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2018

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Abstract

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Disciplines

Engineering | Science and Technology Studies

Publication Details

Wu, H., Zhao, J., Cheng, X., Xia, W., He, A., Yun, J., Huang, S., Wang, L., Huang, H., Jiao, S. & Jiang, Z. (2018). Friction and wear characteristics of TiO₂ nano-additive water-based lubricant on ferritic stainless steel. *Tribology International*, 117 24-38.

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Friction and wear characteristics of TiO₂ nano-additive water-based lubricant on ferritic stainless steel

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Abstract: The tribological behaviour of innovative TiO₂ nano-additive water-based lubricant on ferritic stainless steel (FSS) 445 was characterised on a ball-on-disk tribometer. Non-oxidised (clean) and pre-oxidised FSS 445 disks with original rough surfaces were both applied in the tribological tests at room temperature. The results show that the water-based nanolubricants with concentrations of 0.4-8.0 wt% TiO₂ can significantly reduce the coefficient of friction (COF) on the two types of disks. The 4.0 wt% TiO₂ lubricant exhibits optimal tribological properties, including the lowest COF and the strongest anti-wear ability on the applied balls under all lubrication conditions. The lubrication mechanisms are primarily ascribed to the formation of tribofilm and the ball-bearing effect of the TiO₂ nanoparticles, respectively, on the two different disks.

Keywords: TiO₂ nano-additive; Water-based lubricant; Coefficient of friction; Ferritic stainless steel

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1. Introduction

In recent years, nanoparticles (NPs) have attracted considerable interest due to their outstanding physicochemical properties. Nanotechnology hereby offers an opportunity to improve the performance of lubricants via the application of nano-additives [1]. It has been reported by many researchers that the addition of NPs into base lubricants shows a promising approach towards enhancing the friction-reduction

and anti-wear properties [2-10]. The classification of the utilised NPs as additives in base lubricant includes metals [6, 7, 11-15], metallic oxides [5, 8, 16-20], non-metallic oxides [21-25], sulfides [26-28], composites [9, 18, 29], fullerene [30-32] and other carbon materials [33-36]. Among those additives, nano-TiO₂ demonstrating as one of the best candidate materials has drawn significant attention, because of its low cost, nontoxicity, superb dispersibility and stability in base lubricant, excellent lubricating properties and practical potentiality in engineering applications [8, 10, 18, 19, 37-40].

The reduction of friction and wear by using nanolubricant is greatly dependent on the characteristics of NPs such as size, shape and concentration [3, 9, 17, 23, 25, 41]. Smaller NPs are generally more likely to take effect between friction pairs, and thus bring about smaller coefficient of friction (COF) and less wear [23, 41]. Non-spherical NPs are less likely to roll on the friction surface, and hence lead to worse friction reducing efficacy, compared to spherical ones [3]. The NPs with higher concentrations in lubricants are more readily agglomerated, resulting in a harmful effect on decreasing the friction and wear, and thus an optimal concentration exists [9, 25]. Viscosity is another factor that affects the tribological behaviour of nanolubricants, and it increases with the increase of NP concentration [30, 42, 43]. Wu et al. [44] studied the friction-reduction properties of lubricating oils with nano-additives including nano-CuO, nano-TiO₂ and nano-diamond, and found that the base oil containing nano-TiO₂ presented the lowest COF because it had the highest viscosity of the tested lubricants.

Numerous mechanisms, including rolling/ball-bearing effect [9, 18, 45, 46], protective film/tribofilm [11, 14, 19, 22, 47-51], mending effect [10, 52], polishing effect [18, 46], synergistic effect [53, 54], and third-body effect [28, 45, 55-57], have been proposed to explain the lubrication enhancement of the nanolubricants. The rolling effect means that NPs can act as ball bearings between the rubbing surfaces in case that sliding or ploughing occurs [45]. The protective film, which refers to coating the friction surfaces by separating them from direct contact, is derived from three aspects. NPs are able to be deposited or adsorbed on the rubbing surfaces to form a boundary film [49], or sometimes they are melted as a protective film under friction heat to cover the friction surfaces [11, 14]. At other times, the formation of the film is produced by tribo-sintering of the NPs [50, 51], and the compacted and smooth tribofilm (so called “glaze”) is conducive to the decrease of friction and wear. When it comes to the mending effect, it is defined by the compensation for the weight loss and filling in the surface defects due to the presence of NPs on the friction surfaces [52]. The polishing effect commits to reduce the roughness of the lubricating surfaces with the assistance of abrasion caused by NPs [46]. The synergistic effect involves nano-clusters which integrate two or more nano-additives into base lubricant for a reinforced lubrication effect. Hu et al. [54] reported that the MoS₂/TiO₂ nano-clusters had significant advantages in friction reduction over pure nano-MoS₂, as the size and layer distance of nano-MoS₂ changed when

combined with nano-TiO₂, producing the synergetic effect. Last but not least, the third-body effect is associated with joint effects of wear particles and NPs in the base lubricant. The particles can behave as “third body” like solid lubricants, and thus prevent severe wear by decreasing the friction [55].

With a growing number of concerns about environmental protection in modern society, the green manufacturing and its sustainable development are becoming increasingly more important in the field of engineering applications. Although the conventional oil-in-water emulsions and the novel nano-additive oil-based lubricants exhibit superior lubrication performance, they inevitably generate contamination to the environment when discharged, leading to another issue of recycling. Therefore, it is desirable to develop high-performance green lubricants to make substitutions. In contrast, nano-additive water-based lubricants are expected to serve as perfect candidates. On one hand, water can be used as a coolant, which has the advantages of good environmental compatibility and high thermal conductivity [33]. On the other hand, the addition of NPs into water is dedicated to the improvement of tribological properties of water, even though the results have been rarely reported [6, 10, 29, 58].

Over the past few years, quite few researchers have focused on the tribological behaviour of nano-additive water-based lubricants. Gara et al. [58] investigated the friction and wear characteristics of ZnO and Al₂O₃ nano-additive water-based lubricants with varying concentrations on different rough surfaces. The results showed that the NPs helped to reduce the friction but increase the ball wear, and the lubrication mechanisms were deemed to include the rolling effect and protective film. Zhang et al. [6, 29] examined the tribological properties of as-prepared nano-Cu and Cu/SiO₂ nanocomposites as additives in distilled water, and the reduction of friction and wear was supposed to be executed by a boundary lubrication film and a protective film, respectively. There is a lack of direct evidence, however, to illustrate the lubrication mechanisms of NPs exerting in water. In addition, the effects of NP concentrations on the tribological behaviour and the reasons behind that have not been clearly researched.

Nowadays, the use of nano-TiO₂ in water is prevailing in an ascending trend in relation to engineering applications [38, 40, 59]. Previously, the polished mild steel disks had been applied to the study of the lubrication behaviour of as-prepared TiO₂ nano-additive water-based lubricants [10]. In the present work, the ferritic stainless steel (FSS) 445 rough disks with and without oxidation were investigated using a ball-on-disk tribometer to evaluate the friction and wear characteristics of the TiO₂ nano-additive water-based lubricants. The objective of this study is to reveal the effects of rough surface, oxide scale and NP concentration on the lubrication performance of as-prepared TiO₂ nanolubricants through experimental analysis and interpretation of lubrication mechanisms.

2. Experimental

2.1 Materials

E52100 Cr steel balls and FSS 445 disks were used in this study, and the chemical compositions of these two materials are listed in Table 1. The applied balls with a diameter of 9.5 mm and an identical surface roughness (R_a) of 0.02 μm had Vickers hardness of 780 HV. The clean disk materials were machined to 40 mm in diameter and 8 mm in thickness. The Vickers hardness of the clean disks was 160 HV, and the surfaces were ground to be uniform with an R_a of around 0.51 μm . The pre-oxidised FSS 445 disks were obtained in a high temperature electric resistance furnace at a temperature of 1100 $^{\circ}\text{C}$ for 120 min, and then slowly cooled down to room temperature. In this way, the thickness of the oxide scale on all the pre-oxidised disks can be kept identical, and the R_a of the oxidised surface was maintained homogeneously to be 1.12 μm , which was higher than that of the clean disk. The surface morphologies and 3D profiles of the applied ball, clean disk and pre-oxidised disk are shown in Fig. 1(a)-(f). It can be seen that the ball surface is quite smooth, while both the disk surfaces have rough furrows along a fixed direction. This rough surface was designed to differentiate the smooth one based on the previous study [10], and the lubrication mechanisms of developed TiO_2 nano-additive water-based lubricants would be further analysed. It has been reported that the oxide scale formed on FSS 445 surface is primarily composed of Cr_2O_3 with $(\text{Mn}, \text{Cr})_3\text{O}_4$ spinel located on top of Cr_2O_3 scale [60-62]. The hardness of the formed oxide scale was measured by nanoindentation, showing a value of 13 ± 2 GPa.

The employed TiO_2 nano-additive water-based lubricants were composed of TiO_2 NPs, polyethyleneimine (PEI), glycerol and balanced water. The detailed preparation process of the lubricants was shown in our previous studies, indicating excellent dispersibility and stability [10, 38]. The nano- TiO_2 is P25 containing 75% of anatase and 25% of rutile with a diameter of approx. 20 nm. PEI is a cationic polymer, which behaves as a surfactant of TiO_2 in order to improve the dispersibility of the NPs in water. Glycerol is a colourless, odourless and viscous liquid, which is mainly used to improve the viscosity of solutions. The chemical compositions of as-prepared TiO_2 nano-additive water-based lubricants are outlined in Table 2. The TiO_2 concentrations of these lubricants vary from 0.4 to 8.0 wt%. For a comparison with the lubrication performances of the developed water-based lubricants, dry condition and water lubrication were applied to be benchmarks.

2.2 Tribological tests

An Rtec MFT-5000 Multi-functional Tribometer was utilised to measure the COF values using ball-on-disk tribological tests. The configuration of this tribometer is schematically shown in Fig. 2. The normal force applied to the ball holder was measured by an F_z load cell installed above a spring. The frictional

force was induced by the combination of the rotating motion and the normal load, and it was recorded by an F_x load cell attached to the right point of the arm. The disk holder and disk, which were controlled by a servo motor for rotating, were located in a liquid container. Prior to the tests, both the ball and disk were cleaned ultrasonically in an acetone bath for 5 min, and then assembled in the tribometer. The disk was fastened to the disk holder by a screw, and a small pin was inserted to ensure a combined rotation of the disk and the holder. The arm adjusted by a bubble level needs to be accurately horizontal in order to reduce experimental errors. It should be noted that the disk surface was covered by a layer of lubricant with a fixed volume of 2 ml for each test under liquid lubrication. In this way, the initial conditions of the tribological tests can be well controlled.

The ball-on-clean-disk and ball-on-pre-oxidised-disk tests were carried out at an ambient temperature of around 25 °C under different lubrication conditions, and each test was repeated three times in order to minimise data scattering. The averaged COF and wear values were then calculated as per the obtained data at stable stages and the wear scar diameters after tests, respectively. A constant load of 5 N was applied to press the Cr steel ball against the rotating FSS disk for a period of 30 min. The linear speed and the diameter of the wear track were 50 mm/s and 14 mm, respectively, corresponding to an angular speed of 34 rpm. During each test, COF variations were recorded as a function of the sliding time. It should be noted that the reason of choosing 5 N as an applied load was to protect the oxidised surface from being grooved. This means that the ball-on-pre-oxidised-disk test was confined only to the counterparts between the ball and the oxidised scale. In addition, a sliding linear speed of 50 mm/s was adopted for the minimisation of hydrodynamic effect. A period of 30 min was to stabilise the COF variations. When each test was completed, the ball and disk were disassembled from the holders and cleaned ultrasonically in acetone for 5 min to remove any loose debris and surplus lubricants.

2.3 Characterisation methods

The wear scars of balls and wear tracks of disks after tribological tests were cleaned in an ultrasonic acetone bath for 5 min and then examined under observation under a KEYENCE VK-X100K 3D Laser Scanning Microscope, from which the surface morphologies and 3D profiles of the worn zones were obtained. Both the balls and disks were further analysed using JEOL model JSM-6490LV and JSM-7001F as well as FEI model Nova NanoLab 200 Scanning Electron Microscope (SEM) equipped with an EDS to characterise the lubrication mechanisms.

3. Results

3.1 Ball-on-clean-disk tests

Fig. 3 shows the COF values measured in the process of ball-on-clean-disk tests under different lubrication conditions. The in situ COF curves against time in Fig. 3(a) reveal the variation trend of COF from the beginning to the end of each test. It can be seen that dry condition triggers a COF curve with remarkable fluctuation in the first 250 s, and gradually stabilises it in the rest of period. With the application of water lubrication, differently, the COF level can be lowered down to a stable stage after slight fluctuation in the first 50 s. Similarly, the COF curves under 0.4-2.0 wt% TiO₂ lubrication proceed steadily after 50 s at the beginning of test, but exhibit much lower level than that of water lubrication. When the concentrations of nano-TiO₂ in lubricants increase to 4.0-8.0 wt%, however, the running-in period with severe variation of COF increases to around 250 s, after which the COF curves tend to go downward, and reach a constant level until the end of the tests. In particular, the COF curve of 4.0 wt% TiO₂ lubricant presents the lowest level of all the curves at the stable stage. The variations of averaged COF values from the curves are shown in Fig. 3(b). It can be seen that water and nano-TiO₂ water-based lubricants all demonstrate prominent lubrication effects by significantly reducing the COF of the dry condition. More importantly, the addition of nano-TiO₂ into the water can continuously reduce the COF of the water lubrication with an increase in the concentration of nano-TiO₂, and it reaches the lowest COF value of 0.237 when 4.0 wt% TiO₂ is added. A further increase of TiO₂ concentration to 8.0 wt%, however, shows a higher COF value instead.

Fig. 4 shows the surface morphologies of the worn balls after ball-on-clean-disk tests under different lubrication conditions. It is found that all the wear scars are spherical, and significant scratches are caused on the scar surfaces under the conditions of dry, water, 0.4 and 1.0 wt% TiO₂. In contrast, the 2.0-8.0 wt% TiO₂-containing lubricants result in smooth wear scar with black powders adhered around. The wear scar diameters of the balls in Fig. 4 are quantitatively shown in Fig. 5. With the application of water and water-based lubricants, the diameters of wear scars become gradually smaller than that of dry condition until the smallest one is achieved under lubrication of 4.0 wt% TiO₂. An even higher concentration of nano-TiO₂ lubricant up to 8.0 wt%, nevertheless, is supposed to increase the ball wear, which is similar to that of 0.4 wt% TiO₂. This means that when the TiO₂ concentration exceeds a critical value (4.0 wt%), it will aggravate the ball wear on the contrary.

Fig. 6 shows the wear track morphologies of the clean FSS 445 disks lubricated under the conditions of dry, water and TiO₂ nano-additive water-based lubricants. The corresponding 3D profiles of the wear tracks are shown in Fig. 7. It can be observed that the disk surface under dry condition is severely grooved, and black powders are scattered in the wear track. There are also flat areas (bright zone in Fig. 6(a)) formed on the wear track, corresponding to high positions (red zone in Fig. 7(a)). The wear track lubricated by water, differently, shows no flat areas but holes and deep ditches, as shown in Fig. 6(b) and

Fig. 7(b). When 0.4-2.0 wt% water-based lubricants are applied, however, the furrows on the original disk surfaces are not grooved or ploughed significantly, leading to slight abrasion on the disks, as shown in Fig. 6(c)-(e) and Fig. 7(c) and (d). A high concentration of 4.0 wt% TiO_2 , however, brings about a conspicuous trench, which is wider but smoother than that under water (Fig. 6(f) and Fig. 7(e)). A further increase of TiO_2 concentration up to 8.0 wt%, whereas, causes a slightly shallower wear track (Fig. 6(g) and Fig. 7(f)), compared with 4.0 wt% TiO_2 lubrication. It can be clearly seen that the original disk surface is subjected to apparent deterioration under high TiO_2 concentrations of 4.0 and 8.0 wt%.

3.2 Ball-on-pre-oxidised-disk tests

Fig. 8 displays the COF values measured during ball-on-pre-oxidised-disk tests under different lubrication conditions. The in situ COF curves against time shown in Fig. 8(a) indicate that the COF is almost steady throughout the whole frictional process, except for slight fluctuation during the first 20 s, irrespective of lubrication conditions. The averaged COF values obtained in Fig. 8(b) present a similar variation trend but a quite lower level, compared to those in Fig. 3(b). In particular, the COF caused under dry condition on the pre-oxidised disk shows an average value of 0.453, which is 16.3% lower than that on the clean disk. Besides, the COF on clean disk lubricated by 4.0 wt% TiO_2 can be reduced by 36.4% when a pre-oxidised disk is used as an alternate. Likewise, the lubricant containing 8.0 wt% TiO_2 behaving on the pre-oxidised disk also impedes a further decrease of COF yielded by that containing 4.0 wt% TiO_2 .

Fig. 9 exhibits the surface morphologies of the worn balls after the ball-on-pre-oxidised-disk tests under different lubrication conditions. The wear scar diameters of the balls are quantitatively shown in Fig. 10. It is of great interest that the dry friction can cause the smallest wear scar of the ball, which is different from the results obtained in Fig. 4 and 5. The water and 0.4 wt% TiO_2 lubrication inversely increase the ball wear, which is inclined to be decreased with application of ascending concentrations of TiO_2 nano-additives in lubricants from 1.0 to 4.0 wt%. In particular, 4.0 wt% TiO_2 lubrication results in a comparable wear scar diameter of ball to dry condition. The addition of 8.0 wt% TiO_2 , however, deteriorates the ball wear to some extent. On the other hand, the ball surfaces lubricated by 1.0-4.0 wt% TiO_2 lubricants are much smoother than those lubricated under other conditions.

The wear track morphologies and the corresponding 3D profiles of the pre-oxidised disks after tribological tests are shown in Fig. 11 and 12, respectively. It can be found that there are large and flat zones with bright white colour after dry friction on pre-oxidised disk, as shown in Fig. 11(a). The flat and white zones, which indicate the wear track, correspond to high positions with red colour shown in Fig. 12(a). The water lubrication can decrease the size of the white zones, but increase the width of them, as shown in Fig. 11(b) and Fig. 12(b). With the increasing addition of nano- TiO_2 into the water, the white

zones are found to be gradually decreased in size and area, and they become the smallest and the least when 4.0 wt% TiO_2 -containing lubricant is applied. This phenomenon can be clearly seen from Fig. 11(f) and Fig. 12(e) that the disk surface is nearly intact after the frictional process. On the contrary, a further increase of TiO_2 concentration to 8.0 wt% aggravates the worn zones, as shown in Fig. 11(g) and Fig. 12(f).

4. Discussion

4.1 Analysis of ball-on-clean-disk tests

Fig. 13 shows the SEM images and EDS spectra of the edges of worn balls after ball-on-clean-disk tests. The black powders produced under dry friction around the edge of worn ball in Fig. 13(a) are transferred from the worn disk, suggesting Fe-Cr oxides, as shown in Fig. 13(e). This is in accordance with the result obtained in our previous study [60]. Likewise, the powders are readily adhered to the balls lubricated by TiO_2 nano-additive lubricants, as shown in Fig. 13(b)-(d). It can be apparently seen that higher concentrations of TiO_2 (4.0 and 8.0 wt%) make the lubricants much easier to generate aggregations of powders beside the edges of worn balls. The aggregations and EDS spectra shown in Fig. 13(d) and (f) consist of Fe-Cr oxides and TiO_2 NPs, which may act as a barrier to obstruct the continuous supplies of NPs to the rubbing zone for lubrication [46]. The effective NPs behaving in the rubbing zone originate from two sources, including the ones deposited in the surface valleys [26, 28] and the others outside the contact zone [21, 46].

The analysis of the worn surface of the clean disk after dry friction is shown in Fig. 14. It is observed from Fig. 14(a) that the substrate is severely grooved and ploughed, and loose powders (Point C) together with compacted area (Point B) dominate the components of the worn track. The EDS mappings indicate that the Cr-rich and Cr-poor areas stand for substrate (Point A) and Fe-Cr oxides (Points B and C), respectively. This can be further confirmed by EDS spectra in Fig. 14(b)-(d). The weight percentage of Cr content shown in Fig. 14(b) is 21.5 wt%, which is in line with the one in the substrate, as shown in Table 1. In comparison, Points B and C in Fig. 14(c) and (d) exhibit lower Cr and Fe contents but higher O content, suggesting Fe-Cr oxides. In this case, some loose powders have been pressed and sintered to form the compacted areas (so-called glazes) [50, 63-67]. At the beginning of dry friction (running-in period), the high COF is caused by the severe ploughing as the hardness of the ball is much higher than that of the disk. Then, the majority of the produced powders act as abrasives while few powders are sintered to form glazes, as shown in Fig. 7(a) and Fig. 14(a). On one hand, the wear debris (third-body lubrication) and small amounts of glazes (tribofilm) contribute to the drop and stabilisation of COF,

respectively [55, 57, 67, 68]. On the other hand, the abundant abrasives accelerate the wear damage of the ball [50, 66], which results in the largest wear scar diameter, as shown in Fig. 4 and 5.

Fig. 15 shows the SEM images and EDS mappings of the worn surfaces of the clean disks lubricated by the nano-additive water-based lubricants with TiO_2 concentrations of 0.4, 2.0, 4.0 and 8.0 wt%. It is found from Fig. 15(a) and (b) that the original furrows on the disks remain almost intact under lubrications of 0.4 and 2.0 wt% TiO_2 . The depositions of nano- TiO_2 on the worn tracks reveal a phenomenon of tribo-sintering [50, 69], leading to the formation of tribofilm, which is similar to the glazes (Fe-Cr oxides) formed in dry friction. The tribofilm coupled with the rolling effect [9, 18, 44, 45, 56, 70] of nano- TiO_2 in the wear track is therefore beneficial to the decrease of COF and wear (both ball and disk), as compared to dry condition. When the concentration of TiO_2 increases to 4.0 wt%, however, the nano- TiO_2 tends to agglomerate. The high COF level caused by 4.0 wt% TiO_2 in the running-in period shown in Fig. 3 is ascribed to partial agglomeration of the nano- TiO_2 , which is harder than the disk material. In this case, the disk wear is aggravated. After the running-in period, the formation of tribofilm, as shown in Fig. 15(c), together with the continuous supplies of nano- TiO_2 (shown in the EDS mappings of Fig. 15) inside the disk valley and outside the contact zone facilitates the decrease of COF and ball wear, but deteriorates the disk wear, as compared to the lubricants with TiO_2 concentrations less than 4.0 wt%. When it comes to an even higher TiO_2 concentration of 8.0 wt%, the majority of nano- TiO_2 agglomerates along the edge of the worn disk and ball (Fig. 15(d) and Fig. 13(d)), leading to a scarce supply of nano- TiO_2 from outside of the contact zone. This means that only few nano- TiO_2 in the depleted zone can behave as ball bearings between the ball and the disk, let alone the formation of tribofilm, as shown in Fig. 15(d). In addition, the nano- TiO_2 agglomerated along the ball edge rubs each other and also abrades the ball edge. This means that the lubricant containing 8.0 wt% TiO_2 induces a higher COF value and a larger ball wear scar than that containing 4.0 wt% TiO_2 . It should be noted that in the ball-on-clean-disk tests, a relatively higher TiO_2 concentration is inclined to generate more compacted tribofilm based on the observations from the high-resolution SEM images shown in Fig. 15. The tribofilm formed and the effective TiO_2 NPs supplied dominate the decrease of friction and wear.

4.2 Analysis of ball-on-pre-oxidised-disk tests

Fig. 16 displays the surface morphologies of the worn balls under lubrication conditions of dry, 0.4, 4.0 and 8.0 wt% TiO_2 after ball-on-pre-oxidised-disk tests. The presence of severe scratches in Fig. 16(a) indicates a clear phenomenon of abrasive wear, causing the highest COF, as shown in Fig. 8. In contrast, the relatively mild scratches caused by 0.4 wt% TiO_2 (Fig. 16(b)) signify a lower COF value compared to dry friction. In particular, the worn surface of the ball lubricated by 4.0 wt% TiO_2 appears to be the

smoothest (Fig. 16(c)), corresponding to the lowest COF, as shown in Fig. 8. The lubricant containing 8.0 wt% TiO₂, instead, exhibits a higher COF than 4.0 wt% TiO₂ owing to the agglomeration of the nano-TiO₂ [9], which leads to slight ditches, as shown in Fig. 16(d).

The SEM images and EDS analysis on the worn pre-oxidised disk after dry friction are summarised in Fig. 17. It can be seen from Fig. 12(a) and Fig. 17(a) that the surface of pre-oxidised disk is covered by a smooth and block layer of Fe-rich oxide scale. Point B stands for the compacted layer with rich Fe but poor Cr and Mn contents (Fig. 17(c)), while Point C refers to the loose layer with rich Fe but a bit higher Cr and Mn contents (Fig. 17(d)) than Point B, due to the exposure of substrate (Point A) whose representative elements are in rich Cr and Mn but poor Fe, as shown in Fig. 17(b). As the disk substrate is much harder than the applied ball, the element Fe in the formed layer is definitely transferred from the ball material during the process of dry friction. The Fe-rich oxide scale is formed subsequently because of the frictional heat and loading force. Like the tribofilm formed (Fig. 14 and 15), this smooth and block Fe-rich oxide scale, which is much softer than the disk substrate, plays an important role in decreasing the friction and wear under dry condition, due to a transition from ball-to-Cr-rich-oxide-scale contact to ball-to-Fe-rich-oxide-scale contact. Because of this, it shows a much lower and more stable COF curve in Fig. 8 than that in Fig. 3, and also leads to the smallest ball wear, as shown in Fig. 9 and 10.

Fig. 18 shows the SEM images and EDS mappings of the worn pre-oxidised disks lubricated by 0.4, 4.0 and 8.0 wt% TiO₂-containing nanolubricants. The areas marked with “1” and “2” in Fig. 18(a), (c) and (e) are amplified to present distributions of nano-TiO₂. The EDS mappings shown in Fig. 18(b), (d) and (f) indicate that the Fe-rich phases transferred from ball material adhere onto the worn disk surfaces, suggesting the presence of ball wear. The Fe-rich phases are formed inconsecutively and barely oxidised under lubrication of nanolubricants due to lower frictional heat, in comparison to Fe-rich oxides formed under dry friction (Fig. 17). When the concentration of TiO₂ is low (0.4 wt%), nano-TiO₂-depleted zone appears on the surface of Fe-rich phases (Area “1” in Fig. 18(a)), and there are few nano-TiO₂ acting outside the Fe-rich phases (Area “2” in Fig. 18(a)). This may result in a high COF and severe ball wear. With an increasing concentration of TiO₂ to 4.0 wt%, in contrast, the amounts of effective nano-TiO₂ inside and outside the valleys of wear track become more substantial with a spherical shape (Fig. 18(c)), which provides a ball-bearing effect between the ball and the disk, and thereby decreases the friction and wear to a greater extent. Similar to the situation shown in Fig. 15(d), the 8.0 wt% TiO₂-containing lubricant accelerates the agglomeration of the nano-TiO₂ (Fig. 18(e)), and hereby abrades the ball surface, producing slight ditches, as shown in Fig. 16(d). This indicates a higher COF and more progressive loss of ball materials, as compared to the lubricant containing 4.0 wt% TiO₂. It should be noted here that the pre-oxidised disk is much harder than the nano-TiO₂ and the applied ball, the disk surface, thereby, would

not suffer severe damage under a loading force of 5 N but accommodate the TiO₂ NPs for lubrication effectiveness. Meanwhile, the COF curves can be steadily maintained.

4.3 Lubrication mechanisms

Fig. 19 illustrates the lubrication mechanisms at room temperature when the Cr steel ball encounters the FSS 445 disk with and without oxidation in the tribological tests. For the ball-on-clean-disk test under dry friction (Fig. 19(a)), ploughing dominates the whole abrading process, leading to high friction and wear. The application of TiO₂-containing nanolubricants (Fig. 19(b)-(d)), differently, tends to yield compacted nano-TiO₂ tribofilm by tribo-sintering in the wear track. The tribofilm formed and the effective TiO₂ NPs supplied inside and outside the disk valleys are heavily involved in the decrease of friction and wear. When it comes to the ball-on-pre-oxidised-disk test, as the pre-oxidised disk is harder than the applied ball, dry friction leads to the formation of Fe-rich oxide scale (Fig. 19(e)), which originates from the ball material and covers the disk to produce a protective layer. This layer of oxide scale is beneficial to the decrease of the ball wear rather than the COF, leading to the smallest wear scar diameter of the ball. In contrast, TiO₂ NPs in the employed water-based lubricants shown in Fig. 19(f)-(h) are supposed to behave as ball bearings between the ball and the disk, facilitating the decrease of friction. In particular, the lubricant containing 4.0 wt% TiO₂ exhibits a comparable anti-wear ability to dry condition. In the tribological tests, both clean and pre-oxidised disks can hold the deposited nano-TiO₂ due to the presence of valleys formed on the rough disk surface. The different lubrication mechanisms are attributed to the discrepant hardness levels of the disk surface. Similarly, a lubricant with TiO₂ below 4.0 wt% provides only scarce nano-TiO₂ to take effect, while the lubricant with a high TiO₂ concentration of 8.0 wt% prompts the nano-TiO₂ to agglomerate. On one hand, the agglomeration of nano-TiO₂ acts as a barrier to inhibit the continuous supplies of fine NPs to the contact zone for lubrication. On the other hand, the agglomerated NPs would abrade the ball and disk surfaces to a great extent. Therefore, the lubricant containing 4.0 wt% TiO₂ presents the best comprehensive lubricating performance of all the lubrication conditions.

5. Conclusions

The friction and wear characteristics of TiO₂ nano-additive water-based lubricants on the FSS 445 disks were investigated by the ball-on-clean-disk and ball-on-pre-oxidised-disk tests at room temperature. The conclusions can be drawn as follows:

- (1) When clean disks are used, the TiO₂ nano-additive water-based lubricants result in lower COFs than those obtained under dry and water lubrication conditions. The use of the 4.0 wt% TiO₂-containing

lubricant leads to the lowest COF and the smallest ball wear under all the lubrication conditions. This is attributed to the tribofilm formed by tribo-sintering of nano-TiO₂ in the wear track.

- (2) When oxidised disks are employed under dry condition, the element Fe transferred from the ball material is to be oxidised to form a layer of smooth and block Fe-rich oxide scale to cover the pre-oxidised disk surface. The Fe-rich oxide scale helps stabilise the sliding process and decrease the friction, as compared to the dry friction on a clean disk. It also helps to improve the wear resistance of the ball, leading to the smallest ball wear. The use of the 4.0 wt% TiO₂-containing lubricant again results in the lowest COF, as well as similar ball wear to that under dry friction, owing to the best ball-bearing effect between the ball and the pre-oxidised disk.

Acknowledgement

The authors acknowledge the financial support from Baosteel-Australia Joint Research and Development Centre (BAJC) under project of BA-13012 and the Australian Research Council (ARC) under Linkage Project Program (LP150100591). The first author is greatly thankful for the scholarship support (IPTA & UPA) from University of Wollongong and the scholarship support from China Scholarship Council (CSC). The authors are grateful to Mr. Stuart Rodd and other technicians in the workshop of SMART Infrastructure Facility for their great support on samples machining. The authors also wish to thank Dr. Charlie Kong for technical assistance and use of facilities supported by AMMRF at the Electron Microscope Unit at UNSW. The authors would like to extend special thanks to Dr. Madeleine Strong Cincotta in the final language editing of this paper.

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Table Captions:

Table 1 Chemical compositions of the ball and disk materials (wt%).

Table 2 Chemical compositions of employed lubricants.

Figure Captions:

Fig. 1 Surface morphologies and 3D profiles: (a, b) applied ball, (c, d) clean disk and (e, f) pre-oxidised disk.

Fig. 2 Schematic of the ball-on-disk tribometer used for tribological tests.

Fig. 3 COF values measured during ball-on-clean-disk tests under different lubrication conditions: (a) in situ COF curves against time, and (b) variation of averaged COF values.

Fig. 4 Surface morphologies of the worn balls after ball-on-clean-disk tests under lubrication conditions of (a) dry, (b) water, (c) 0.4 wt% TiO₂, (d) 1.0 wt% TiO₂, (e) 2.0 wt% TiO₂, (f) 4.0 wt% TiO₂ and (g) 8.0 wt% TiO₂.

Fig. 5 Wear scar diameters of applied balls after ball-on-clean-disk tests under different lubrication conditions.

Fig. 6 Wear track morphologies of the clean disks under lubrication conditions of (a) dry, (b) water, (c) 0.4 wt% TiO₂, (d) 1.0 wt% TiO₂, (e) 2.0 wt% TiO₂, (f) 4.0 wt% TiO₂ and (g) 8.0 wt% TiO₂.

Fig. 7 3D profiles of the clean disks under lubrication conditions of (a) dry, (b) water, (c) 0.4 wt% TiO₂, (d) 2.0 wt% TiO₂, (e) 4.0 wt% TiO₂ and (f) 8.0 wt% TiO₂.

Fig. 8 COF values measured during ball-on-pre-oxidised-disk tests under different lubrication conditions: (a) in situ COF curves against time, and (b) variation of averaged COF values.

Fig. 9 Surface morphologies of the worn balls after ball-on-pre-oxidised-disk tests under lubrication conditions of (a) dry, (b) water, (c) 0.4 wt% TiO₂, (d) 1.0 wt% TiO₂, (e) 2.0 wt% TiO₂, (f) 4.0 wt% TiO₂ and (g) 8.0 wt% TiO₂.

Fig. 10 Wear scar diameters of applied balls after ball-on-pre-oxidised-disk tests under different lubrication conditions.

Fig. 11 Wear track morphologies of the pre-oxidised disks under lubrication conditions of (a) dry, (b) water, (c) 0.4 wt% TiO₂, (d) 1.0 wt% TiO₂, (e) 2.0 wt% TiO₂, (f) 4.0 wt% TiO₂ and (g) 8.0 wt% TiO₂.

Fig. 12 3D profiles of the pre-oxidised disks under different lubrication conditions of (a) dry, (b) water, (c) 0.4 wt% TiO₂, (d) 2.0 wt% TiO₂, (e) 4.0 wt% TiO₂ and (f) 8.0 wt% TiO₂.

Fig. 13 SEM images of the edges of worn balls after ball-on-clean-disk tests under lubrication conditions of (a) dry, (b) 0.4 wt% TiO₂, (c) 4.0 wt% TiO₂ and (d) 8.0 wt% TiO₂, and EDS spectra of (e) dry and (f) 8.0 wt% TiO₂.

Fig. 14 SEM image and EDS analysis of the worn surface of clean disk after dry friction: (a) worn track morphology, and (b, c, d) EDS spectra of Points A, B and C, respectively.

Fig. 15 SEM images and EDS mappings of the worn surfaces of clean disks lubricated by (a) 0.4 wt% TiO₂, (b) 2.0 wt% TiO₂, (c) 4.0 wt% TiO₂ and (d) 8.0 wt% TiO₂.

Fig. 16 SEM images of the worn surfaces of balls under lubrication conditions of (a) dry, (b) 0.4 wt% TiO₂, (c) 4.0 wt% TiO₂ and (d) 8.0 wt% TiO₂ after ball-on-pre-oxidised-disk tests.

Fig. 17 SEM image and EDS analysis of the worn surface of pre-oxidised disk after dry friction: (a) worn track morphology, and (b, c, d) EDS spectra of Points A, B and C, respectively.

Fig. 18 SEM images and EDS mappings of the worn surfaces of pre-oxidised disks lubricated by (a, b) 0.4 wt% TiO₂, (c, d) 4.0 wt% TiO₂ and (e, f) 8.0 wt% TiO₂.

Fig. 19 Schematic illustration of the lubrication mechanisms using (a-d) ball-on-clean-disk and (e-h) ball-on-pre-oxidised-disk tests under lubrication conditions of (a, e) dry condition, (b, f) 0.4 wt% TiO₂, (c, g) 4.0 wt% TiO₂ and (d, h) 8.0 wt% TiO₂.

Table 1 Chemical compositions of the ball and disk materials (wt%).

Materials	C	Si	Mn	Cr	Cu	Mo	Ti	Nb	P+S
Ball-E52100	1.0	0.25	0.35	1.5	0.30	0.10	-	-	≤ 0.03
Disk-FSS 445	≤ 0.01	0.30	0.15	21.5	0.10	0.60	≤ 0.20	0.12	≤ 0.03

Table 2 Chemical compositions of employed lubricants.

Lubrication type	Description
1	Dry condition
2	Water
3	0.4 wt% TiO ₂ +0.004 wt% PEI + 10.0 vol% glycerol + balance water
4	1.0 wt% TiO ₂ +0.01 wt% PEI + 10.0 vol% glycerol + balance water
5	2.0 wt% TiO ₂ +0.02 wt% PEI + 10.0 vol% glycerol + balance water
6	4.0 wt% TiO ₂ +0.04 wt% PEI + 10.0 vol% glycerol + balance water
7	8.0 wt% TiO ₂ +0.08 wt% PEI + 10.0 vol% glycerol + balance water

Fig. 1 Surface morphologies and 3D profiles: (a, b) applied ball, (c, d) clean disk and (e, f) pre-oxidised disk.

Fig. 2 Schematic of the ball-on-disk tribometer used for tribological tests.

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Fig. 5 Wear scar diameters of applied balls after ball-on-clean-disk tests under different lubrication conditions.

Fig. 6 Wear track morphologies of the clean disks under lubrication conditions of (a) dry, (b) water, (c) 0.4 wt% TiO_2 , (d) 1.0 wt% TiO_2 , (e) 2.0 wt% TiO_2 , (f) 4.0 wt% TiO_2 and (g) 8.0 wt% TiO_2 .

Fig. 7 3D profiles of the clean disks under lubrication conditions of (a) dry, (b) water, (c) 0.4 wt% TiO_2 , (d) 2.0 wt% TiO_2 , (e) 4.0 wt% TiO_2 and (f) 8.0 wt% TiO_2 .

Fig. 8 COF values measured during ball-on-pre-oxidised-disk tests under different lubrication conditions: (a) in situ COF curves against time, and (b) variation of averaged COF values.

Fig. 9 Surface morphologies of the worn balls after ball-on-pre-oxidised-disk tests under lubrication conditions of (a) dry, (b) water, (c) 0.4 wt% TiO_2 , (d) 1.0 wt% TiO_2 , (e) 2.0 wt% TiO_2 , (f) 4.0 wt% TiO_2 and (g) 8.0 wt% TiO_2 .

Fig. 10 Wear scar diameters of applied balls after ball-on-pre-oxidised-disk tests under different lubrication conditions.

Fig. 11 Wear track morphologies of the pre-oxidised disks under lubrication conditions of (a) dry, (b) water, (c) 0.4 wt% TiO₂, (d) 1.0 wt% TiO₂, (e) 2.0 wt% TiO₂, (f) 4.0 wt% TiO₂ and (g) 8.0 wt% TiO₂.

Fig. 12 3D profiles of the pre-oxidised disks under different lubrication conditions of (a) dry, (b) water, (c) 0.4 wt% TiO_2 , (d) 2.0 wt% TiO_2 , (e) 4.0 wt% TiO_2 and (f) 8.0 wt% TiO_2 .

Fig. 13 SEM images of the edges of worn balls after ball-on-clean-disk tests under lubrication conditions of (a) dry, (b) 0.4 wt% TiO_2 , (c) 4.0 wt% TiO_2 and (d) 8.0 wt% TiO_2 , and EDS spectra of (e) dry and (f) 8.0 wt% TiO_2 .

Fig. 14 SEM image and EDS analysis of the worn surface of clean disk after dry friction: (a) worn track morphology, and (b, c, d) EDS spectra of Points A, B and C, respectively.

Fig. 15 SEM images and EDS mappings of the worn surfaces of clean disks lubricated by (a) 0.4 wt% TiO_2 , (b) 2.0 wt% TiO_2 , (c) 4.0 wt% TiO_2 and (d) 8.0 wt% TiO_2 .

Fig. 16 SEM images of the worn surfaces of balls under lubrication conditions of (a) dry, (b) 0.4 wt% TiO₂, (c) 4.0 wt% TiO₂ and (d) 8.0 wt% TiO₂ after ball-on-pre-oxidised-disk tests.

Fig. 17 SEM image and EDS analysis of the worn surface of pre-oxidised disk after dry friction: (a) worn track morphology, and (b, c, d) EDS spectra of Points A, B and C, respectively.

Fig. 18 SEM images and EDS mappings of the worn surfaces of pre-oxidised disks lubricated by (a, b) 0.4 wt% TiO₂, (c, d) 4.0 wt% TiO₂ and (e, f) 8.0 wt% TiO₂.

Fig. 19 Schematic illustration of the lubrication mechanisms using (a-d) ball-on-clean-disk and (e-h) ball-on-pre-oxidised-disk tests under lubrication conditions of (a, e) dry condition, (b, f) 0.4 wt% TiO_2 , (c, g) 4.0 wt% TiO_2 and (d, h) 8.0 wt% TiO_2 .