, while it was not observed in the O K-edge curve of WT Na₃PO₄ further suggesting the little depolymerization of orthophosphate.
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Figure 5-11 O $K$-edge XANES spectra in TEY model within the lubricated surfaces (WT) by NaPO$_3$, Na$_4$P$_2$O$_7$ and Na$_3$PO$_4$, and their corresponding model compounds.

The chemical state of Fe in the wear track was analyzed by the Fe $L$-edge XANES spectra in Figure 5-12a. There are two main peaks (a and b) in the Fe $L$-edge XANES spectra, which are assigned to transitions from Fe 2p to the unoccupied Fe 3d orbitals [157]. The distinct splitting at L$_3$-edge remains for all three films, with a small pre-peak followed by a main peak, suggesting the dominant presence of Fe$^{3+}$ valence form [157].

Figure 5-12b compares the Na $K$-edge XANES spectra of the lubricated surfaces by three sodium phosphates. The Na $K$-edge XANES spectrum in lubricated track by NaPO$_3$ is similar to that of Na$_4$P$_2$O$_7$, the wide edge doublet can be found with a small pre-peak and a wide smooth resonance. This indicates similar chemical environment of sodium in WT NaPO$_3$ and Na$_4$P$_2$O$_7$. In WT Na$_3$PO$_4$, only one peak at 1079 eV with a small pre-peak at 1074 eV and a broad feature at 1111 eV can be observed. The position of the main peak is intermediate between that of peaks b and c in WT NaPO$_3$ and Na$_4$P$_2$O$_7$, and could thus
result from a merging of these two peaks [155]. The presence of a small pre-edge peak is due to atom-forbidden transition from 1s to 3s state that contains partial waves of p character in the presence of crystal field [158, 159], suggesting a complex coordination environment for Na in this study. The broader peak c, which is caused by the transition from 1s to 3p, in WT NaPO$_3$ and Na$_4$P$_2$O$_7$ than that of Na$_3$PO$_4$ suggests that the coordination environment around Na atoms in the tribofilm formed by NaPO$_3$ and Na$_4$P$_2$O$_7$ lubricants are more periodic disorder than that of Na$_3$PO$_4$ [159].

Figure 5-12 (a) Fe L-edge and (b) Na K-edge XANES spectra in TEY mode recorded within the wear tracks lubricated by NaPO$_3$, Na$_4$P$_2$O$_7$ and Na$_3$PO$_4$.

In hot metalworking operations, high temperature lubricants are also required to protect freshly exposed and chemically active metal surfaces from oxidation. Figure 5-13 showed the cross-sectional SEM micrographs of the OT area on mild carbon steel discs after tribological test. As Na$_3$PO$_4$ appeared as loose particle at the contacting surfaces, it cannot resist the permeation and diffusion of oxygen, thus an oxide scale with a drastic thickness of 142 μm was formed on the disc lubricated by Na$_3$PO$_4$. Furthermore, severe
cracks and fractures were observed within the oxide scale, which posed a severe threat to the surface quality. When longer-chain Na₄P₂O₇ and NaPO₃ were applied, a uniformly adsorbed phosphate film was formed on the disc surface and totally isolated the hot steel surface from air, as a result a negligible oxide layer could be found.

Figure 5-13 Cross-sectional SEM images of the mild carbon steel discs after tribological tests in the OT area lubricated by (a) Na₃PO₄, (b) Na₄P₂O₇ and (c) NaPO₃.

5.4 Discussions

The tribological results shown in Figure 5-6 and Figure 5-7 indicate that three types of sodium phosphates with different chain-lengths can all reduce friction by 45~65% and wear rate by 80~90% at 800°C. The SEM images of tribo-stressed surface, shown in Figure 5-8, reveal a compact and smooth film covering the worn surface with clear shear tracks. EDX mapping demonstrates that the film was composed of Fe, Na, O, and P elements covering the worn scar uniformly, which suggests the existence of a layer of tribo-boundary phosphate film between the sliding surfaces. The state of lubricant and the interfacial tribo-chemical interaction of phosphate lubricants with the heated steel/steel surfaces are the causes of different friction behavior.

Sodium orthophosphate is thermally and chemically stable [156], it did not melt at 800°C, as evidenced by the in situ High Temperature Laser Scanning Confocal
Microscopy shown in Figure 5-3, where a large number of orthophosphate particles are present. O 1s and P L-edge spectra both confirm that short-chained Na₃PO₄ lubricant does not to polymerize in the thermal film. When subjected to high pressure and shear stress, there was almost no polymerization as well, and O K-edge also excludes the formation of mixed Na/Fe phosphate. Thus the tribofilm formation of orthophosphate at an elevated temperature is believed to associate with modifications to sodium orthophosphate’s initial crystalline structure, where the crystalline sodium orthophosphate particles have been sheared, deformed and smeared transforming them into a disorder tribofilm at the stressed interface at 800°C [76, 77]. At the first stage of friction curve, the sodium orthophosphate might be involved in a partial granular lubrication regime leading to the reduction of friction coefficient. After a short time of sliding, a nascent and thermally-softened tribofilm grown on the flat surface reduces the coefficient of friction. However, once the tribofilm is built up, a dynamical equilibrium is reached, with a stable average coefficient, as shown in Figure 5-12a. The melting point of Na₄P₂O₇, is at around 980°C (see Figure 5-4), while hydrated sodium pyrophosphate often has a melting point of ~79.5°C. Na₄P₂O₇ normally contains some hydrated water, thus it will partially melt during the heating process to form the liquid/solid composite phases between the rubbing surfaces, as shown in Figure 5-14b. As a consequence, a real viscous fluid film spreads out onto the deformed steel surface, with some solid particles existing in the fluid film. The friction curve shows an unstable track, which is possibly related with the third body particles between the sliding surfaces. Tribo-interaction between Na₄P₂O₇ and Fe₂O₃ forms mixed Na/Fe phosphate compounds at 800°C and 0.87 GPa, which is demonstrated by the XPS and XANES results. O 1s and P L-edge...
spectra both indicate that a slight polymerization of pyrophosphate occurs to form mixed short-chained Na/Fe phosphate with a chain-length between Fe$_4$(P$_2$O$_7$)$_3$ and Na$_3$PO$_4$, as shown by in Figure 5-11 and Figure 5-10. For metaphosphate, NaPO$_3$ is polymeric, and has a melting point at 628°C. Figure 5-14c shows a uniformly melting film covering the steel surface. P L-edge and O 1s spectra confirm depolymerization reactions in the WT and OT areas. In the non-contact OT area, the notable diffusion of iron atoms from steel substrate to a phosphate thermal film, together with the chemical reaction between iron oxide and bridging oxygen (P-O-P) according to the principles of hard and soft bases [21], is believed to be the fundamental reason for depolymerization in the thermal film. The diffusion of iron atoms into the top ~5 nm surface of thermal film was demonstrated by the detection of the Fe 1s signal shown in Figure 5-12b. Depolymerization also occurs because the exchange of Na$^+$ with Fe$^{3+}$ needs more negative charges to balance the reaction, and shortens the chain-length [160]. A comparison with the depolymerization in thermal film shows that metaphosphate in wear track suffers more severe depolymerization, and the BO/NBO ratio decreasing from 0.30 to 0.23. The O 1s spectrum also indicates that the concentration of non-bridging oxygen is higher in WT area than that in the OT area, which indicates the reaction between iron oxide and BO is facilitated in WT by tribological stress. As sliding proceeds, the chain length of metaphosphate decreases due to the replacement of the P-O-P bond by a P-O-Fe bond.

The O K-edge spectrum demonstrates the formation of short-chained Fe/Na polyphosphate glass with a a/c value of 0.27 within tribofilm, where the Fe$^{3+}$ resides predominantly. The tribofilms formed by NaPO$_3$ and Na$_4$P$_2$O$_7$ exhibit similar chain-lengths supported by similar BO/NBO intensity ratios and a/c peak intensity ratios of P
L-edge. It is in good correlation with their frictional performance, as shown in Figure 5-6 and Figure 5-7. However, the uniformity of phosphate film by NaPO$_3$ ensures a lower and more stable coefficient of friction.

Figure 5-14 shows the *in situ* optical images of phosphate thermal films on steel surfaces at 800°C and the magnified images of tribofilm. The differences in thermal film morphology can be attributed to their chemical reactivity difference due to different chain-length, such that: longer-chain polyphosphate is more chemically reactive with iron oxide, as XPS and XANES results indicate. Once the thermal films, shown in Figure 5-14a, b and c, are subjected to high pressure and shearing stress, complex tribo-chemical reactions occur to produce different phosphate compounds leading to different frictional behaviors. The layered structure of ZDDP’s tribofilm is composed of zinc polymer-like metaphosphate at the top surface with a a/c ratio of 0.72 after 30 min friction [79, 145]. However, that formed by NaPO$_3$ and Na$_4$P$_2$O$_7$ presents a different phosphate structure which shows a short-chained Fe/Na polyphosphate (soften and melting point at approximately 500 and 1050°C, respectively) on the top surface with a a/c ratio of 0.27 and 0.25, respectively. Thus, a softened phosphate film was believed to exist at the interface. The structure of mixed short-chained Na/Fe polyphosphate structure was extensively investigated and interpreted: a FeO$_6$ octahedron shares all its apices with PO$_4$ tetrahedra, PO$_4$ tetrahedral shares its corners with octahedra and tetrahedra, Na$^+$ ions are enclosed in the cages formed by PO$_4$ tetrahedral. The Fe$^{3+}$ adopts octahedral symmetry and contributes to the network [161]. The structures of these Na/Fe phosphates can show the great adaptability of the PO$_4$ groups to the octahedra, and the coordination between PO$_4$ tetrahedral and iron ions can also increase as high pressure induced cross-linking
through the iron ions, thereby increasing the hardness of material [161]. For example, it was reported that at a higher pressure (0.6 GPa) and elevated temperature (1000°C), the degree of cross-linking during friction is able to increase the mechanical strength by factor of 3 [162]. Therefore, high pressure, shearing stress combining with elevated temperature transform NaPO$_3$ and Na$_4$P$_2$O$_7$ lubricants to more chemically advanced glass structures in the tribo-stressed area, which will improve resistance of wear. Compared to NaPO$_3$ and Na$_4$P$_2$O$_7$, Na$_3$PO$_4$ is more thermally and chemically stable. The crystalline orthophosphate is mainly deformed and smeared and incorporated into the tribofilm in a disordered form without the state of polymerization. A comparison with the tribofilm formed by Na$_4$P$_2$O$_7$ and NaPO$_3$ lubricant with steel oxide suggest that the tribofilm formed by Na$_3$PO$_4$ possesses a shorter chain-length with an intensity ratio of peak a/c of 0.13, a higher softening point and a higher mechanical properties with a 25% higher hardness and 15% higher elastic modulus [163], as a result, the higher antiwear resistance was obtained.

Figure 5-14 Fine structure and real state of phosphate lubricants at the tribo-surfaces

120
5.5 Conclusions

An investigation has been carried out to study the friction and wear behaviors of steel/steel pairs lubricated by three types of sodium phosphates (ortho-, pyro- and metaphosphate), and the following conclusions can be drawn:

(1) In this chapter, phosphate compounds with different chain-lengths, such as ortho-, pyro- and meta-phosphates, were investigated in terms of the contribution of individual phosphate to the tribological efficiency (anti-wear and friction-reducing capability) of the tribofilm. Sodium orthophosphate ($\text{Na}_3\text{PO}_4$) provides the lowest friction and wear value, while sodium polyphosphate ($\text{NaPO}_3$) produces a more stable friction coefficient.

(2) A tribo-boundary film of phosphate contributes to their performance, which is composed of Na, Fe, P and O elements. Crystalline orthophosphate is short-chained, and little depolymerization/polymerization was observed in the wear track. Sodium metaphosphate decomposes in the tribo-stressed area (WT) and non-contact area (OT), whereas sodium pyrophosphate becomes slightly polymerized.

(3) The short-chained phosphate mainly leads to better anti-wear efficiency, due to the tribo-chemical reaction of iron oxide wear debris with phosphate agents. The long-chained phosphate facilitates the lubrication of the rubbing surface, leading to a stable friction of sodium metaphosphate. Furthermore, sodium metaphosphate is very resistant to oxidation at elevated temperatures and is the best candidate for hot metalworking applications.
6 Effect of loading on the friction and interface microstructure of lubricated tribopairs

6.1 Introduction

The tribochemical interaction between inorganic alkali polymers and oxide scale has been investigated, but it remains controversial. Dancheko [164] suggests that the chemical products between phosphate glass and steel at high temperature possess similar properties as the initial glass melt, and still work as excellent lubricants, even though the mutual dissolution of lubricant and scale changes the melting temperature and viscosities of the glass lubricants. The lubricity mechanism of the products can be explained that the reaction between phosphate and scale on metal surface transform the melt into a material with the same polymeric structure as the initial glass. The researcher also claims that the stable feeding of glass lubricant in tube rolling can improve the quality of the tubes and reduces the wear and friction. Grunze [165] and Danchenko [164] 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 [166] disputed that the oxides produced during metal forming dissolve into the polyphosphate glass and destroy its polymer structure and lubricity properties. In chapter 4, alkali polyphosphates with different chain-length, i.e. metaphosphate, pyrophosphate and orthophosphate, have been studied as a lubricant at an elevated temperature. Metaphosphate produces desirable performance in terms of friction reduction, wear inhibition and anti-oxidation, 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. 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 [66]. Although the application of inorganic phosphate glass as a hot metal forming lubricant has attracted attention, the effects of applied load on the tribological behavior and interface evolution are still poorly understood.

This chapter uses a ball-on-disc high temperature tribometer on which the disc surface is pre-coated with sodium metaphosphate before heating, this lubricant is found to have an excellent wettability with a steel surface at high temperature [61]. This layer of phosphate film can form a viscous tribofilm in the contacting zone and help to reduce the friction and wear [78, 167]. This chapter considers the effect of applied load on the tribological behavior of sodium metaphosphate, which includes the evolution of the microstructure and the mechanical properties of phosphate film on the ball, supported by SEM, FIB/TEM and nanoindentation.

6.2 Experimental details

The preparation details of 20w.r% sodium metaphosphate lubricant and the pre-coating procedures with a thickness of around 50 μm on the mild steel disc were introduced chapter 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 are shown in Table 6-1. The frictional sliding test started when the
temperature of the furnace was in a steady state at 800°C for 5 min. every test was 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 in the furnace.

Table 6-1 ball-on-disc test conditions

<table>
<thead>
<tr>
<th>Ball</th>
<th>Material</th>
<th>GCr15 steel: 0.98%C-1.48%Cr-0.27%Mn-0.35%Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diameter</td>
<td>6.35 mm</td>
<td></td>
</tr>
<tr>
<td>Disc</td>
<td>Material</td>
<td>Mild steel: 0.20%C-0.40%Mn-0.50%Si</td>
</tr>
<tr>
<td>Size</td>
<td>Φ50 mm×5 mm</td>
<td></td>
</tr>
<tr>
<td>Sliding speed</td>
<td>0.094 m/s</td>
<td></td>
</tr>
<tr>
<td>Temperature</td>
<td>800°C</td>
<td></td>
</tr>
<tr>
<td>Load (N)</td>
<td>5 (0.68 GPa), 10 (0.86 GPa), 20 (1.09 GPa) and 30 (1.24 GPa)</td>
<td></td>
</tr>
</tbody>
</table>

### 6.3 Results

#### 6.3.1 Effect of phosphate coating on oxidation of steel

![Figure 6-1](image)

Figure 6-1 Geometric positions of sodium metaphosphate, Au and substrate layers (a) before and (b) oxidation after heating, (c) the EDX spectra of the circle position in (b).

...to investigate 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 ($R_a$) was measured to be 87 nm. The sample was sprayed by lubricant to form a layer of phosphate on top, as shown in Figure 6-1a. Then, the sample was put into the furnace heating up to 800°C for 900 s. After oxidation, the sample was taken out and cooled in air. Then the cross sections of samples were analyzed by SEM&EDX, shown in Figure 6-1b. 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 4-8. 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 [168]. 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 [168]. With the continuous dissolution 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 6-1b.
6.3.2 High temperature tribological tests

Figure 6-2 (a) Curves of friction coefficient as a function of sliding time for tribotests at different loads where friction coefficient curves at 30 N are inserted. (b) Average friction coefficients as a function of load at both unlubricated and lubricated conditions.

Figure 6-2 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 A-7 in the Appendix. At 20 N, the friction is reduced from 0.41 to 0.21 by 49% shown in Figure 6-2b. 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 6-2a exhibits an substantially unsteady and fluctuating trend. But when NaPO$_3$ lubricant is 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 6-2b.

![Graphs showing friction and wear rate](image)

Figure 6-3 Specific wear rates of (a) GCr15 ball and (b) mild steel disc at different loads at 800°C with a 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 as shown in Figure 6-3, 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 an increase of applied load except at 20 N, which presents a slightly lower wear rate than that at 10 N. This phenomenon has also been reported by reference [6], attributed to the improvement of glaze layer in compaction with load. The wear rate under lubricated condition is proportional to the applied load, which increases monotonously with load. A comparison
of the wear rate between lubricated and unlubricated tribopairs shows that the polyphosphate lubricant can reduce the ball and disc wear by approximately 65%~86% and 64%~90%, respectively.

6.3.3 SEM analysis

Figure 6-4 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 6-4 shows the SEM micrographs of the wear surfaces and the corresponding cross section of the unlubricated ball scars at different loads. Figure 6-4a shows that at 10 N the worn ball surface of 2200 μm diameter is 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 is increased to 20 N, a smaller wear scar with smooth and compacted worn surface is observed. However, spalling of the oxide glaze layer is also observed at some spots shown in Figure 6-4c, which may be a reason for the slight fluctuation of friction in Figure 6-2a. The corresponding cross-sectional micrograph in Figure 6-4d shows that the oxide layer has a thickness of 10 μm. At 30 N, a large number of oxide lumps transferred from the mild steel disc accumulated unevenly on the ball scar. Furthermore, a large number of cracks and fractures were observed within these oxide lumps, which were confirmed by the highly magnified SEM images in the Appendix Figure A-9.
Figure 6-5 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 6-6 SEM/EDX elemental mappings of cross-section of ball track lubricated by NaPO₃ 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 in the Appendix Figure A-10.

Figure 6-5 shows the SEM micrographs of ball scars lubricated by sodium metaphosphate at different loads. At 10 N, a layer of distinct film was observed to cover the wear scar on the ball with a mean diameter of 1080 µm, which is about half of the unlubricated one. The cross section of the ball scar in Figure 6-5b shows that a distinct tribofilm was located above the oxide scale with a thickness of 5 and 20 µm, respectively. The wear scars on the balls at 5 (Figure A-8 in the Appendix), 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 at 20 and 30 N were 4.5 and 4 µm, respectively. The EDX
mappings in Figure 6-6a 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 6-6b. This indicates the phosphate tribofilm cannot support the 30 N load continuously for 900 s at 800°C.

6.3.4 Nanohardness

![Graphs showing film thickness and nanohardness](image)

Figure 6-7 (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 6-7a 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, the phosphate tribofilm became monotonously thinner with increase of load. The reason is that the high pressure will squeeze the soft viscous phosphate fluid out of the wear track.
Figure 6-7b 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 6-4 and Figure 6-5. 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 down slowly. As a result, the increase in disc hardness due to deformation and compaction in sliding was reduced by the annealing behavior during 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.

6.3.5 XRD characterization
Figure 6-8 XRD characterization of tribofilm scale collected in the wear track of disc.

Figure 6-8 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°/min. The crystallized compounds at room temperature can provide clues about the parent glass at high temperature. The XRD results agree well with those in Figure 4-15 indicating that the peaks of $\text{NaFePO}_4$, predominate the spectra with some $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$, and $\text{Na}_3\text{PO}_4$, this phenomenon 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.

6.3.6  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 6-5. The corresponding STEM bright field micrograph, high-angle annular dark-field imaging (HADDF), EDX mappings and the selected area diffraction (SAD) patterns are shown in the following figures.

**With sodium metaphosphate**

![STEM HADDF micrograph and corresponding EDX elemental mappings of the phosphate tribofilm formed at 10 N at 800°C on the ball.](image)

Figure 6-9 STEM HADDF micrograph and corresponding EDX elemental mappings of the phosphate tribofilm formed at 10 N at 800°C on the ball.
Figure 6-10 (a) STEM 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 6-9 shows the HADDF micrograph and corresponding EDX elemental mappings of the cross-section of lubricated contact surface at 10 N on the ball, where there are many nanoparticles with an average diameter of 360 nm within the matrix. The EDX mappings reveal that the matrix consists of Na, P, Fe, Mn and O elements, while the nanoparticles dissolved in the matrix 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 6-9b. The phosphate tribofilm is composed of soft phosphate phase and hard oxide particles indicating that the integral hardness of tribofilm should be between those two phases, as shown in Figure 6-7b. The corresponding SAD patterns shown in Figure 6-10b and c indicate that the matrix is mainly amorphous, but they do have crystalline nanoparticles embedded within it. The SAD pattern of these nanoparticles indexed in Figure 6-10b indicates that the nanoparticles consist of both Fe$_3$O$_4$ and Fe$_2$O$_3$. 
Figure 6-11 TEM HADDF micrograph and corresponding EDX mappings of phosphate tribofilm at 20 N at 800°C on the ball.

Figure 6-12 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 6-11 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 6-11b 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, while Na, P, Fe and O elements were found in the bottom layer. There are also numerous particles distributed in the matrix, but less than that produced at 10N. The phosphate layer mainly presents an amorphous morphology with some grains showing clear boundary with a mean grain diameter of around 1μm. The corresponding SAD pattern of this grain (position 1) in Figure 6-12 indicated that the crystalline grain was maricite (NaFePO$_4$), which is consistent with the report that the short-chained oligomers crystallize more easily [169].
Figure 6-13 TEM HADDF micrographs and EDX elemental mappings of phosphate tribofilm at 30 N at 800°C on the ball.

Figure 6-13 shows the TEM&EDX analysis of the FIB milling cross-section of ball scar lubricated by sodium metaphosphate lubricant at 30 N. Only one layer structure was identified in the tribofilm with an average thickness of 4.7 μm shown in Figure 6-13a, 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 6-13b, but less than both of those at 10 and 20 N. The EDX mapping of Figure 6-13b 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.
6.4 Discussions

For the an unlubricated tribo-system of GCr15/Mild steel at 800°C 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 high wear rates of both ball and disc shown in Figure 6-3 are 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 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 metal transfer occurs. The severe surface damage to the protective oxide ‘glaze’ layer, such as fractures and cracks shown in Figure 6-4e, which leads to a fresh metal-to-metal contact, is thought to be mainly responsible for the massive metal transfer and fluctuating friction [9]. 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 advantageous to the sintering and compaction of fine wear debris, and facilitates the formation of the protective oxide ‘glaze’ layer [6]. Furthermore, a higher applied load had the effect of raising the surface temperature, leading to a higher rate of oxidation [14]. 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 the thinning of oxide scale,
which also promotes clean metal/metal contacts, increases the metal transfer and causes fluctuation of friction [6, 9]. The higher hardness of oxide layer on the ball scar surface at 20 N than that at 30 N can be 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 [170]. At 20 N, a smooth and compact oxide layer is shown in Figure 6-4c. However, when the load increases to 30 N in Figure 6-4e, part of this layer of oxide glaze is transferred from the opposite disc, it shows a loose and fragmented morphology, which has in a much lower hardness value. The different wear rates in Figure 6-3 between the ball and disc occur because the ball is in continuous contact with the mating disc surface, while 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 [171]. 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 hard Chromium carbide in the iron matrix [122]. This is also a significant reason for the higher hardness of ball than that of disc, shown in Figure 6-7b. In summary, with extreme conditions of pressure and temperature, high wear of tool, unsteady friction and the massive metal transfer will occur, which synergistically re damage 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 is in a melting state as determined by the DSC&TG curves in Figure 4-8. 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. Both the wear rate and friction
coefficient lubricated by sodium metaphosphate increase linearly with load. The thickness of phosphate tribofilm is reduced monotonously with an increase of load, while the hardness of phosphate tribofilm experiences little change around 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 applied load due to coordination transformations at high pressure and shear [172]. The little variation of phosphate tribofilm hardness with load at high temperature indicates that the impact of high pressure on the mechanical properties of viscous glass state is not as evident as viscoelastic solid state at room temperature.

The chemical compounds in the phosphate film were predominated by NaFePO₄ some Na₃Fe₂(PO₄)₃ and Na₃PO₄, and they change little in the load range from 10 to 30 N. This finding supports the view that the interaction between oxide scale and polyphosphate destroys its polymer structure, and produces short-chained orthophosphate. However, this structural change exerts little negative influence on its tribological performance. The similar types of chemical compound at different applied load can also explain the similar hardness performance at room temperature in Figure 6-7b. 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 Fe³⁺ to strengthen the phosphate chains [173, 174]. 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; (i) it facilitates the breakup of P-O-P bonds and reduces the viscosity of the phosphate network [174, 175], (ii) take parts 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. STEM 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 [21, 65, 176]. The extensive wear debris reintroduced into the soft phosphate matrix can perform multiple contributions to the improvement of tribological performance: Firstly, the abrasive wear caused by hard Fe$_2$O$_3$ debris was alleviated [21, 33], which can be observed by comparison of SEM micrographs of wear scar in Figure 6-4, 6 and 7. Secondly, the digestion of oxide debris into the phosphate matrix can enhance the integral mechanical properties of tribofilm shown in Figure 6-7, which shows the tribofilm is four times harder 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 [177], 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, where 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 composed mainly 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 6-10 and Figure 6-11: 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 suggested in this study 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 observed in the static oxidation test in Figure 6-1. 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 increase sharply, which is twice that at 20 N shown in Figure 6-3. 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.

6.5 Conclusions

The tribological tests at 800°C show that the inorganic alkali polyphosphate lubricant can reduce the friction coefficient and wear rate significantly, by around 24–49% and
64–90%, respectively, although they show a monotonous increase trend with load. 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 the wear track, composed of short-chained amorphous NaFePO$_4$ and some Na$_3$Fe(PO$_4$)$_2$. The thickness of phosphate tribofilm monotonously decreases with the increase of load, while the corresponding hardness shows little change. However, when the load increases to 30 N, the phosphate tribofilm deteriorated significantly.
Chapter 7 - Lubrication mechanics of polyphosphate glass in hot rolling

7 Lubrication mechanics of polyphosphate glass in hot rolling

7.1 Introduction

In hot rolling, a lubricant is used to enable the strip to slide over the roll surface under controlled and/or reduced frictional conditions. Lubrication in hot rolling is an ongoing topic for researchers in hot metal forming and lubrication field, driven by the global competition in steel product price and the manufacturing cost. Furthermore, complex and harsh tribological conditions in hot rolling, as described in section 2.2.3, pose significant challenges for the selection of lubricant.

Currently, o/w emulsion lubricant is commonly applied in hot rolling to reduce the forces/torques, roll wear [178], surface defects and tertiary scale thickness [103]. The effectiveness of lubrication depends on the oil film thickness as compared to the separation between the roll and the strip surfaces, the deformation of the oil film and the activity of the load bearing additives. Azushima et al. [106] pointed out that the increase of oil concentration increases the lubrication film thickness, which in turn influences the friction coefficient. However, when it exceeds a critical value, the friction coefficient becomes constant, and is independent of the film thickness in the interface, in this case, the contact interface was fully covered by a uniform lubrication film, as shown in Figure 2-12a. The inaccessibility of the contact zone in hot rolling significantly limits the understanding of lubrication behavior at the roll-strip interface. An influential factor is the failure in identification and characterization of the lubrication film as the oil undergoes pyrolysis, even burn-off after hot rolling leaving no residual lubricant traces, which makes the oil film impossible to be analyzed offline. Furthermore, as discussed in
references [38, 43, 179], there exist some disadvantages with the use of oil, such as serious emissions to environment and health issue due to harmful smoke caused by the pyrolysis of organics, etc. Therefore, the use of some inorganic lubricants is highly recommended in hot rolling to avoid such problems.

Many publications have proposed a number of inorganic glass lubricants for metal forming process, as suggested in section 1.2.2. The tribological performances of different lubricants in hot rolling, including distilled water, commercial o/w emulsion, layered solid talc, borax and metaphosphate glass, were compared in Chapter 4 when tested on pin-on-disc and hot rolling under controlled conditions. The results reveal that sodium metaphosphate has the best lubrication performance among all the tested lubricants. Furthermore, the sodium metaphosphate glass lubricant can bring about a significant reduction of tool wear. However, it shows little impact on the antioxidation behavior of hot steel. This was inferred that the low concentration of sodium metaphosphate results in a very thin lubricating film, which contributes little to prevent the diffusion of iron ions to the interface of oxide and oxidized atmosphere.

Kong et al. [86] performed hot rolling tests with interstitial-free steel at warm rolling temperatures 600-800°C, lubricated by a mixture of sodium and potassium polyphosphate with a total weight concentration of 20%. They found that the friction coefficient in hot rolling was halved, and the lubrication ability grows with an increase of temperature. The detailed analysis on the cross section of rolled surface reveals that a uniform lubrication film with a thickness as thin as 50-100 nm was detected. It is evident that from the literature survey [53] on high temperature tribology in hot metal forming that there are several aspects that need to be studied further, such as the influence of inorganic glass lubricant on microstructure and
properties of hot rolled strip, properties of oxide scale and substrate, and in particular there is little studies into practical interfacial layer structure which still remains unclear. Some studies suggested the use of phosphate-based chemicals as antiwear additives in hot metal forming lubricants. Tomla et al. [180] tested a commercial solid lubricant containing zinc phosphate chemicals as antiwear additives in the lubricant at 500°C and 800°C. The results show that this type of solid lubricant not only reduced the friction coefficient, but also completely protected the tool from adhesion. A similar phosphate additive was also tested by Hao et al. [181] to prevent the sticking defects during the hot rolling of ferritic stainless steel strip. The results show that the formation of phosphate film at the top surface can narrow the crack sizes and suppress the crack propagation, which in turn can alleviate the sticking problem at the interface. Besides the lubrication and antiwear advantages, the use of polyphosphate glass in hot rolling can also provide some information about the lubricant entry amount, its whereabouts, and the relation between rolling conditions and lubricant entry, because the Na and P elements allow the researcher to characterize and follow the lubricant. As a result, more detailed information in the contact zone with sodium metaphosphate glass can be revealed, resulting in a clear understanding of the structure of the lubricating film. How the interfacial structure contributes to the lubrication mechanics will be discussed in this chapter.

This chapter concentrates on the front section of hot rolling production line from reheating to roughing mill, as shown in Figure 1-2a. A high concentration (40 w.t. %) of sodium metaphosphate aqueous solution is used to study its effect on lubrication and oxidation under different reductions. Through FIB and TEM, close attention is given to the detailed interfacial structure at the contact zone built up with sodium metaphosphate
glass lubricant. In this chapter, we are only concerned about the interfacial structure formed in hot rolling, since the excellent lubricating performance of sodium metaphosphate has already been demonstrated in Chapter 4. Furthermore, the effect of high concentration of polyphosphate lubricant on surface roughness, oxide scale growth and its mechanical properties is also studied in this chapter.

7.2 Experimental details

7.2.1 Lubricant preparation

The high purity (AR Grade) and amorphous sodium metaphosphate (NaPO₃) compound from Sigma-Aldrich Corporation is the principle composition of aqueous phosphate glass solutions. As 40 g sodium phosphate compounds were dissolved into 60 ml distilled water, forming the transparent solutions of 40 wt% concentration. The component was weighed on a balance that provided measurements accurate to ±0.001 g. The aqueous sodium metaphosphate solution was tested previously by high temperature ball-on-disk tribometer, and shows an excellent lubricity and antiwear attributes [61]. Mild steel plates with the chemical composition listed in Table 7-1, were selected and machined into the specimen size of 65 (W) × 203 (L) × 20 (H) mm for the experiments. In order to help entry of the sample into the roll bite, the front of the specimen was tapered to a thickness of 6 mm and a length of 50 mm.

7.2.2 Hot rolling test

The rolling experiments of mild carbon steel were performed on a 2-high Hille 100 rolling mill with rolls of 225 mm diameter × 254 mm roll body length and with a roll
surface roughness ($R_a$) of 1.0 µm. Rolling forces were measured by two load cells on the mill, and rolling speed can be set from 0.12 to 0.72 m/s. In this study, three different reductions (20, 40, and 60%) were applied. The heat treatment of mild steel specimens was conducted in an electrical resistance furnace in air atmosphere at 1150°C for 30 min to ensure a homogeneous temperature distribution and a uniform scale thickness. After heat treatment, the hot specimen was mechanically descaled before rolling. The temperature after hot rolling was measured to be 900°C. It needs 260 s to cool down to below 570°C, over which time the oxide scale will develop on steel surfaces [182].

A thick layer of aqueous inorganic polymer glass lubricant was sprayed on the rolls. After rolling, the rolled samples were put into a tank purged with inert gas $N_2$ to minimize the oxidation during the cooling. All experiments have been done twice to ensure repeatability. Representative samples were taken in the middle of the strip for further study of the oxide layer. The samples were prepared for metallography, etched, and the thickness of the oxide scales was evaluated.

<table>
<thead>
<tr>
<th>Elements</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Cu</th>
<th>Ni</th>
<th>Cr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight, %</td>
<td>0.1356</td>
<td>0.1795</td>
<td>0.695</td>
<td>0.00875</td>
<td>0.0235</td>
<td>0.1807</td>
<td>0.0528</td>
<td>0.1444</td>
</tr>
</tbody>
</table>

### 7.2.3 Characterization methods

After hot rolling, the rolled surface and cross-section perpendicular to the rolling direction were analyzed by JEOL JSM-6490LV with a 30 kV conventional tungsten filament, and the obtained EDX mapping was analyzed by Aztec software. Lamella specimen was obtained using FEI Helios NanoLab G3 CX focused ion beam FEGSEM.
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The JEOL 1400 transmission electron microscope with an accelerating voltage up to 120 kV was used to analyze the FIB lamella.

7.3 Results and discussions

7.3.1 Hot rolling force and torques

![Graph showing comparisons of hot rolling forces and corresponding torques with different hot rolling reductions at 1150°C and 0.5 m/s.]

Figure 7-1 Comparisons of (a) hot rolling forces and (b) corresponding torques with different hot rolling reductions at 1150°C and 0.5 m/s.

Figure 7-1 shows the roll separating forces and rolling torques as a function of the reduction under the condition of dry and lubrication. With a higher reduction, as expected, the rolling forces and torques all grow regardless of the lubricated and un lubricated conditions. This trend was associated with the increase of strain and strain rate hardening, as indicated by Equation 2.2 and Equation 2.3. Furthermore, the larger contact area and heat transfer at the interface also contribute to this trend. The results also show that the lubrication performance of metaphosphate glass becomes weaker with a decrease of reduction, and it shows a very small effect on lubrication at 20% reduction. The reason behind this trend will be discussed in detail in the following sections.
7.3.2 Surface morphology and roughness characterization

Figure 7-2 SEM micrographs of the rolling mild steel surfaces lubricated by: (a) dry, (b) sodium metaphosphate solution (c) magnification of Figure 7-2(b) at 60% reduction, 1150°C and 0.5 m/s.

Figure 7-3 EDX spectrums of two different positions in Figure 7-2b

Figure 7-2 shows the SEM micrographs of the rolled surface with different lubricating conditions at 60% reduction. For the dry rolled surface in Figure 7-2a, the rolled samples seem to have a smoother surface with an Ra of 1.17 μm, however, the surface appears severely cracked. For the strip lubricated by sodium metaphosphate solution, it has a slightly rougher surface with an Ra of 1.37 μm. Two types of morphology are observed on the sample surface; a small ratio of rolled surface is covered by residual lubricant. The
lager magnification of residual lubricant in Figure 7-2c shows that it has a banded morphology with a rough topography, which is reflected in the higher roughness of the rolled strip lubricated by sodium metaphosphate. The EDX analysis in Figure 7-3 of the residual lubricant show that it was mainly composed of Na, Fe and O with only a very small content of P element. Phosphorus is hardly detected from the rolled surface which indicates the partial separation between phosphorus and sodium in sodium metaphosphate.

As described in Chapter 3, when 20\textit{w.t.}\% sodium metaphosphate solution was used, EDX analysis shows that lubricant elements (Na and P) were hardly detected from the top surface and the corresponding cross-section. It was possible that the thin polyphosphate film was absorbed by the following oxide growth during the cooling down period, and it was diffused and integrated into the oxide scale. Consequently, it has little influence on the surface roughness, and the detection also becomes more difficult. When the weight concentration was increased to 40\%, a larger amount of sodium polyphosphate was dragged into the roll bite to lubricate the hot plastic deformation of strip. The amount of lubricant is large such that its complete integration becomes almost impossible.
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7.3.3 Surface roughness

Figure 7-4 3D surface profiles of hot rolled steel strip with a reduction of 60% (a) pre-entry, (b) dry condition and (c) lubricated by 40w.t.% sodium metaphosphate aqueous solution.

Figure 7-5 Average surface roughness (Rₐ) of rolled strip with different reductions at 1150°C and 0.5 m/s.

The rolled surface was measured by a 3D surface profilemeter as shown in Figure 7-4, and the measured average surface roughness (Rₐ) shown in Figure 7-5. The descaled surface is quite rough with a large number of valleys and peaks. The Rₐ was measured to be 5.03±0.28 μm. After undergoing a 60% reduction under dry condition, the surface is flattened, and becomes fairly smooth with an Rₐ of 1.17 μm. The sodium metaphosphate
lubricant roughens slightly the surface to 1.37 µm. This difference was associated with the lubricant residual formed on the surface, as shown in Figure 7-2b, and the surface roughness differences between dry and lubricated were found to become smaller with a higher reduction. Furthermore, it can be observed that the pre-entry image in Figure 7-4a and lubricated rolled strip in Figure 7-4c contain a relatively high number of potential lubricant pockets which may support lubricant entrapment and reduce the asperity contact area between the tool and sample sheet. The roughness data shows that the use of inorganic glass introduces the possibility that the residual can increase the surface roughness slightly.

### 7.3.4 Cross-sectional analysis

**EDX analysis of cross section**
Figure 7-6 EDX cross-sectional mapping of rolled steel plate lubricated by sodium metaphosphate under different reductions (a) 60%, (b) 40%, (c) 20% at 1150°C and 0.5 m/s, perpendicular to the rolling direction of the test pieces.

Figure 7-6 shows a representative EDX cross-sectional mapping of the rolled mild steel strip. After rolling at a reduction of 60%, the scale thickness was fairly even, and no partial flaking off the base metal surface. A structure with four layers was identified in the
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oxide scale; Layer 1 has a thickness of 9 ± 2 μm, showing a solid and compact morphology with few cracks or porosities. This layer was attributed to the newly grown oxide layer formed during the cooling period. As described in the “Experimental Section”, after hot rolling, the rolled plate still has a temperature at approximately 900°C, and it takes at least 260 s to cool down to below 570°C. This duration is judged to be sufficient to form a fairly thick oxide scale based on the literature survey on the oxidation of mild steel [183, 184]. Layer 2 is a uniform layer of polyphosphate film, which is consisted of Na, P, Fe and O elements. This layer of phosphate shows a discontinuous film, which is believed to be damaged by the outward growth of oxide scale in the cooling process, and some thin areas of phosphate film are penetrated by columnar iron oxide. At high temperature, it is expected that this layer of phosphate film is located at the top surface and is continuous. Layer 3 shows a cracked and porous structure of the deformed secondary oxide scale layer formed during the rolling process. Layer 4 also shows a thin and intermittent layer of phosphate lubricant film existing at the interface between oxide scale and steel substrate. The formation of layer 4 is due to part of phosphate melt in layer 2 moving to the interface to form this layer after rolling. The high temperature after rolling allows the metaphosphate to maintain a melt state for over 260s, as revealed in Figure 4-9 that it shows a melting behavior at around 520°C. Furthermore, the porous and cracked secondary oxide scale provides the passageway for the fluidic lubricant to enter into the interface and left some traces in the secondary oxide scale.

The oxidation of rolled strip during the cooling period was reported in many literature, which indicates that the surface at room temperature is not a realistic reflection of surface in the contact zone [4]. The practical tribo-interface in hot rolling was covered with new-
grown oxide scale formed during the cooling period, and it needs to be explored in further details.

![Calculated lubricating film thickness of phosphate lubricant](image)

**Figure 7-7** Calculated lubricating film thickness of phosphate lubricant

The sodium metaphosphate glass can provide a quantitative analysis of entrapped lubricant in the roll bite. The thickness of phosphate film at 60% reduction is measured at around 4 μm, as shown in Figure 7-6a. However, this thickness was subject to the influence of element diffusion and the oxide growth during cooling, which does not reflect accurately the realistic working film thickness. Therefore, one method to obtain the practical film thickness is proposed here. The total amount of metaphosphate lubricant entry is calculated by adding up the entire areas occupied by phosphorus element in Figure 7-6, then the total area occupied by phosphorus element was divided by the length to obtain an effective phosphate film thickness, as shown in Figure 7-7. As suggested in the introduction (section 7.1), the effectiveness of the lubrication is mainly determined by the lubricating film thickness and the chemical activity of glass lubricant. Other factors such as the surface roughness of roll and workpiece, the sensitivity of lubricant viscosity to temperature also have some influence on the loads, but not as
important as the first two parameters. At 20% reductions the use of sodium metaphosphate aqueous solution creates conditions under which the lubricating ability of the polyphosphate solution may have been diminished due to the little amount of lubricant that enters the contact zone.

7.3.5 Thickness of oxide scale

As described in the “Experimental Detail” section, the primary scale formed in the reheating furnace was descaled mechanically. However, mild steel can be oxidized readily such that the secondary scale can rapidly form on the surface. The existence of secondary scale at the roll-strip interface has significant effects on the tribology, such as heat transfer, surface protection, lubrication etc. However, shortcomings such as various types of surface defects, steel yield loss, also come with it.

Figure 7-8 SEM cross-sectional micrographs of hot rolled plate lubricated by sodium metaphosphate under different reductions (a) 20%, (b) 40% and (c) 60%.
Figure 7-9 Oxide scale thickness (a) after hot rolling and (b) various layers with sodium metaphosphate lubrication in Figure 7-8, under the reduction of 60%, 1150°C and 0.5 m/s.

Figure 7-8 shows the cross-sectional images of hot rolled samples. It can be observed that the lubrication film always located in the middle of the oxide scale under all the reductions. The deformed oxide scales (layer 3) under 40 and 60% show more cracks and a more porous morphology than that at 20% reduction.

No exposure of iron substrate was observed for all the three reductions in Figure 7-8 which implies that the scale was capable of elongating together with base metal to maintain adhesion, although cracks formations were observed. Under 20%, tiny cracks are seen to run along the grain boundaries, this is aligned with the statement that the formed secondary scale can deforms uniformly if the reduction is less than 20% [4]. The compact structure of deformed oxide scale under 20% reduction can prevents the phosphate melt from flowing down into the interface of oxide/substrate, as indicated by its EDX mapping in Figure 7-6c. Under a higher reduction, the grain boundary cracks...
become wider, and the scale crystals become separated from each other. At 60% reduction, each oxide scale crystal is deformed and pressed into the base metal, which indicate that FeO is capable of plastic deformation at high temperatures, but its grain boundaries are easily broken, as shown in Figure 7-8a.

Figure 7-9 compares the thickness of oxide scale formed under different rolling conditions followed by cooling in nitrogen box. The results show scale was rolled thinner as the reduction ratio increased, which indicates that the scale was elongated during hot rolling, and that the 40w.t.% sodium metaphosphate lubricants can reduce the thickness of oxide scale. A reduction in oxide scale thickness by 5–37.6% was obtained at a reduction of 20–60%. The antioxidation effect becomes more evident at a higher reduction, as indicated in Figure 7-9b that the formed oxide scale in the cooling stage (layer 1) becomes thinner with an increase of reductions due to the formation of a thicker phosphate film. This is because the thicker lubricating phosphate film at a higher reduction, shown in Figure 7-6 and Figure 7-7, blocks the outward movement of iron and produces a thinner layer 1. It has been stated that the use of rolling lubricant functions to reduce the tertiary scale thickness [103]. Although secondary oxide scale will be decaled before the finishing mill, it is preferred to minimize the growth of secondary scales to improve the materials yield loss.

7.3.6 Grain size statistic

The question that how the microstructure of hot rolled strip is affected by the lubricant remains controversial. Though a few publications report that the lubricant can reduce the grain size of hot rolled strip to some extent, such claims were not widely accepted.
Because the deformed grains recrystallize into fine grains after hot rolling, the cooling parameters such as after-rolling temperature, cooling speed, oxide scale thickness etc. exert a more vital influence on the growth of grains.

The author also had done some preliminary study into the microstructure evolution of hot rolled strip, the results were shown in Figure 7-10 and Figure 7-11, which reveals that the impact of lubricant on grain growth is very weak, and its dominant function is to lubricate the roll/strip interface, no conclusive results regarding the impact of lubricant on grain size could be obtained.

Figure 7-10 Optical microscope photo of cross-section of hot rolled strip by different lubrication at 60% reduction, 1150°C and 0.5 m/s

Figure 7-11 Statistics of grain size at different reductions

Figure 7-10 shows the comparison in microstructure of subsurface of hot rolled strip at 60% reduction. Little difference with the lubricants in subsurface microstructure evolution was observed.
The statistical average grain size versus reductions was plotted in Figure 7-11, which shows that the use of lubricant appears to reduce the grain size at the reduction of 20% and 40%. However, the grain size is statistically averaged around 500 grains, and both of their differences are all within the error bar. Consequently, the conclusion that the reduction in grain size by lubricant could not be established. In summary, the writer suggests that the use of lubricant has no significant impact on the grain size during processing.

7.3.7 FIB and STEM analysis

Figure 7-12 (a) SEM cross-sectional micrographs of rolled sample at 60% reduction, (b) TEM bright field micrographs of the cross section in position A, where the selected area diffraction was inset, and (c) corresponding EDX mapping spectrum of cross section (b).

FIB&TEM apparatus was used to acquire a clear image of the interface. Figure 7-12a shows the SEM cross-sectional micrographs where the FIB milling was undertaken. Two different locations, region A and B, were being milled. In region A (Figure 7-12a), it was observed that two different contrasts exist, and the top grey layer in region A has a thickness of 4±1 µm. The first FIB milling was conducted from the top surface with a depth of 7.2 µm, as shown in Figure 7-12b, which is still a part of layer 1. A clear top layer consisting of large columnar grains was observed which is characterized to be
magnetite ($\text{Fe}_3\text{O}_4$) by the inset selection area diffraction pattern. The thin layer above the magnetite is hematite ($\text{Fe}_2\text{O}_3$), and the bottom layer belongs to wüstite ($\text{FeO}$) with large-grained size. The three-layered structure is similar to that formed under dry conditions [8], and the magnetite precipitate in wüstite was also observed. It was noted that the thickness of hematite and magnetite layer ($4 \pm 0.5 \, \mu\text{m}$) in Figure 7-12b is consistent with the top layer in Figure 7-12a to confirm that this contrast difference is caused by the oxide phase difference. The measured thickness ratio $\text{FeO}: \text{Fe}_2\text{O}_3: \text{Fe}_3\text{O}_4$ is 4: 33: 100. Furthermore, few porosities and cracks were found in Figure 7-12b. These indicate that these grains did not undergo severe plastic deformation. EDX analysis of the cross-section in Figure 7-12b suggests that little phosphorus and sodium element were detected. The compact structure of layer 1 and failure in detection of lubricant within it rule out the possibility that the lubricating film is moved down from the top surface. It supports the view that layer 2 is the working tribo-surface in the contact zone.

![Figure 7-13 TEM bright field images, EDX mapping and SAD of the polyphosphate lubricating film under 60% reduction](image_url)
Region B in Figure 7-12a, which represents the working lubricating film at the hot rolling interface was also milled, and the corresponding TEM characterization was shown in Figure 7-13. It reveals that the lubricating layer has loose and porous structures, and the lubricant stays in these positions, as confirmed by the EDX mapping. The polyphosphate lubricant shows an amorphous morphology with no observation of grains. The EDX mapping shows that the cracked and porous oxide scale caused by the significant plastic deformation provides some reservoirs for the metaphosphate glass. SAD analysis of these oxide grains show that they are composed of hematite, a representative diffraction pattern was given in Figure 7-13c. The polyphosphate film exerts insignificant influence on the structure of tertiary oxide scale, as it shows a three-layered structure similar to that without this film.

### 7.3.8 Mechanistic analysis of the hot rolling lubrication process

![Schematic illustration of the lubrication mechanism in hot rolling](image)

Figure 7-14 Schematic illustration of the lubrication mechanism in hot rolling
The interfacial structure of roll/strip was proposed as Figure 7-14, the contact area can be classified into two areas based on the model suggested by Matsubara [45]; A direct contact of roll/strip through asperities and detached large oxide scale flakes or particles, the other area is the contact between adsorbed polyphosphate film on roll surface and chemical reaction film (between phosphate and oxide scale) on hot strip. The total friction coefficient can be expressed by the combination of these two areas.

\[ \mu = \alpha \mu_d + (1 - \alpha) \mu_b \]  

Equation 7.1

Where, \( \mu_d \) and \( \mu_b \) represents the friction coefficients produced in dry contact and boundary lubrication conditions, respectively. Usually, the \( \mu_d \) is higher than \( \mu_b \). The parameter \( \alpha \) is the contact area percentage through reaction film in the whole contact area. The direct oxide/oxide contact account for the large fraction of contact. When the reduction increases, it is expected that more asperities and oxide flakes will be in contact and increase \( \alpha \), as a result, the friction coefficient was increased. When the temperature decreases, it means the reaction between polyphosphate and hot iron oxide also slows down. This will reduce the amount of polyphosphate being adhered on oxide surface, and those free polyphosphates molecular will be expelled out of the contact zone, which will reduce the lubricant capture and form a thin lubrication film.

As generally accepted [34] that the roll surface experiences an instant heating with the surface temperature reaching around 500–700°C in \( 10^{-2}–10^{-3} \) s, however, the hot strip surface temperature was estimated to be around 900–1000°C. Therefore, it is proposed that the polyphosphate compound shows a different chemical nature on the two surfaces, as suggest in Figure 7-14, in which a thin polyphosphate adsorbed layer forms on the roll
surface and a thick phosphate chemical layer on the hot strip surface. Severe plastic deformation of oxide scale on strip also generates fractures and cracks in scale leading to detached oxide scale. Since the phosphate reaction film was postulated to have a thickness of ~ 4µm, therefore, it can only digest debris with a diameter less than 4µm, and those with larger size will act as third-body abrasives at the interface. The use of polyphosphate glass can create a higher percentage area of boundary lubrication contact than that of hot rolling oil, because of the strong phosphate bond on hot steel, which is also reflected by their friction coefficients in Figure 4-18b. For hot rolling, the roll/strip contact is extremely short varying between 10^{-2}~10^{-3} s, as described in the “Introduction” section. This contact time is too short for the diffusion of phosphate melt and as well as transport of reactants etc, consequently, the lubrication film was still composed of pure sodium metaphosphate melt. Based on this point, the schematic interface was proposed (Figure 7-14) where all the polyphosphate glass concentrates and covers the top surface to lubricate the rolling. As for the digestion of debris, it significantly depends on the size of debris; the phosphate film can only digest these debris with the diameter smaller than the phosphate film thickness, for those with a larger diameter, they still exist at the interface acting as third-body abrasives. However, the abrasive wear is still reduced due to the partial digestion of abrasives.

7.4 Conclusions

Hot rolling tests lubricated by sodium metaphosphate compound had been performed at different reductions. The lubricant performs more ideally at a higher reduction, where a larger amount of polyphosphate lubricant was captured into the contact zone. The rolled
strip surface becomes a little rough due to the residual melt caused by the high concentration of metaphosphate. When 40\text{w.t.\%} sodium metaphosphate was used at temperature of 1150°C and rolling speed of 0.5 m/s, the lubrication film thickness was calculated to be 2.2, 2.4 and 4.3 \text{μm} for the 20, 40 and 60\% reductions, respectively. The formed lubricating film can reduce the oxidation of rolled plate, and its effect is more evident at a higher reduction with a thicker antioxidation film.
8 Conclusions and suggestions

8.1 Introduction

Inorganic alkali metaphosphate glass was proposed as a lubricant in hot rolling in this thesis, where the tribological behaviors and the working mechanism were studied. Before the tribological tests, the physical and chemical properties as well as thermal behaviors of alkali polyphosphate glass at high temperature were determined. Then laboratory ball-on-disc tribometer combined with experimental hot rolling were used to evaluate the glass lubricants, in terms of lubricity, antiwear, antioxidation, surface quality as well as prevention of material transfer. In the final chapter of this thesis, a hot rolling simulation as real as industrial product line was carried out to test the glass lubricant and reveal the structure of the tribo-interface. These carefully controlled experiments are expected to provide a better understanding of the mechanism of alkali polyphosphate glass in hot metal forming.

8.2 General conclusions

8.2.1 Evaluation of sodium metaphosphate glass by ball-on-disc

High temperature ball/pin-on-disc machine has been used to simulate hot rolling as it is an ideal tool to determine tribological performance of a lubricant under controlled conditions. It has been suggested in some publications that the high temperature tribometer can only focus on a number of simulation aspects such as pressure, temperature, speed, etc., while disregarding other parameters such as modes of lubrication, oxidation during heating and cooling etc.. However, it needs to be cautious to
correlate the lubricating behavior from the ball/pin-on-disc to that in hot rolling, even under similar tribological conditions. As shown by the tribological result in Chapter 3, where the talc solution shows a contradictory performance when tested by the two equipment; ball-on-disc test reveals that the talc solution increases the friction, however, hot rolling experiment indicates that the talc solution is an acceptable lubricant, by reducing the rolling force by 8.3%. It is also suggested that the thermal environment difference is the main influential factor. The contact time in hot rolling was in the magnitude of millisecond, which is believed too short to heat talc to the decomposition temperature (845~915°C). It is also possible that the oil lubricating film can still survive and lubricate the sliding between roll and hot strip, by reducing the rolling force by 10.2%, which suggests the interface temperature is not so high, otherwise, the pyrolysis of the oil film will occur instantly.

High speed ball against mild steel disc tribological tests were carried out at 900°C at a velocity of 0.05 m/s to evaluate the lubrication performance of a number of lubricants involving distilled water, 20\textit{w.t.}% sodium metaphosphate, 5\textit{w.t.}% borax, 20\textit{w.t.}% talc, oil-in-water emulsion. The ranking on the basis of friction coefficient was shown as: sodium metaphosphate < borax< oil-in-water < distilled water = dry< talc powder. The sodium metaphosphate shows the best friction reduction.

On the ball-on-disc tribometer at 800°C, 0.87 GPa and 0.094 m/s, firstly, three types of sodium phosphates with different chain-lengths were coated on the disc with similar thickness. Their capabilities were compared in terms of friction and wear reduction, antioxidation. Although sodium orthophosphate provides the lowest friction and wear it shows a limitation in protecting steel substrate from oxidation due to the formation of
porous and solid tribofilm, with an oxide scale as thick as 142 μm. Hot metal forming requires a minimal antiwear and antioxidation with a certain level of friction, a significantly low friction coefficient may cause the slippage problem between tool and workpiece, for example, the hot strip was dragged into the roll bite by frictional force, and an excessively low friction will lead to non-entry into the roll bite. Therefore, sodium metaphosphate glass was preferentially recommended in hot metal forming application if friction and wear are the main focuses.

A phosphate tribofilm was detected in wear track to be associated with the tribological improvement, which is composed of Na, Fe, P and O elements. The three sodium phosphates also show different tribochemical behaviors when exposed to the similar tribological conditions. Sodium metaphosphate undergoes depolymerization in both the tribo-stressed and non-contact area, whereas sodium pyrophosphate experiences a slight polymerization. Little depolymerization or polymerization was detected in both the tribo-stressed and non-contact area, while the crystalline structure underwent irreversible amorphization by the pressure and shear stress when sodium orthophosphate was used.

8.2.2 Loading effect on the tribological performance of glass compound

Hot rolling was usually performed at a wide range of reheating temperatures and reductions depending on the types of steels, which will lead to a variation of rolling pressures.

Sodium metaphosphate was tested by ball-on-disc under pressure range of 0.68~1.24 GPa at 800°C and 0.094 m/s. The results show that load has a vital impact on the lubricity and antiwear performance of polyphosphate glass. Both of friction coefficient and wear rate
rise with an increase of load, and the polyphosphate glass can produce a friction and wear reduction by 24–49% and 64–90% in the load range of 0.68–1.24 GPa at 800°C and 0.094 m/s.

This improvement of tribological performance is the result of a build-up of phosphate tribofilm in the wear track, which was mainly composed of short-chained amorphous NaFePO$_4$ and a little Na$_3$Fe(PO$_4$)$_2$ and Na$_3$PO$_4$. The thickness of phosphate tribofilm monotonously decreases with an increase of load. However, when the load increases to 1.24 GPa, the phosphate antiwear film deteriorated severely. Hot rolling was usually conducted below 1 GPa [34], therefore, sodium metaphosphate glass can meet the demand of the pressure requirement in hot rolling.

The microstructure evolution of antiwear film with loading accounts for the tribological behaviors. The antiwear film is mainly composed of viscous phosphate matrix and oxide nanoparticles generated by the cyclic refinement of wear debris. The relative position of these two phases is affected by loading, where a moderate increase of pressure can facilitate the migration of oxide nanoparticles towards the top surface forming a sintered and compact solid nanoparticles layer above the phosphate matrix. In this case, an oxide/oxide contact between occurs replacing oxide/phosphate contact, which increase the interfacial friction. When the pressure increases further above a critical value, the wear mode changes into severe wear where the phosphate protective film is worn away, as a result, a contact between oxide/substrate metal occurs which causes a severe wear problem.
8.2.3 **Lubrication mechanics of polyphosphate glass in hot rolling**

Hot rolling tests were performed in this thesis to examine the lubrication behaviour of sodium metaphosphate solution, where the mild steel was heated in a well-sealed tube furnace filled with inert gas. Under this circumstance, the thickness of primary scale and entry temperature were controlled accurately. Furthermore, the lubricant concentrations were all set at 20%, except borax salt, which has a low solubility in water. These measures were taken to avoid their influences on the rolling force. By applying a wide range of lubricants, several conclusions can be obtained.

The lubrication ranking based on calculated friction coefficient is shown as: sodium metaphosphate < oil-in-water < borax < talc powder < distilled water = dry, when they were evaluated by experimental hot rolling at 1150°C, 0.5 m/s and 40% reduction. Combined with the ranking result obtained by ball-on-disc tests at 900°C, it was concluded that 20w.t.% sodium metaphosphate solution always shows the best lubrication performance among all the tested lubricants regardless of the testing tribometer. 20w.t.% sodium metaphosphate can reduce the rolling force by 11.5% in hot rolling.

The influence of sodium metaphosphate glass on the surface roughness of hot rolled strip was associated with the weight concentration. A 20% concentration affects the surface topography negligibly, whereas, some lubricant residual forms on rolled surface roughening the surface slightly, when the concentration was increased to 40%. Since the hot rolled strip will be descaled before entry to finishing mill, the residual on surface will be removed and does not exert influences on the properties of the strip.
In the second hot rolling test in chapter 6, the hot mild steel plate was descaled before entry to the roll after being reheated in an electrical furnace at 1150°C in air atmosphere. This was designed to simulate the hot rolling product line more closely. As suggested in section 6.1, the use of sodium metaphosphate glass brings an advantage over commercial oil-in-water lubricant in that it enables the tracking of the lubricant elements in subsequent characterization of lubrication film. Therefore, the information relating to the structure of tribo-interface was investigated, and several conclusions can be obtained. The thickness of lubrication film by sodium metaphosphate solution in hot rolling was calculated to be 0.6~2.8 μm for reductions of 20~60% at 1150°C and 0.5 m/s, the lubrication film decreases with a decrease of reduction, i.e. less lubricant was dragged into the roll bite at a lower reduction. Furthermore, a thicker lubrication film can reduce the oxidation of hot rolled workpiece with the formation of a thinner scale above the deformed scale. Hot rolling tests suggest that the use of polyphosphate glass can form a lubricating film thickness at 2.8 μm, the maximum value obtained in this thesis when 40w.t.% sodium metaphosphate solution is applied by spraying on the roll.

An in-situ interfacial lubrication structure was established, in which the contact area was divided into direct oxide contact and the contact through polyphosphate film. A larger reduction increases the fractional area of direct contact and a lower temperature decreases the polyphosphate reaction film thickness indirectly. Both factors increase the direct contact area, and result in a high friction coefficient.
8.2.4 Antioxidation function of alkali polyphosphate glass

It is not realistic to prevent the occurrence of oxidation completely at hot metal forming; furthermore, the existence of oxide scale between the tribo-surfaces also lubricant acts to prohibit the direct metal-to-metal contact, which is the main cause for severe adhesion and material transfer, even seizure. However, if the oxide scale grows to an excessive thickness, it will break, detach and spall to produce large amounts of third-body abrasive oxide debris, and some oxide fragments also indents into the substrate causing deterioration of the surface and affecting the surface quality of the workpiece, and even tool. Therefore, a proper control of the oxidation in hot metal forming is necessary.

Sodium metaphosphate glass has demonstrated an excellent ability to protect the workpiece from oxidation. When it was coated on mild steel disc with a thick metaphosphate glass film, little oxidation was observed after heating to 800°C for 15 mins. In hot rolling test, the oxide scale thickness experiences little change when 20% sodium metaphosphate lubricant was used. However, when hot rolling test was conducted with 40\% w.t. sodium metaphosphate, excellent antioxidation function was also obtained, reducing the oxide scale thickness by 5~37.6% at 20~60% reduction, and the antioxidation is more evident at a higher reduction due to a thicker protective phosphate film.

Sodium metaphosphate glass has the intrinsic advantages to protect the hot worked sample attributed to the wide fluidic temperature window (>520°C). Viscous polyphosphate glass film can prevent the inward penetration of oxygen molecules to contact the hot steel substrate. However, the outward diffusion of iron atom through the
phosphate melt to the scale/air interface cannot be prevented completely. The phosphate film thickness determines the diffusion length of iron atom; as a result, it plays a decisive role in determining the oxidation extent of workpiece. The thicker the glass films is, the longer time the migration is, thus a less number of iron atoms migrated to the surface forming a thinner oxide scale in a certain time. The oxide structure formed through phosphate lubrication film shows a similar structure as that at dry condition with Fe$_2$O$_3$ at the top followed by Fe$_3$O$_4$ and FeO. The measured thickness ratio for FeO: Fe$_2$O$_3$: Fe$_3$O$_4$ is 4: 33: 100.

8.2.5 Suggestion for future work

- In this thesis, the most consumed mild steel was tested as the workpiece, which is easily to be oxidized. As a result, the practical tribo-interface is extremely difficult to be preserved due to the oxidation during cooling. Consequently, the lubrication film will be damaged to some extent by the growth of oxide scale, which brings some trouble to the following characterization. To avoid such problem, stainless steel with a strong antioxidation ability is suggested to be applied, under this circumstance, the characterization of lubrication film can be performed without the effect of oxidation during cooling.

- It is recommended that some additives with easily-sheared layered structures are added into polyphosphate-base lubricant contributing to the reduction of friction and wear. These additives can be selected from talc, MoS$_2$, BN, some nanoparticles etc., which can survive hot rolling due to the extremely short
contact time. Furthermore, when polyphosphate glass melts, it also can cover the layered solids from oxidation by isolating them from air.

- Temperature has a significant influence on the properties of inorganic glass; the typical one is the viscosity. Due to the heating limitation of the high temperature tribometer, the higher temperature ranges from 900~1200°C was not studied in this thesis. Practical hot rolling is usually performed at the higher temperature range, therefore, to explore the potential lubrication capability of inorganic alkali polyphosphate glass at 900~1200°C is of vital significance.

- Borax salt shows high lubrication efficiency when tested by both ball-on-disc and hot rolling in Chapter 3, considering that the weight concentration is only 5%, far below 20% of other salts. Thus, it is suggested that some modification should be conducted on borax compound to increase its water solubility. Then the relation between lubrication efficiency and weight concentration should be established.

- The most widely used mild steel was tested in the thesis to indicate the large broadness of the glass lubricant. However, because the sodium metaphosphate glass contains a high concentration of phosphorus elements (30.4w.t.%), consequently, the polyphosphate lubricant may be not suitable for those types of steel grades or alloys which have a strict demand of phosphorus element control. More tests should be carried out in the future to study the effect of polyphosphate lubricant on the phosphorus content in steel strip.
References

References


[112] Kong N. Lubrication mechanics of inorganic polyphosphate in ferrite strip rolling of IF steel: University of Wollongong; 2014
Figure A- 1 SEM&EDX analysis of cross section of hot rolled sample lubricated by talc lubricant. The rolled specimen was cooled in nitrogen purged box to avoid the contamination of quench oil.

Figure A- 2 SEM&EDX analysis of cross section of hot rolled sample lubricated by borax lubricant. The rolled specimen was cooled in nitrogen purged box to avoid the contamination of quench oil.
Figure A-1 and Figure A-2 show the typical EDX mapping analysis of the cross section of rolled mild steel plate lubricated by talc and borax, respectively. These rolled samples were cooled in a nitrogen purge box instead of quenching in oil to avoid the oil contamination. The result shows that no lubrication film was detected for both lubricants.

Figure A-3 EDX mapping of the lubricated steel/steel pair by NaPO₃ at 800°C: (a) the wear scar of ball; (b) the wear track of disc. The magnified image of white dashed rectangular area is present as shown by the arrow.
The EDX mappings of the steel/steel surfaces lubricated with NaPO$_3$ in Figure A-3 indicate the presence of Na, P, Fe and O elements on the worn surface of the ball (Figure A-3a) and disc (Figure A-3b). The lubricant elements were distributed over tribo-stressed area fairly uniformly. The SEM images in Figure 5-8 shows clear shear tracks on the smooth and compact phosphate film, thus indicating a layer of phosphate film composed of Na, Fe, P and O exists on the worn surface when subjected to high pressure and shearing stress at 800°C.

Figure A-4 SEM&EDS images of the lubricated steel/steel pair by NaPO$_3$:(a) the wear scar of steel ball and (b) the wear track of steel disc.

Figure A-4 shows the EDX mapping of tribo-stressed areas of ball (Figure A-4a) and disc (Figure A-4b) lubricated by Na$_4$P$_2$O$_7$. P, Na, Fe and O elements were observed to distribute uniformly on the load bearing area. The worn surfaces are very smooth and compacted. It is noted that Na and P elements of the Na$_4$P$_2$O$_7$ lubricant are mainly distributed in the worn area. Furthermore, a smaller number of wear debris are observed on the worn surfaces than that of unlubricated pairs.
The elemental composition of the worn surfaces of the ball and the disc lubricated by Na₃PO₄ are shown in Figure A- 5. The worn scar of ball presents a smooth and compact surface as well. There are less Na and P elements from lubricant elements on the worn surface than that of Na₄P₂O₇ due to the chemical inertness of Na₃PO₄. A large amount of wear debris is observed at the edge of ball scar, which is composed of Na, P and O elements. Furthermore, a strong signal of Na was detected in the wear track, but that of phosphorus is not evident in Figure A- 5a, which is due to the atomic radius difference of Na⁺ ions and PO₄³⁻ group.
Figure A-6 P 2p XPS spectra recorded within the wear track (WT) and outside the wear track (OT) lubricated by NaPO₃, Na₄P₂O₇ and Na₃PO₄ at 800 °C.

Figure A-6 illustrates the XPS curve of P 2p where there are normally two peaks of P 2p₃/2 and P 2p₁/2 in the phosphorus signal, due to the spin-orbit coupling of the 2p orbital.¹ The fitting results are listed in Table A-1. The difference in binding-energy between the P 2p₃/2 and P 2p₁/2 signal was not constrained and the mean value was found to be 0.90±0.1 eV. Since the thermal stability is different among the three phosphates, although the interaction of lubricant with iron/iron oxides occurs at the rubbing surfaces, the basic PO₄³⁻ structure does not change significantly in response to the elevated temperature of 800°C. The binding energy of the P 2p₃/2 in the orthophosphate group of PO₄³⁻ is found at ~133.2 eV, whereas the P 2p₃/2 in the iron phosphate (FePO₄) is at ~133.5±0.5 eV.² According to the fitting result, the binding energy of the P 2p₃/2 peak upshifts from 132.0
in the OT area to 132.3 eV in the WT area for NaPO₃, which is indicating more depolymerization of the NaPO₃ within the tribo-track. The P 2p₃/2 peak of Na₃PO₄ remains almost unchanged, which implies little polymerization of orthophosphate.

Table A-1 Peak positions of P 2p XPS spectra in steel discs lubricated by three phosphates and their model compounds: NaPO₃, Na₄P₂O₇ and Na₃PO₄.

<table>
<thead>
<tr>
<th>P/eV</th>
<th>2p</th>
<th>P 2p 3/2</th>
<th>P 2p 1/2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na₃PO₄</td>
<td>132.5</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>Na₄P₂O₇</td>
<td>133.4</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>NaPO₃</td>
<td>134.5</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>WT Na₃PO₄</td>
<td>133.0</td>
<td>132.2</td>
<td>133.0</td>
</tr>
<tr>
<td>OT Na₃PO₄</td>
<td>132.8</td>
<td>132.1</td>
<td>133.1</td>
</tr>
<tr>
<td>WT Na₄P₂O₇</td>
<td>132.4</td>
<td>132.1</td>
<td>133.0</td>
</tr>
<tr>
<td>OT Na₄P₂O₇</td>
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<tr>
<td>WT NaPO₃</td>
<td>132.6</td>
<td>132.3</td>
<td>133.2</td>
</tr>
<tr>
<td>OT NaPO₃</td>
<td>132.4</td>
<td>132.0</td>
<td>132.9</td>
</tr>
</tbody>
</table>

a) Na₃PO₄, Na₄P₂O₇ and NaPO₃ represent the original chemical powders;
b) WT Na₃PO₄ represents the wear track lubricated by Na₃PO₄;
c) OT Na₃PO₄ represents the outside track area formed by Na₃PO₄, i.e. static thermal film.

Figure A-7 Curves of friction coefficient as a function of sliding time at 5 N and 800°C. The frictional result shows that the CGr15 ball/mild steel tribopair lubricated by sodium
metaphosphate shows a steadier and lower friction coefficient. The average friction coefficient was reduced by 24% with the lubrication of sodium metaphosphate.

Figure A- 8 SEM&EDX analysis of the ball scar with the lubrication of sodium metaphosphate at 5 N and 800°C. Figure 2 shows that the ball scar was covered by a distinct film, which was composed of Na, P, Fe and O elements, i.e. the Na-Fe phosphate film.
Figure A-9 Magnified micrographs of the red circle area in Figure 6-4 at the load of (a) 20 N and (b) 30 N.

Figure A-10 SEM/EDX mapping of cross-section of ball track lubricated by NaPO₃ glass at 10 N and 800°C. It shows that a layer of Na-Fe phosphate film locates above the oxide scale in the wear track, which contributes to the friction and wear reduction. The average thickness of the phosphate film was 4.5 μm.
Appendix

Alexander model for calculation of rolling force and inverse calculation of friction coefficient

Figure A-9 Geometry and related parameters in rolling process [30]

Consideration the equilibrium of the elemental slice of material in the plastic arc of contact depicted in Figure A-9, Von Karman [31] put forward the basic linear first-order differential equation, as shown in Equation A-1.

\[
d\left[h(s - 2k \pm \tau \tan \phi)\right]/d\phi = 2R'(s \sin \phi \pm \tau \cos \phi) \quad \text{Equation A-1}
\]

Where \( \phi \) denotes the angle of considered elemental section as shown in Figure A-9, \( h \) the total thickness, \( s \) is the local normal pressure on the deformed roll surface, \( R \) the original roll radius, \( k \) the yield shear stress at the section, \( \tau \) surface shear stress at the section, \( R' \) radius of deformed contact arc.
This equation is based on the assumption that dry slipping occurs over the whole arc of contact between the rolls and the rolled material. This solution also claims that the frictional force $\tau$ is directly proportional to the value of the local normal pressure $(s)$, i.e.

$$\tau = \mu s$$

Equation A-2

Where $\mu$ represents the friction coefficient.

One of the comprehensive of these was that developed by Orowan [32], he proposed a homogeneous graphical method of solution, including an attempt to allow for the inhomogeneity of deformation throughout the volume of the plastically deforming material in the arc of contact.

The mathematical modeling of the rolling process involves several parameters that may lead to non-linear equations of difficult analytical solution. Thus the Alexander's model [30], being considered one of the most complete in the rolling theory. With the assistance of modern computers, Alexander showed the ways that rolling problem can be solved accurately using the basic approach proposed by Orowan [32], who developed a homogenous graphical method of solution. Unlike Orowan’s method, no allowance was made in the computer program for inhomogeneous deformation through the contact arc.

The calculation method of roll force proposed by Alexander was on the assumption that the deformed arc of contact is circular and neglecting the elastic arcs, the roll force must act midway along the angular arc of contact and be directed towards the centers of the deformed arcs as indicated for one roll in Figure A-9. With these assumptions the roll force per unit width is made up of the resolved components of $s$ and $\tau$ in that direction, as expressed by the A-3:
\[ P = R \int_{0}^{\theta_1} s \cos(\theta - \frac{1}{2} \theta_1) d\theta + R \int_{\theta_N}^{\theta_1} \tau \sin(\theta - \frac{1}{2} \theta_1) d\theta - \\
R \int_{\theta_0}^{\theta_N} \tau \sin(\theta - \frac{1}{2} \theta_1) d\theta \]

Equation A-3