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Tribochemistry and lubrication of alkaline glass lubricants in hot steel manufacturing

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Abstract

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Review

Tribochemistry and Lubrication of Alkaline Glass Lubricants in Hot Steel Manufacturing

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Abstract: Nowadays, the increasing demand to reduce energy consumption and improve process reliability requires an alternative lubricant with an effective tribological performance and environmentally friendly properties to replace traditional lubricants in hot steel manufacturing. The current work reviews recent comprehensive experimental and theoretical investigations in a new generation of alkaline-based glass lubricants, with phosphate, borate, and silicate being intensively researched. This class of lubricants showed an outstanding friction reduction, anti-wear, and anti-oxidation performance on coupled steel pairs over a wide range of temperatures (from 650 °C to 1000 °C). Each type had different tribochemical reactions within itself and with oxidized steel surfaces, which were largely determined by their chemical nature. In addition, the critical role of each structural component was also determined and corroborated by computational simulation. The theoretical studies at quantum and atomic levels reinforced our experimental findings by providing insights into the reaction mechanism using the static and dynamic simulations of the adsorption of lubricant molecules onto iron oxide surfaces. Additionally, the new reactive molecular dynamics (MD) model developed for alkali phosphate will need to be extended further to consider the realistic operating conditions of these lubricants at the atomic scale.

Keywords: glass lubricants; hot steel manufacturing; tribochemistry; lubrication

1. Introduction

Hot metal forming has existed for centuries, however, efforts have always been made to constantly increase the overall productivity. There is a growing interest in the tribology of steel hot rolling, which refers to the multidisciplinary science of contacting bodies during the hot rolling of steel. Steel is often preheated at 800–1200 °C before undergoing a series of rolls at high speed (1–10 m/s) [1] and under high loading conditions (~0.5–1 GPa). The interface between the cold work tools and heated workpiece governs heat transfer, friction, and wear mechanisms [2]. During the pre-heating stage, oxidation invariably occurs on the steel workpiece surface, forming a thick oxide layer with a thickness up to several millimetres [3]. The oxide scale is deemed to be the cause of high friction, severe roll wear, and increased chances of seizure. In addition, if the oxide scale remains on the workpiece surface after rolling, it requires costly removal processing to meet the required final quality specifications. To minimize energy consumption, and to reduce oxidation and prolong the roll service life, there is a pressing demand to achieve the optimum lubrication during rolling. The use of lubricant has proven to be an effective approach to address the above concerns.

An oil-in-water emulsion was used widely in the rolling industry in the early stages, followed by other alternatives, like graphite, MoS₂, and oxide nanoparticles. However, most of them undergo thermal decomposition upon contact with the heated steel surface and subsequently lose their lubrication function. Factoring in potential environmental concerns, the use of those traditional

lubricants is consequently discouraged. Glass-based lubricants are essentially alkaline-based inorganic polymers with exceptional thermal stability. They are compositionally constructed by alkaline elements and glass-forming compounds (phosphates, borates, silicates) which are accountable for their polymeric nature. The lubricants generally melt at the working temperature, wet the oxidized steel surface, and provide viscous fluid lubrication. Thermally driven and tribological reactions determine frictional and wear behaviors. This set of reactions is complex by nature and varies from one lubricant to another. The following part details the experimental findings of the tribological properties of three types of glass lubricants (polyphosphate, borate, silicate) whose working mechanisms were elaborated by in-depth chemical characterization, in combination with computational simulations at different scales. It is noted that the review mostly revolves around sodium-based glasses, however, potassium- and lithium-based counterparts are occasionally mentioned.

2. Results and Discussion

2.1. Experimental Studies

High temperature lubricants, as summarized in Figure 1, can be divided into five different types depending on their working temperature range, molecular structure, thermal stability, and reactivity with the atmosphere [4]. Oil-based lubricants with an oil-in-water mixture are classified as conventional lubricants and are commonly used in the hot rolling of steel because of the reduction in rolling force due to a lower friction and a longer life of the work roll due to the reduced roll wear [5–7]. Nevertheless, their thermal decomposition at high temperatures, cost, and from the environmental perspective, the usage of fossil fuel, are the drawbacks of this type of lubricant [8]. Apart from soluble additives of phosphorus, chlorine, and sulfur, a solid lubricant of fine powder can be applied to tribological surfaces. The well-known lamella solid lubricants, such as graphite, h-BN, transition metal dichalcogenides (MX_2 with $\text{M}=\text{W}, \text{Mo}, \text{Nb}, \text{Ga}$, and $\text{X}=\text{S}, \text{Se}, \text{Te}$), mica, and talc are also often formulated in the lubricant to enhance its lubricating performance due to the weak van der Waals interactions between 2D layers [9]. However, transition metal dichalcogenides degrade rather quickly in moist and oxidizing environments. Moreover, most these 2D materials lose their intrinsic lubricity above 500 °C due to thermal degradation [10,11]. Solid lubricants of soft metals (Au, Ag, Pb, In, Sn), single (B_2O_3 , Re_2O_7 , MoO_3 , TiO_2) and mixed oxides ($\text{CuO-Re}_2\text{O}_7$, CuO-MoO_3 , $\text{PbO-B}_2\text{O}_3$, CoO-MoO_3 , $\text{Cs}_2\text{O-MoO}_3$, NiO-MoO_3 , $\text{Cs}_2\text{O-SiO}_2$), fluorides (CaF_2 , BaF_2 , SrF_2 , LiF , MgF_2), and sulfates of alkaline earth metals (CaSO_4 , BaSO_4 , SrSO_4) have also been considered as alternatives [12,13]. The self-lubricating behavior of ternary ceramic and its composite coating materials containing different solid lubricants, such as $\text{Ni-CoCrAlY-Cr}_2\text{O}_3\text{-Ag-Mo}$, VN-Ag , NbN/Ag , and TaN/Ag , performed well from room temperature to 1000 °C [14–16]. In comparison with liquid and grease, solid lubricants can withstand a high pressure while being relatively insensitive to temperature [13]. However, this type of lubricant can still have major shortcomings, which include: (i) poor thermal conductivity, (ii) a relatively high and unstable friction coefficient, (iii) having a short wear life and difficult replenishment, (iv) degradation during service, and (v) irreversible structural–chemical changes [13]. At extreme temperatures, the melt products that can function effectively are glasses, such as alkali phosphates, borates, and silicates. These glasses gain lubricity when they transition into viscous melt phases above their melting point to produce a tribofilm that reduces friction, wear, and oxidation. The last type of lubricant is reactive gases, such as gaseous halogen-substituted methane derivatives, which are used under extreme conditions with the excessive chemical reactions that are manifested in corrosive wear [17]. This paper is focused on a series of glass lubricants with regard to their tribological performance and the underlying mechanochemical mechanism for tribofilm formation between sliding steel surfaces at high temperatures.

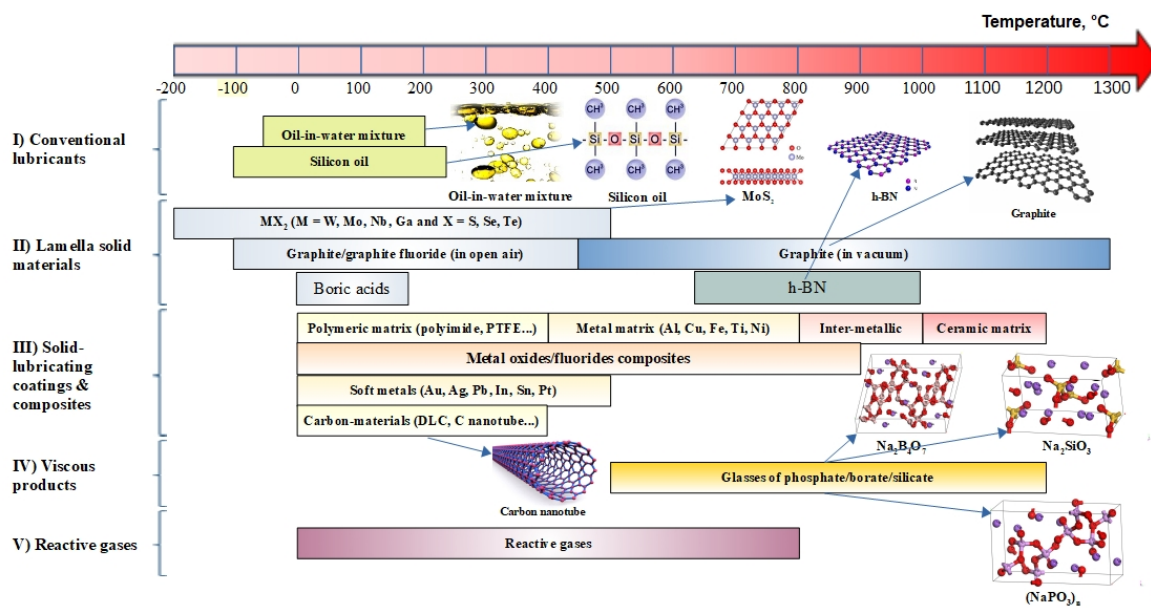


Figure 1. Working temperature range of different lubricant classes.

2.1.1. Sodium Polyphosphate

Potassium/sodium (K/Na) polyphosphate begins melting at 600 °C and demonstrates exceptional friction- and wear-reducing ability on steel tribopairs from 600 °C to 900 °C. Friction was lowered by more than 50%, while the wear rate reduction varied with temperature, but often fell in the range of 30–90% [18,19]. On the rubbing surface, the tribofilm structure was characterized by two layers of K/Na polyphosphate sandwiching a thick iron oxide layer [19]. The complex tribofilm structure was a result of thermal diffusion and tribochemical reactions between composite polyphosphate and iron oxides. Chemical analysis (XPS) revealed a significant reduction in polyphosphate chain length induced on the lubricated surface while a wear reduction mechanism via chemical digestion was also observed [18,20]. Using energetic synchrotron radiation, the fine chemical structure of the K/Na polyphosphate tribofilm was studied in detail, showing a long chain–short chain hierarchy as a function of tribofilm depth. As a result of this tribochemical reaction, iron oxide was disintegrated and digested into the polyphosphate network to form ferric orthophosphate (FePO_4), as well as iron and sodium mixed phosphates, such as (NaFePO_4) [20] and $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$ [19]. The digestion of iron oxide is accountable for the excellent wear resistance of polyphosphate tribofilm. As presented in Figure 2, this tribofilm contains a 5 nm short-chain polyphosphate layer on the top, above a 5 nm long-chain polyphosphate layer below, which adheres to the oxide surface through a short-chain layer [21]. However, this polyphosphate film was mainly covering the valley area of the worn surface and was chemically inhomogeneous at the submicron level [19,21]. Interestingly, Na and P existed not only in the top sodium layer, but they were also found in the grain boundary of iron oxide layer [19]. The phosphate glass was also beneficial for the pickling of silicon steel surfaces, with a quicker scale removal and a thinner fayalite layer than an unlubricated one [19].

It was proposed that the tribochemical reaction occurs on the basis of hard–soft acid–bases (HSAB) principles, in which Fe^{3+} from oxide surfaces actively reacted and diffused into a polyphosphate bulk under shearing stress, depolymerizing the network while simultaneously strengthening the whole tribofilm. Later, a series of sodium polyphosphates (ortho-, meta-, and pyro-) with different molecular structures was examined regarding their tribological properties. It was found that the extent of polymerization in the starting materials exerts distinguishable effects on their friction and wear behaviors on a steel tribopair. An abundance of Na_2O was produced as a consequence of the tribochemical reaction between sodium polyphosphate and different iron oxides [19]. Having an abundance of Na without the ability to polymerize, sodium orthophosphate demonstrated the best

tribological performance among the three, while the depolymerization of meta- and pyrophosphate was triggered by both thermal and tribological reactions [20]. In addition, higher loading was proven to accelerate the diffusion of Fe into polyphosphate networks [20], while an increase in temperature resulted in a reduction of long-chain polyphosphates on the rubbing surface [18].

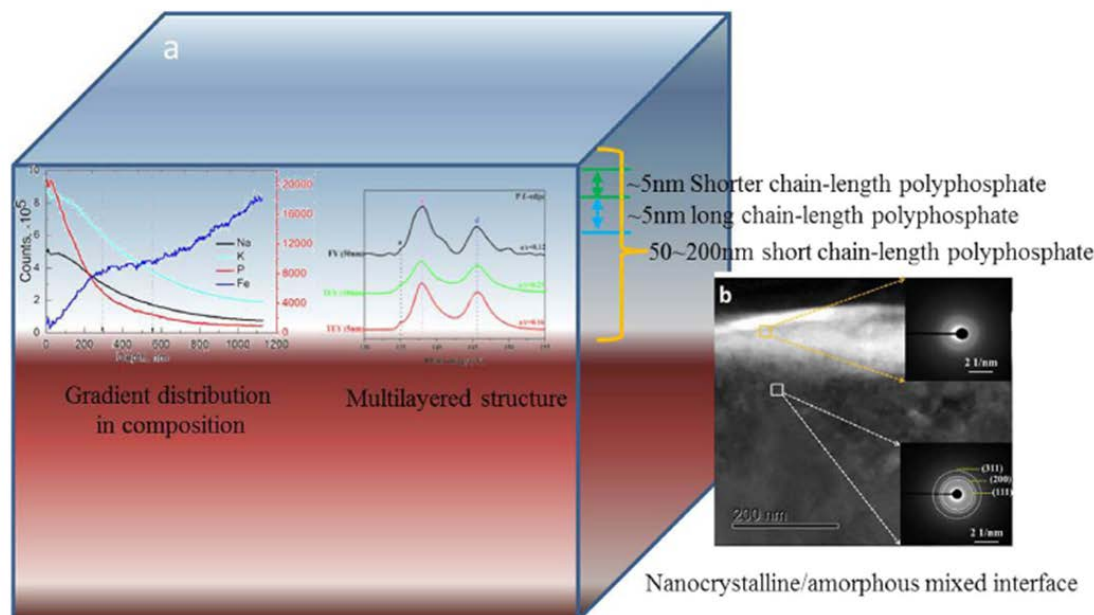


Figure 2. Schematic illustration of hierarchical structure of tribofilm obtained from the work by Wan et al. [21], with (a) depth profile of the composition in the worn steel disc at 800 °C by secondary ion mass spectrometry (SIMS), and P L-edge X-ray adsorption near edge structure (XANES) spectra of the polyphosphate tribofilm in fluorescence yield (FY) and total electron yield (TEY) modes, respectively. (b) Transmission electron microscopy (TEM) images and the corresponding selected area electron diffraction pattern (SAED) of the tribofilm.

2.1.2. Sodium Borate

Sodium borate, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, begins melting around 525 °C and can provide good lubricity on sliding steel surfaces over 600–800 °C [22,23]. Results from ball-on-disc tribotesting showed different tribofilm structures on different mating surfaces. On the disc, the tribofilm was composed of a bottom layer rich in Na and an upper layer of condensed boron oxide with a total thickness of 60 nm (Figure 3). There were signs of the polymerization of boron oxide networks, which could be the result of tribochemical reactions within the lubricant film. The tribofilm was notably depleted in oxygen, which consequently improved its oxidation resistance on the steel surface. On the ball, the tribofilm experienced a drastic molecular transformation, evidenced by a dominant presence of BO_3 species. Subsequently, complementary experiments revealed that the adsorption of Na occurred independently of tribological exposure. In other words, it is thermally driven, which establishes a necessary adhesion between the lubricant and the iron oxide surface and allows borate to lubricate effectively. The profound role of Na in sodium borate was later discovered, as it provides anchoring effects due to electrostatic interactions with the iron oxide surfaces. Without Na, the boron oxide system (B_2O_3) failed to adhere on the surface, thus leading to a lubrication failure, which could be attributed to a weak interaction between boron oxide and iron oxides. A sodium element was also believed to alleviate direct asperity contact due to its strong adsorption and high mobility. Borate tribofilm provides an amorphous low-shearing layer, which lowers the frictional resistance, while its wear-reducing mechanism relies on the tribologically activated condensation of the boron oxide network with good endurance. In comparison with phosphate glass at 900 °C, sodium borax showed a better anti-wear performance than the other, but it has a lower friction reduction [20]. The lower

friction of borax glass could be the consequence of a high temperature of 900 °C, which is out of its optimal working condition and it was in a molten state.

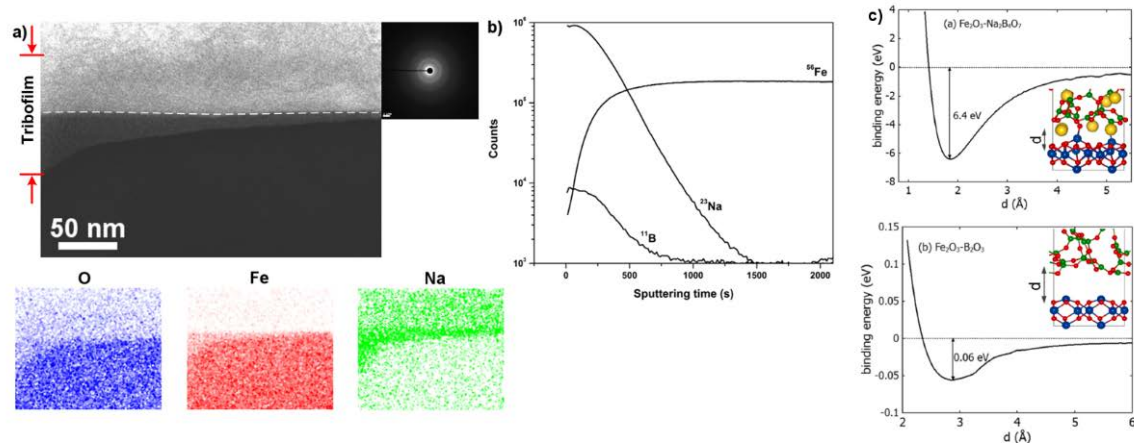


Figure 3. (a) STEM image of the tribofilm on the lubricated disc and according EDS mapping, (b) SIMS depth profile of the contact interface for B, Na, and Fe elements (800 °C, normal load 30 N, sliding speed 0.1 m/s) from the experimental work by Tran et al. [24]; and (c) binding energies of $\text{Fe}_2\text{O}_3\text{-Na}_2\text{B}_4\text{O}_7$ and $\text{Fe}_2\text{O}_3\text{-B}_2\text{O}_3$ as a function of the separate distances obtained from the DFT calculation by Ta et al. [25].

2.1.3. Sodium Silicate

Sodium metasilicate ($\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$), having a relatively high melting point (920 °C), has proven to be an effective lubricant around 1000 °C [26,27]. The silicate melt stimulates the outward migration of Mn from a steel bulk to the sliding surfaces, which, in combination with Na adsorption, forms a unique tribofilm layer [28]. The composited tribofilm reduces friction and wear effectively, while simultaneously providing anti-oxidation resistance. The formation of a Na-rich layer is relatively similar to what was observed in the case of sodium borate. An addition of expandable graphite lowered the minimum operating temperature of metasilicate to 850 °C [29]. This is a result of the in situ formation of sodium carbonate melts and spinels (MnFe_2O_4 , Na_5FeO_4), with crystallographic planes favouring low friction and wear.

2.2. Theoretical Simulations

Despite the significant progress that has been made in surface characterization, an in situ observation of tribochemical processes and the measurement of tribological properties under harsh operating conditions remains a critical challenge for the experiments, or may not even be feasible. To tackle this challenge, the atomic-scale simulations using quantum mechanics (QM), ab initio molecular dynamics (AIMD), and reactive MD have been used to observe these chemical phenomena. During the working conditions, the inorganic lubricant melts and adsorbs onto the iron oxide surface as a result of thermal effects; this adsorption includes the chemical reaction and dissociation, as well as polymerization. It is well known that adhesion is one of the most important properties of lubricants since their anti-wear performances consistently depend on the adhesion capability [30]. Although experiments have successfully characterized the hierarchical structure and tribological performance of the tribofilms at room temperature, the chemical heterogeneity of the tribofilm formed at elevated temperatures and its spatial distribution at the atomic level were not understood with a high degree of certainty. Furthermore, alkali cations played an important role in the tribological performance of glass lubricants, but the detailed reaction and the influence of temperature and pressure need more work, especially on the theoretical calculation, to provide a full understanding of the mechanism. It is important to investigate the chemical mechanism of how a glassy lubricant works when it is applied in practice at high temperature and pressure in metal forming. We have carried out some

theoretical investigations of the adsorption and thin film lubrication of $\text{Na}_4\text{P}_2\text{O}_7$ and $\text{Na}_5\text{P}_3\text{O}_{10}$ [31–34], sodium tetraborate ($\text{Na}_2\text{B}_4\text{O}_7$), and boron oxide (B_2O_3) molecules [25,35,36], as well as sodium silicate, $\text{Na}_6\text{Si}_2\text{O}_7$, on iron and iron oxide surfaces [37,38]. These studies have overcome the drawbacks of previous experiments and provided a deep insight into the chemical reactions in the tribofilm.

2.2.1. Phosphate Glass

Unlike organic phosphite/phosphate additives used in automotive applications, where the direct Fe–P bonding was found on iron surfaces because of the chemical dissociation of phosphite/phosphate under friction, leading to the formation of Fe_2P [39,40], the AIMD simulations in Figure 4 revealed that the cross-linking with the Fe–O–P bond between phosphate and the iron substrate was the main chemical structure in phosphate glass [31,32]. The Fe–P bond only occurred in a combination of an elevated temperature of 1500 K, a high exposure of Fe, and an appearance of under-coordinated P [33]. The pure ionic Na–O bond, the moderate covalent P–O interaction, and the mixed ionic/covalent Fe–O bond exist inside the tribological system [32]. Among these bonds, the P–O_b (bridging O) bond has the highest chance to dissociate because it is the weakest, which results in depolymerization when the phosphate lubricant contacts the iron and iron oxide surfaces [31,32].

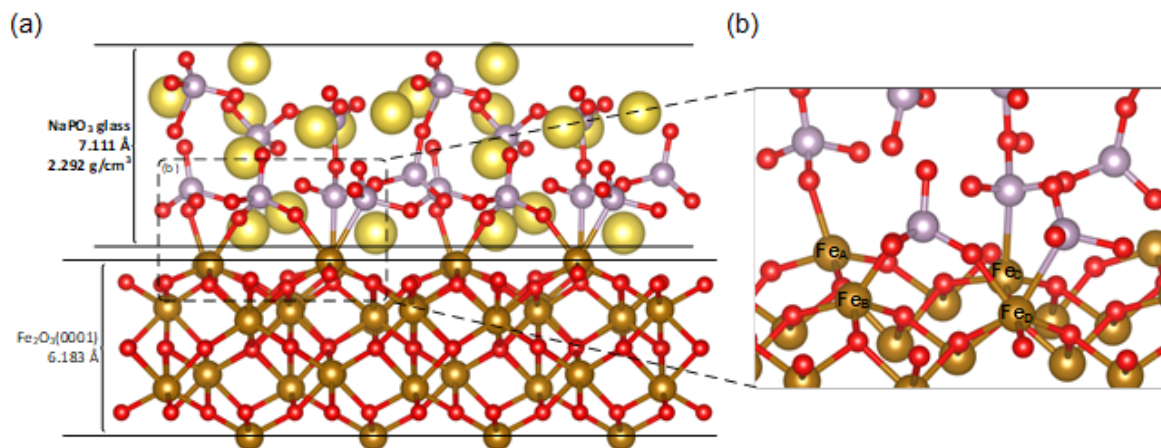


Figure 4. (a) NaPO_3 glass layer and Fe_2O_3 (0001) surface dimension; (b) enlarged and tilted structure of the glass–oxide interface from the work by Le et al. [33], sodium atoms have been removed for clear visualization. O atoms are colored in red, Fe in gold, P in purple, and Na in yellow.

It is thermodynamically preferable that both pyrophosphate, $\text{Na}_4\text{P}_2\text{O}_7$, and triphosphate, $\text{Na}_5\text{P}_3\text{O}_{10}$, clusters, which are different from each other by their molecular chain length, are chemisorbed on the surface first, followed by the P–O_b dissociation. There was a slight difference in the total energy of absorbed clusters and their decomposed products, which indicated that the breaking and non-breaking phosphate bonds can coexist during the tribological process. A deformed FeO_4 tetrahedral structure between a surface iron cation and four oxygen anions (three oxygens from the surface and one from the lubricant) was found, and its number of coordination of 4 was lower than the value of 6 from FeO_6 octahedra, which are found in Fe(III) oxide crystals. These FeO_4 tetrahedra connection with PO_4 tetrahedra by a strong chemical P–O–Fe linkage, which provides a strong adherence of phosphate chains to the surface, although the oxide still maintains the flexibility of the phosphate chain due to the partial anchor. Thus, the lubricant network could produce a durable layer which provides a wear reduction and oxidation prevention in the rolling process.

Temperature, especially at the working conditions of the hot rolling process, is a factor that contributes to the depolymerization process. An AIMD simulation at 1100 K indicated that the monodentate linkage was the most observable interaction between the lubricant and the surface. However, there was no P–O_{nb} (non-bridging O) bond cleavage at neither normal nor high temperatures. The chain length also has an influence on the depolymerization behavior. In fact, $\text{Na}_4\text{P}_2\text{O}_7$ indicated

no bond breaking for the P–O_b bond at 1100 K, while there was a coexistence of bond breaking and reforming during simulation for Na₅P₃O₁₀ on the iron oxide surface [32]. This simultaneous depolymerization and polymerization of phosphate chains from AIMD simulations affirmed the previous XPS experimental characterizations [1]. The smaller P–O_b dissociative energy and bond overlap population, as well as the longer bond length calculated for Na₅P₃O₁₀ compared with Na₄P₂O₇, could be an explanation for this behavior, as a longer bond length results in a weaker bond strength [32]. The better anti-wear performance of short-chain phosphate compounds in the aforementioned experiment is promoted by their better adhesive strength, which is characterized by their larger bond order population of O_{glass}–Fe bonds than that in long-chain molecules [31,32].

Experimental characterization indicated that iron oxide was digested into polyphosphate glass to form a hierarchical structure including iron, sodium, and phosphate oxides [20]. The AIMD simulations of (NaPO₃)_n glass and iron/iron oxide clusters at high temperatures unveiled a transformation mechanism, in which the dominant chemical Fe–O_{glass} bond caused the weakening of the oxide surface topmost Fe–O bond and resulted in the removal of the top Fe atoms from the iron oxide surface [33].

2.2.2. Borate Glass

For sodium borate, Na₂B₄O₇, O_{nb} from its structure also approaches the nearest Fe atoms to form the Fe–O–B covalent bond [25]. The AIMD simulation indicated that this bond resulted in a strong adsorption of Na₂B₄O₇ onto the Fe₂O₃ (0001) surface [25]. This molecule decomposed at 1073 K to transform the BO₄ complexes into BO₃ and O_{nb} by activating sodium mobility. When the lubricant was subjected to an applied pressure, the confined sodium borate layer started a geometrical rearrangement because of volume change [35]. This arrangement was more favourable for higher sodium concentrations as the large ratio of sodium could break long polymer chains into shorter ones [41]. An increase in pressure yielded to a chemical modification; however, when this pressure rose up to a critical value, the BO₃ group transformed into BO₄ with an increase in the boron coordination number from three to four [35]. This critical pressure for polymerization was varied with sodium concentration, with the largest triggering pressure at 33% of Na₂O. As explained in Figure 5, the chemical mechanism for this polymerization was that the boron atoms created new bonds with molecular oxygen via the lone-pair electrons to form cross-links between long borate chains, which increased linearly with applied pressure [35]. This polymerization was more preferable in the system with fewer BO₄ groups and sodium cations [35]. This mechanism also revealed the anti-oxidation mechanism for borate glass, in which the diffused oxygen is digested by BO₃ groups to form BO₄ in harsh conditions. Conversely, there was an insignificant decomposition of BO₄ into BO₃ in the decompression process, indicating that the formed polymer was retained after mechanical impact [35].

2.2.3. Silicate Glass

With a sodium silicate lubricant, the silicate cluster chemically adsorbs onto the iron surface by forming multiple Fe–O_{nb} bonds, which have a strong covalent characteristic compared to the Si–O bonds [38]. This strong covalent bond confirms the adhesion capability of the sodium silicate to the metal surface. The number of O_{nb} involved in this reaction increases gradually from one to three during the simulation. An increase in Fe–O_{nb} bonds consequently resulted in the negative charges on Fe surface atoms, which attracted positively charged atoms from the lubricant by the Coulombic interaction to form the tribofilm. In contrast, the strength of Si–O_{nb} bonds within the molecule was reduced significantly. This influenced its bond dissociation and resulted in the instability of the tribofilm, which caused the higher wear and friction at high temperatures. In fact, previous experiments reported an increase in the CoF of sodium silicate lubricant when the temperature rose above 1000 °C [27].

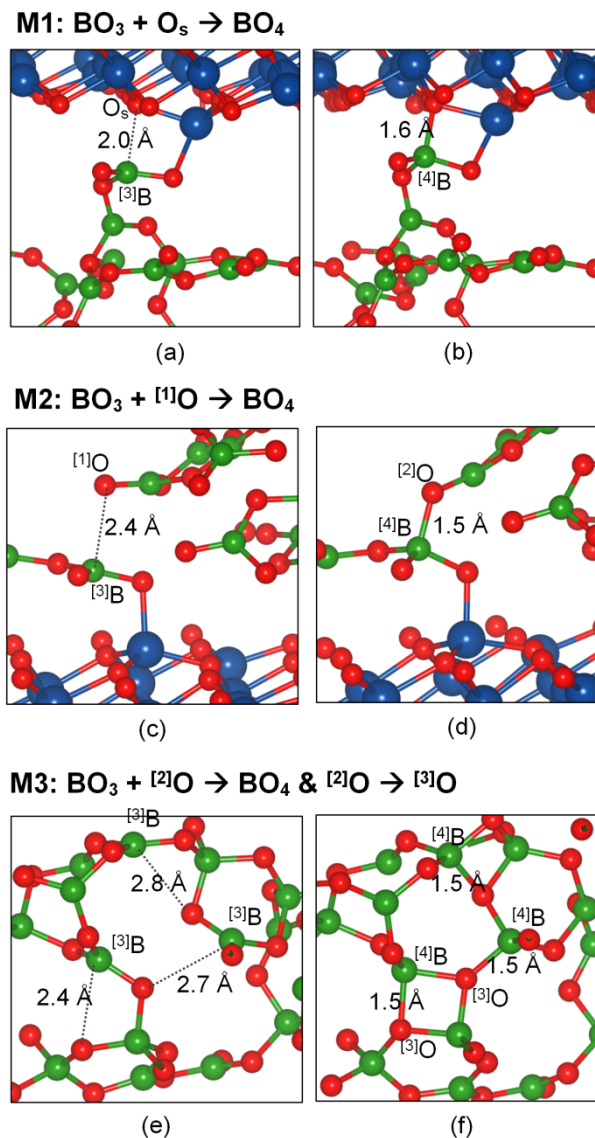


Figure 5. Ball and stick model of the selective configurations before (left) and after (right) the polymerization in the system following three mechanisms: M1 (a,b), M2 (c,d), and M3 (e,f) from the work by Ta et al. [35]. These configurations before and after the chemical reactions were captured from two consecutive steps with $\Delta z = 0.05 \text{ \AA}$. Sodium has been removed for better visualization.

Interestingly, the depolymerization and formation of small fragments were observed for sodium phosphate at 1100 K and for sodium silicate at 1500 K, but these phenomena resulted in different tribological performance. The friction and wear were reduced with a sodium phosphate lubricant [1], whilst they were increased for sodium silicate [27]. The cause of this contrasting behavior may have originated from the strength of the Fe– O_{nb} bonds, which were stronger for $\text{Na}_6\text{Si}_2\text{O}_7$ than $\text{Na}_4\text{P}_2\text{O}_7$ and $\text{Na}_5\text{P}_3\text{O}_{10}$ molecules. These data indicate that sodium silicate adsorbs more strongly onto iron surfaces than sodium phosphate.

Similarly, with borate glass [35], the level of polymerization increased when the proportion of Na_2O decreased from 50% to 33% [37]. Silicate glass also formed covalent bonds between O_{nb} and surface iron atoms, while some Si atoms formed direct covalent bonds with surface oxygen [37]. As presented in Figure 6, an AIMD simulation at 1361 K and 1 GPa demonstrated a continuous process of polymerization and depolymerization in the glass lubricant. As described in scheme 1 of Figure 4d and the stable adsorption configuration in Figure 4b, the depolymerization of the sodium silicate molecules formed active sites that strengthened the adhesion of the lubricant to metal oxide surfaces

via these covalent bonds. Due to the excessive complexity and lengthy processing time, studies on sodium silicate have not taken into account the effects of other steel components (e.g., the diffusion of Mn) on surface chemistry at high temperatures. This will be considered in future investigations. Nevertheless, experimental findings on sodium silicate suggested very complex interactions between the lubricant and oxide surfaces, in which thermally driven reactions should not be underestimated.

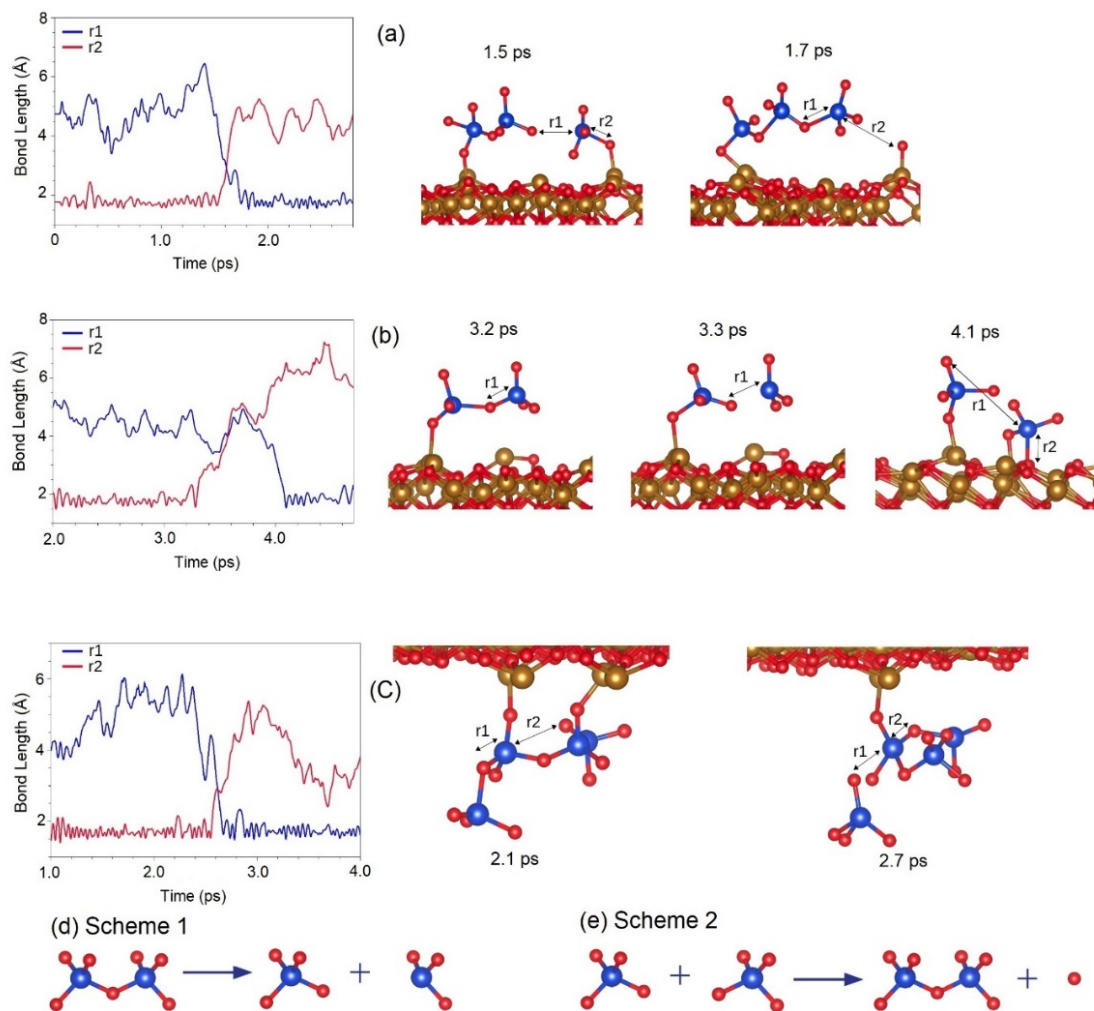


Figure 6. Evolution of the Si–O bond lengths and different snapshots taken during the AIMD simulation at 1361 K and 1 GPa obtained from Tran et al. [37]. (a,b) illustrate the polymerization and dissociation of the FeNSO11 system, respectively. (c) shows the bond exchange in the FeNSO12 glass network. (d,e) demonstrate the reaction schemes for the polymerization and depolymerization, respectively.

2.2.4. The Roles of Na in Glass Lubricants

All of the considered inorganic compounds contain a sodium element, which has a vital role in the tribological performance of these glassy lubricants. Na attacks the O_b and stimulates the $P-O_b$ bond dissociation by reducing the bond dissociation energy [32]. In addition, the weak network former role, along with the dominant network modifier role of sodium, has been observed, along with its prominent network modifier role. The phenomena in which the mobile sodium atoms either terminate O_{nb} or occupy three oxygen on the surface were observed in both static QM calculations and high temperature AIMD simulations. An investigation of the adsorption of sodium atoms on Fe_2O_3 (0001) surfaces indicated that sodium preferred to adsorb on hollow positions where it could bind with three surface oxygens [42]. Therefore, the presence of the iron oxide surface attracts sodium atoms in a glass

lubricant onto the surface oxygens and reduces the interaction between these alkaline atoms and the O_b of the lubricant. Consequently, this surface affects the decomposition caused by sodium cations.

When the adsorption of $Na_2B_4O_7$ on the Fe_2O_3 (0001) surface at 1073 K was investigated, we also observed a movement of Na atoms toward this surface via an interaction with surface oxygen to form a Na-rich layer [25,35], which agrees with previous experiments [22]. A comparison between $Na_2B_4O_7$ and B_2O_3 lubricants was made to investigate the influence of Na. The results indicate that $Na_2B_4O_7$ adsorbs onto the surface more strongly than B_2O_3 . The main reason leading to the different behavior between these lubricants was the absence of Na and O_{nb} in B_2O_3 , which results in the absence of Na–O ionic bonds and Fe– O_{nb} covalent bonds for the Fe_2O_3 – B_2O_3 system. In contrast, for the Fe_2O_3 – $Na_2B_4O_7$ system, a sodium-rich layer was formed mainly through strong electrostatic interactions between Na cations, the surface, and lubricant oxygen. In this borate system, along with O_{nb} atoms, Na ions acted as bridging elements which connected the surface and lubricant. Meanwhile, the absence of Na cations induced a weak interaction because there was a rich layer of negatively charged oxygen at the surface–lubricant interface.

In addition, the anti-wear property has benefited from the polymerization of discrete borate chains with the contribution of O_{nb} to create the cross-links between molecules [35]. Na_2O is considered as an appropriate compound to deliver the necessary O_{nb} atoms. When this O_{nb} joined the polymerization process, the modification role of Na^+ cations was inevitably reduced, so they were attracted to surface oxygen to create a Na-rich layer. In shearing conditions, the higher concentration of sodium oxide resulted in smaller energy barriers, which indicated that lower friction could be obtained because of this Na-rich layer [36]. Moreover, the energy barrier of sodium borate with 33% Na_2O was close to potassium, but the confined systems with a higher concentration of Na showed much smaller energy barriers than those using K and Li elements [36]. Among the considered alkali elements, Li provided the highest energies barriers at low and high applied pressures [36]; this unveiled that friction in this system could be higher than in the others. The calculation of the number of bonds between Fe and O in borate molecules showed that this number is under five for systems with Na_2O concentrations larger than 33%, whilst values larger than six were found for Li and K systems [36]. This calculation revealed that the Li and K systems have larger energy barriers due to their larger numbers of Fe– O_{borate} bonds. Additionally, the small shearing energy barrier in borate glass with a high Na concentration was also contributed by the layering structure of sodium borate layers in tribofilm [36]. When considered the sole role of Na elements, it has been reported that the stacking of sodium onto hematite (0001) surfaces could yield a surface adhesive strength of only a half, and a much smaller lateral friction force than that calculated for pure oxide surfaces [42].

The Na-rich layer was also found in silicate glass. In fact, the confined system of $Na_2O.SiO_2$ and $Na_2O.2SiO_2$ displayed this layer at surface–silicate interfaces due to the migration of Na atoms out of the glass network to adsorb onto Fe_2O_3 (0001) surfaces. The rearrangement of sodium elements promoted the polymerization process in the middle of the glass lubricant [37]. When considering the influence of a shearing effect on silicate glass, Tran et al. [37] confirmed the previous observation by Ta et al. [36] for sodium borate glass that silicate lubricants with a higher Na_2O concentration provided a better tribological performance than the lower one because of its greater adhesive strength. The better tribological performance was because of the sodium-rich layer, which worked as a lubricating layer thanks to the nature of their weak electrostatic interaction [37].

2.2.5. Reactive Molecular Dynamics Lubrication Simulations

The experimental findings indicated that tribofilm formation is thermally and mechanically driven under extreme pressure and sliding velocity. The quantum mechanics modeling has described the adsorption mechanism and chemical reactions between alkali glass lubricants and iron oxide surfaces in static conditions well. However, the model scale is limited to several hundred atoms due to a high computational cost. Therefore, the realistic tribosystem with surface roughness, a large number of molecules, and a long-chain molecular structure could not be handled by QM/AIMD simulations.

The critical role that the tribo-mechanical effect plays in driving the first steps of tribofilm formation reactions has not been described yet on a larger scale. The reactive MD simulation with several thousand atoms has been used to understand how these reactions take place when the lubricant was subjected to a continuous applied load and shear force. Additionally, this simulation also helped to design the new and optimized additives by altering the ratio of mixed glass lubricants under a wide range of applied loads and sliding velocities. Unfortunately, the current tribological system contains many different elements in combinations for which the ReaxFF parameters are not available. Recently, we have developed a new set of ReaxFF parameters for Fe/Na/P/O systems to simulate the tribological performance of $\text{Na}_4\text{P}_2\text{O}_7$ confined between Fe_2O_3 surfaces. The developed force field properly reproduced the quantum data of relative energy, the heat of formation, partial charges, bulk modulus, and crystal cell parameters of binary, ternary, and quaternary oxides for the considered system. The chemical reaction between sodium and iron oxide, which caused a penetration of Na atoms into oxide surfaces, as well as the removal of iron cations from the glass lubricant because of its reaction with phosphate, have been observed. Moreover, as presented in Figure 7, the Na-rich layers were observed at the Fe_2O_3 – $\text{Na}_4\text{P}_2\text{O}_7$ interface. These phenomena confirmed our scanning electron microscopy with energy dispersive X-ray (SEM/EDX) analysis from the experiments well [20]. However, the current work is still limited for sodium phosphate lubricants, while the determination of ReaxFF parameters for sodium borate and sodium silicate lubricants confined between iron oxide surfaces is still under progress. Following the successful development of the ReaxFF parameters for sodium phosphate and iron oxide tribosystems, future work to complete the new set of parameters for sodium borate and silicate lubricants will help to understand the influence of the ratio of oxidation inhibitor/anti-wear compound on: (i) chemical properties of the tribofilm under shear effects and (ii) tribological performance, such as shear stress/friction at the shear sliding interface at elevated temperatures. These outputs will help researchers to design the optimum lubricant composition ratio used in metal forming.

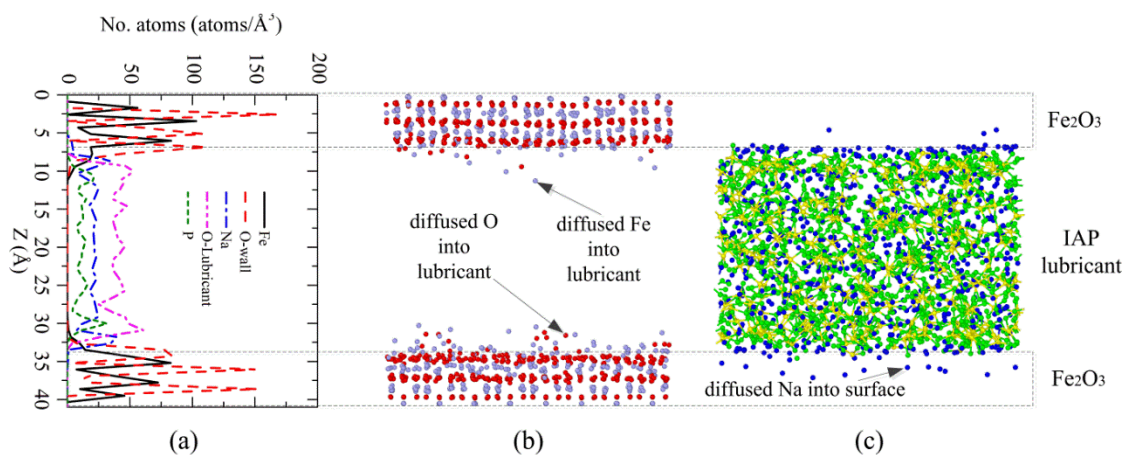


Figure 7. (a) Atomic density of different elements across the thin lubricant film thickness of sodium polyphosphate confined between Fe_2O_3 (001) surfaces; (b) snapshot of Fe_2O_3 (001) surfaces; and (c) phosphate glass obtained from the work by Ta et al. [34].

3. Conclusions

The tribological performance of glass lubricants of alkaline-based inorganic polymers at temperatures up to 1000 °C has been investigated. The lubricating mechanism of phosphate glass was characterized by the chemical reactions between this lubricant and iron oxide surfaces to form an amorphous iron phosphate glass. The tribochemical reaction was triggered by the combination of thermal and shearing mechanisms, resulting in the iron oxide being disintegrated and digested into polyphosphate networks. Our theoretical and experimental results showed that the improvement of the chemical and mechanical stability of phosphate lubricant was attributed to the strong Fe–O–P

formed during the reaction between the Fe_2O_3 surface and $\text{P}_2\text{O}_7^{4-}$ groups. Sodium borate lubricant provides a low coefficient of friction at low applied loads, but this lubricating performance decreased with increasing load. A distinct Na-rich layer (20 nm), residing on the tribosurface interfaces, has been observed from the experiments.

The quantum simulation revealed that this was the result of weak interactions between borate and iron oxide surfaces. Under extreme temperature and load, a metallic silicate tribofilm was generated due to the reaction between sliding metal substrates and the silicate lubricant. The melt of sodium silicate contributed to the diffusion and aggregation of Mn atoms from the iron substrate, and the formed Na-rich layer was also found. These layers contributed significantly to the anti-oxidation performance. The QM calculation indicated that the Fe–O_{nb} bond between the iron oxide surface and silicate was the mechanism for the tribofilm formation of this lubricant. This calculation also revealed that a higher wear could be found at a temperature higher than 1000 °C because of the dissociation of silicate molecules. A realistic reactive MD simulation was carried out for sodium polyphosphate confined between iron oxide surfaces, which confirmed the vital role of sodium in phosphate tribofilms, as well as the digestion and diffusion of iron cations into the glass lubricant.

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