Tribochemistry of Bismuth and Bismuth Salts for Solid Lubrication

Pablo Gonzalez-Rodriguez,†‡ Karin J. H. van den Nieuwenhuijzen,‡ Walter Lette,§ Dik J. Schipper,§ and Johan E. ten Elshof†‡

†Materials Innovation Institute (M2i), Elektronicaanweg 25, 2628 XG Delft, The Netherlands  ‡Inorganic Materials Science, MESA+ Institute for Nanotechnology, University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands  §Surface Technology and Tribology, Faculty of Engineering Technology, University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands

Supporting Information

ABSTRACT: One of the main trends in the past decades is the reduction of wastage and the replacement of toxic compounds in industrial processes. Some soft metallic particles can be used as nontoxic solid lubricants in high-temperature processes. The behavior of bismuth metal particles, bismuth sulfide (Bi2S3), bismuth sulfate (Bi2(SO4)3), and bismuth oxide (Bi2O3) as powder lubricants was studied in a range of temperatures up to 580 °C. The mechanical behavior was examined using a high-temperature pin-on-disc setup, with which the friction force between two flat-contact surfaces was recorded. The bismuth-lubricated surfaces showed low coefficients of friction (μ ≈ 0.08) below 200 °C. Above the melting temperature of the metal powder at 271 °C, a layer of bismuth oxide developed and the friction coefficient increased. Bismuth oxide showed higher friction coefficients at all temperatures. Bismuth sulfide exhibited partial oxidation upon heating but the friction coefficient decreased to μ ≈ 0.15 above 500 °C, with the formation of bismuth oxide-sulfate, while some bismuth sulfate remained. All surfaces were studied by X-ray diffraction (XRD), confocal microscopy, high-resolution scanning electron microscopy (HR-SEM), and energy-dispersive X-ray spectroscopy (EDS). This study reveals how the partial oxidation of bismuth compounds at high temperatures affects their lubrication properties, depending on the nature of the bismuth compound.

KEYWORDS: solid lubricant, high temperature, bismuth, bismuth oxide, bismuth sulfide, bismuth sulfate, pin-on-disc, friction coefficient

INTRODUCTION

Solid lubricants are used in many industrial processes, especially those related to metal processing. Although metals as structural materials are in some cases being replaced by more lightweight or sustainable solutions, like composites or ceramics, the production of high-end products is still linked to the mechanical properties and workability of metals. Metal–metal sliding contacts are present in a wide variety of applications, including conduits, automotive gears, sliding electrical contacts, and biological implants. In the upstream industry, the production of steel requires the use of large amounts of lubricants, and nowadays the most common products are aqueous suspensions of graphite, molybdenum disulfide, or polytetrafluoroethylene (Teflon). Nevertheless, some problems are associated with their use, for instance pitting corrosion on the steel surface caused by partial decomposition of the lubricants at high temperature, and, more in general, a dirty working environment. Bismuth has been used for many years as an active part in self-lubricating alloys because of its natural softness and as an additive for lubricating oils. This element has found its major applications as an alternative for lubricants based on lead. Both metals have a high density, malleability, softness, and low melting temperature. The one important difference between the two is that bismuth is not toxic for living organisms, in contrast to its counterpart, lead. Despite both being heavy metals, bismuth may be considered as a green alternative to lead. Bismuth has already been used in protective lubricating coatings for solid lubrication. It has been found that bismuth particles can form nonbonded films on steel that are easily removed from lubricated surfaces, and which are due to the poor solubility of bismuth in iron. Other compounds of bismuth have also been studied as active additives in lubricants. The presence of sulfur has a synergetic effect on the lubricating properties of bismuth. Bismuth sulfide (Bi2S3) is known to have lubricious properties, forming a stable tribolayer on lubricated pairs. Bismuth organometallic...
compounds are used as additives in oil-lubricated systems, together with sulfur carriers that promote the formation of a Bi&ndash;S tribolayer between the interfaces of metal&ndash;oil&ndash;metal. However, under conditions where the use of organic-based products is unfavorable, i.e., at high temperatures, employing solid lubricants in the form of powders is a solution to reduce friction and energy consumption.2 Powders are typically applied in the form of a suspension in a liquid solvent or compressed to act as a part on the sliding system.20 Application of the lubricant together with treatment of the waste after its use should be performed in a controlled manner. Therefore, it is important that the lubricant itself is not toxic in small concentrations for living organisms. Bismuth is present as an important that the lubricant itself is not toxic in small concentrations for living organisms. Bismuth is present as an additive in cosmetics and paints,21,22 anti-inflammatory agents,23 dental and intestinal tracts.24 Therefore, in this research we explore the applications of bismuth and several bismuth compounds as high-temperature lubricants. Bismuth and bismuth salts have hardly been studied as lubricants in the form of free powders, and little is known about the chemical modifications that bismuth undergoes when present in the contact between two sliding surfaces.

\section*{EXPERIMENTAL SECTION}

\subsection*{Preparation of Bismuth Suspensions.}
Bismuth metal powder (Bi, ABCR, 99.99%), bismuth(III) sulfide (Bi&ndash;S, ABCR, 99.99%), bismuth(III) oxide (Bi2O3, Alfa Aesar, 99%), and bismuth(III) sulfate (Bi2(SO4)3, Alfa Aesar, 99%) were used as received, without further purification. The powders were suspended in water to a concentration of 2 wt% in closed bottles. The suspensions were placed on a rolling bench with zirconium oxide beads (ϕ = 1 mm) to grind suspended powders. The suspensions were then transferred to a suspension in a liquid solvent or compressed to act as a part on the sliding system. Application of the lubricant itself is not toxic in small concentrations for living organisms. Bismuth is present as an additive in cosmetics and paints, anti-inflammatory agents, dental and intestinal tracts. Therefore, in this research we explore the applications of bismuth and several bismuth compounds as high-temperature lubricants. Bismuth and bismuth salts have hardly been studied as lubricants in the form of free powders, and little is known about the chemical modifications that bismuth undergoes when present in the contact between two sliding surfaces.

\subsection*{Characterization: Pin-on-Disc.}
The lubricating properties of the bismuth and bismuth salt powder films were assessed by the use of a high-temperature pin-on-disc (PoD) tribometer for CSM instruments. This technique allows to record friction forces between two sliding surfaces when a lubricant is present in between them. The granular nature of the lubricant made it necessary to adapt the classical PoD configuration, because the use of a bearing ball implies a single contact point between the two metal surfaces. In our experiments the balls were flattened so that the lubricant could be applied on the surface of the pins and could be employed when the discs had reached the set temperatures. The pins consisted of flattened steel bearing balls (10 mm diameter, SKF). The surface of the steel pin was 27 mm2 (disc diameter of ϕ = 5.9 mm), giving a surface concentration of lubricant of 75 &mu;g/mm2 (or 75 &mu;g/m2). The applied load was 10 N, resulting in an effective contact pressure of 370 kPa. The rotating disc was made of EN 10278 steel and was polished, as well as the flattened bearing balls, with SiC paper with a maximum mesh of 2000 and diamond paste of 3 &mu;m particle size. The calculated arithmetic roughness of the steel surfaces was Ra = 0.90 ± 0.25 &mu;m. The measurements consisted of recording the friction force for a maximum of one rotation of the pin over the disc, at a velocity of 1 mm/s. Data were collected from the first data points after contact between the pin and lubricant and the disc at temperatures varying from 35 to 580 °C. The coefficient of friction (CoF) was averaged over a minimum of 5 repetitions. The typical time scale of an experiment lasted up to 30 s, since the powder films were susceptible to be worn out due to the limited testing surface.

The measurement of particle size was performed using a laser diffraction particle size analyzer (Masterizer 2000). The particle size distributions (PSDs), i.e., particle size at 10% (D10), 50% (D50), and 90% (D90) of the volume distribution, were all calculated automatically using the Masterizer 2000 software. The characterization of the crystallographic changes by X-ray diffraction (XRD) was conducted with an X'Pert Powder Pro (PANalytical) instrument using Cu Kα irradiation (λ = 1.5418 &AA;) and recorded with a 1D PIDXel detector. Scans from 2θ = 20–70° were measured with step sizes of 0.013° and 150 s per step. High-resolution scanning electron microscopy was executed on a Merlin field emission microscope (Zeiss) coupled with elemental analysis performed by energy-dispersive X-ray spectroscopy (EDS; TEAM EDS system). Further surface analysis was performed with a laser confocal microscope VK 9700 from Keyence at a magnification of 10 times and a z-axis resolution of 1 nm. Surface images of different tribolayers were obtained and the profile roughness parameters were determined.

\section*{RESULTS AND DISCUSSION}
The performance of bismuth metal (Bi) and bismuth compounds as lubricants was studied by means of PoD measurements. The diverse compounds have different melting/softening points that may influence the tribological properties. The lowest melting point is that of bismuth metal at 271 °C, followed by Bi2(SO4)3 at 405 °C, Bi2O3 at 817 °C, and Bi2S3 at 850 °C. Only the two first compounds have melting points below the maximum testing temperature in this study (580 °C). The powders of all bismuth compounds were suspended in water and grounded for 48 h, and the particle size distributions in volume are displayed in Table 1. The thicknesses of the dried films varied from 100 to 300 &mu;m for the different films. The thickness difference was caused by density differences between the individual compounds, while keeping the mass of the powders constant.

The friction properties of Bi were directly compared with those of Bi2O3, see Figure 1. The recorded dynamic friction force was translated to the coefficient of friction (CoF) for different temperatures, from 35 to 580 °C using eq 1.

\begin{equation}
F_D = \mu F_N
\end{equation}

where \( F_D \), \( \mu \), and \( F_N \) are the dynamic friction force, CoF, and the normal force, respectively.

The CoF of the contact between the unlubricated surfaces of the pin and the disc were recorded as reference, resulting in values of 0.32 ± 0.02 at different temperatures. The CoF of graphite as the state-of-the-art lubricant was also determined, with values of 0.05 ± 0.005. For the sake of clarity and simplicity, the data points of both reference measurements are represented in Figure 1 in the form of colored bands. The measured values can be found in Figure S1 in the Supporting Information. The average CoF of the Bi films was lower than the metal-to-metal contact at all temperatures below 500 °C. The maximum effectiveness of Bi as lubricant was reached in

\begin{table}
\centering
\caption{Summary of Particle Size Distributions by Volume of the Different Lubricants}
\begin{tabular}{llll}
\hline
compounds & \multicolumn{3}{c}{particle size distributions (PSDs)} \\
 & \multicolumn{1}{c}{D10 (μm)} & \multicolumn{1}{c}{D50 (μm)} & \multicolumn{1}{c}{D90 (μm)} \\
\hline
Bi & 2.09 & 6.42 & 20.462 \\
Bi2O3 & 1.38 & 11.14 & 69.56 \\
Bi2S3 & 1.51 & 11.51 & 67.14 \\
Bi2(SO4)3 & 1.86 & 11.71 & 45.67 \\
\hline
\end{tabular}
\end{table}
the low temperature range (up to 200 °C) with a reduction of the CoF by a factor of 3 compared to the reference. This is due to the fact that bismuth metal has a closed packed quasi-metallic layered structure at room temperature.\textsuperscript{25} This structure may be at the basis of its enhanced properties as solid lubricant. When a force is applied the atoms slide along the same crystallographic direction, forming a slip system where dislocations can propagate. The value of the CoF increased steadily between 200 and 500 °C, to reach typical values of metal–metal contact eventually. The variation of the recorded values also increased with temperature, which could be related to changes experienced by the Bi film. Above the melting temperature (271 °C), liquid bismuth can wear out faster compared to the solid powder form. Thus, the performance of bismuth metal as lubricant was only comparable with graphite at temperatures below 200 °C. On the other hand, the CoF of Bi\textsubscript{2}O\textsubscript{3} was higher than the metal–metal contact for all tested temperatures. Bismuth atoms in the structure of Bi\textsubscript{2}O\textsubscript{3} are not completely screened by the surrounding oxygen atoms due to their large size (117 pm). The lack of surrounding makes it so that the metal cations can interact with each other and form covalent or ionic bonds leading to a network that is difficult to shear.\textsuperscript{26}

The variation in the friction properties of Bi powders can be directly linked to changes in the chemistry and crystallography of the lubricant. The friction experiments led to the formation of transferred films from the surface of the pin to the surface of the discs and the Bi powders underwent crystallographic changes within the measurement time. Figure 2 shows the X-ray diffraction patterns of the Bi transferred films at different temperatures, up to 580 °C. It was found that, upon heating, partial oxidation of the Bi film resulted in Bi\textsubscript{2}O\textsubscript{3}. The oxidation happened even at room temperature and was accelerated in samples tested at 300 °C and higher. Figure 2b displays the 2\textdegree\theta region from 26 to 28.5°. It can be seen that three Bi\textsubscript{2}O\textsubscript{3} peaks emerged from the background, i.e., the (110), (120), and (012) peaks, resulting in an overall intensity decrease of the Bi (012) peak with increasing temperature. The intensity of the (012) peak increased up to 400 °C as an artifact of the irradiated surface. Bismuth metal seemed to adhere stronger to the surface of the disc after measurement around and above the melting point. The measurements at high temperature also induced the oxidation of the surface of the steel discs, and peaks of iron(III) oxide (Fe\textsubscript{2}O\textsubscript{3}) were present in samples tested above 400 °C. Evidence of intermetallic compounds of bismuth and iron was not found in the employed films, which could be due to the short measurement times. The transferred Bi powders may not have had enough time to react with the surface of the steel before the samples had cooled down. The lubrication mechanism at low temperatures (below the melting point) is not based on the formation of a bound layer of lubricant and substrate, but on the deformation and sliding of Bi particles between the two sliding metal surfaces. Previous reports in literature found the same behavior when using Bi as additive in lubricant oils.\textsuperscript{11,17}

Bismuth has a low melting point compared to those of the majority of metals in the periodic table.\textsuperscript{25} The oxidation of Bi was accelerated above the melting point, as can be seen by the XRD data in Figure 2. The partial oxidation of the lubricant films beyond the melting point could be related to the higher friction coefficients at higher temperatures. The CoF of Bi powders increased upon heating and approached the behavior of Bi\textsubscript{2}O\textsubscript{3} films, as can be seen in Figure 1. Apparently, the formation of a stiffer oxide phase decreased the deformability of the bismuth film, hindering its good friction properties. In addition, the molten bismuth was worn out faster, which implied a friction increase when a thinner bismuth film is present in between the contact asperities.

The melting of Bi could also be seen in the morphology of the transferred films. Confocal microscopy imaging of Bi samples after investigation above 300 °C showed regions with varying light refraction and amorphous shapes that could be attributed to molten Bi powder, see Figure 3. A close-up of the molten droplets showed that their core was formed by microcrystals and not by a glassy structure. The molten areas may have been the nucleation points for the accelerated oxidation of Bi. Despite the formation of molten Bi, the increasing CoF with increasing temperature can be directly linked to the formation of Bi\textsubscript{2}O\textsubscript{3} crystals in the matrix of molten Bi droplets. The transferred Bi films at 300 °C had thicknesses in the range of 30–50 μm and a roughness of 0.8 μm, in contrast to Bi\textsubscript{2}O\textsubscript{3} transferred films that had thicknesses in the
range of 70–110 μm and an average roughness of 3.9 μm, see Figure 3. The lower film thickness and roughness of Bi could be linked to the plasticity of the metallic phase in comparison to the more brittle behavior of Bi2O3.

In another series of friction experiments, the compounds Bi2S3 and Bi2(SO4)3 were compared. Results of the average CoF for both compounds are displayed in Figure 4. Both ceramic materials performed above the metal–metal contact for the majority of friction tests at different temperatures. Nevertheless, Bi2S3 showed a steady decrease of the average CoF from 100 °C. The coefficient of friction dropped abruptly above 500 °C, and the lubricant showed values of only half of the CoF of metal–metal contact. The spread in the measurement data increased at 500 °C, which may be considered as a transition temperature for the lubricant, and reached more reproducible values at 580 °C. Bi2(SO4)3 showed more erratic behavior, and no trend could be deduced from the measured values of friction. The ceramic showed friction forces well above normal metal–metal contact and the scatter in the measurement data was high. The relatively large scatter in the data may be an indication of the lack of deformability of these ceramic powders. The particles tend to slide and roll between the asperity contact of the metal surfaces. The stiffness of the ceramic particles affects the stability of the measured friction force baseline.

The crystallographic changes of Bi2S3 upon heating were studied by XRD and the patterns are displayed in Figure 5. The transferred films consisted exclusively of Bi2S3 up to 400 °C. At 500 °C and higher, new peaks, resulting from a partially oxidized species of bismuth and sulfur, emerged. On the basis of its crystallographic reflections, the new compound
corresponded to bismuth oxysulfate \([\text{Bi}_2\text{O}_3\text{g}(\text{SO}_4)_{10}]\), with 65% of \(\text{Bi}_2\text{S}_3\) oxidized. The disappearance of some reflections of \(\text{Bi}_2\text{S}_3\) and the increase in intensity of the peaks of the new phase suggest that its formation was directly linked to the partial oxidation of \(\text{Bi}_2\text{S}_3\) during the tribological tests. The effect of oxidation was especially visible by prolonging the typical experiment from 1 cycle (or 60 s) to 5 cycles (or 5 min); these samples are denoted 580 °C and 580 °C, respectively. The peaks of the oxidized \([\text{Bi}_2\text{O}_3\text{g}(\text{SO}_4)_{10}]\) phase increased in intensity with prolonged thermal treatment, as can be seen in Figure 5. None of the growing peaks could be attributed to the \(\text{Bi}_2\text{O}_3\) phase. It is known in the literature that \(\text{Bi}_2\text{S}_3\) undergoes oxidation in both Bi and S sites upon heating, leading to mixed oxides—sulfates at these temperatures.\(^{27}\) The peaks of the stainless steel substrate are visible in the patterns, accompanied by ferrite (Fe_{0.4}O), and magnetite (Fe_{0.4}O) peaks. The oxidation in both Bi and S sites may have influenced the difference in performance between \(\text{Bi}_2\text{S}_3\) and its oxidized form \([\text{Bi}_2\text{O}_3\text{g}(\text{SO}_4)_{10}]\) compared with \(\text{Bi}_2(\text{SO}_4)_{3}\). \(\text{Bi}_2(\text{SO}_4)_{3}\) is a typical ionic bonded ceramic, showed more “ceramic” behavior, with less plastic films, leading to higher CoFs and more scatter in the measurement values.

The transferred films were also studied by means of HR-SEM and EDS. The analysis resulted in values of 63 mol% of the bismuth atoms combined with oxygen, which is in line with the oxygen composition of \([\text{Bi}_2\text{O}_3\text{g}(\text{SO}_4)_{10}]\), with 65% percent of \(\text{Bi}_2\text{S}_3\) oxidized. The HR-SEM image of the surface of the film and the elemental analysis can be found in the Supporting Information, Figure S2. The morphology of the Bi films was studied by means of confocal microscopy. The transferred \(\text{Bi}_2\text{S}_3\) films at high temperatures had thicknesses in the range of 15–20 μm and a roughness of 2.7 μm. Despite \(\text{Bi}_2\text{S}_3\) films being rougher than Bi films, their low thickness is also related to their plasticity of that lubricant. The topographical profile of a \(\text{Bi}_2\text{S}_3\) model film at 300 °C can be found in the Supporting Information, Figure S3.

Figure 5. Powder XRD patterns of \(\text{Bi}_2\text{S}_3\) transferred films after treatment between 35 to 580 °C. The phases are represented as follows: Bismuth(III) sulfide (\(\text{Bi}_2\text{S}_3\), JCPDS 01-084-0279), bismuth oxysulfate (\([\text{Bi}_2\text{O}_3\text{g}(\text{SO}_4)_{10}]\), JCPDS 01-077-1727), stainless steel (Fe−Cr−O, JCPDS 03-065-7775), iron(III) oxide (Fe_{0.4}O, JCPDS 01-073-0603), and iron oxide magnetite (Fe_{0.4}O, JCPDS 01-086-1358).

CONCLUSIONS

The effectiveness of Bi and \(\text{Bi}_2\text{S}_3\) as solid free-standing powders for lubrication has been demonstrated. The morphological, crystallographic, and chemical characterization of all Bi compounds helped to describe their behavior as lubricants. Bi powders perform better at temperatures below 500 °C, with an overall reduction of the CoF by a factor of 3 compared to the reference metal—metal contact. In contrast, \(\text{Bi}_2\text{S}_3\) performed best as a lubricant above 500 °C, with a reduction in CoF by a factor of 2. The oxidation of both lubricants influenced their tribological behavior in a different way. Despite oxidation of the lubricants, no reaction with the substrate was found, which makes the cleaning process of the lubricant from the surface easier. This may help to avoid wastage of water and other cleaning agents, and, thus, help the sustainability of high-temperature processes. This study allowed for the choice of the best solid lubricant for processes occurring at different temperatures.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.6b02541.

Pin-on-disc measurements of unlubricated metal surfaces and graphite; HR-SEM of a \(\text{Bi}_2\text{S}_3\) transferred film; and confocal micrographs of a \(\text{Bi}_2\text{S}_3\) transferred film (PDF).

AUTHOR INFORMATION

Corresponding Author

*E-mail: j.e.tenelshof@utwente.nl

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This research was carried out under the project number M41.7.11434 in the framework of the Research Program of the Materials innovation institute (M2i) Delft, The Netherlands. The authors thank E. G. de Vries for technical assistance during friction data acquisition and M. Smithers for his advice during HR-SEM imaging.

REFERENCES


(8) Becker, J. Light, Graphite Free Lubricants are Born. *World Cem.* **2001**, *32*, 78.