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Dry Sliding Wear Behavior of Experimental Low-Cost Titanium Alloys

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ABSTRACT

The high cost and potential toxicity associated with the common commercial Ti-6Al-4V alloy are major concerns against its continued use in the biomedical industry. Low-cost, less toxic titanium alloys have been developed as a possible alternative to Ti-6Al-4V. Because of the various wear processes that take place in the human body, it is imperative to have a good understanding of the wear properties and wear resistance of these alloys. This study, therefore, investigated the resistance to wear of the low-cost Ti-3Fe, Ti-4.5Al-1V-3Fe, and Ti-4.5Al-1V-3Fe alloys under dry sliding conditions in contrast to the common commercial alloy, Ti-6Al-4V. The findings revealed that among the tested alloys, Ti-3Fe exhibited the lowest resistance to wear as it displayed the highest coefficient of friction (0.55) and wear rate (5.55E-06 mm^3/Nm). The Ti-4.5Al-1V-3Fe alloy demonstrated superior wear resistance compared to the rest of the alloys, including Ti-6Al-4V, as it had the lowest wear rate (4.27E-06 mm^3/Nm) and wear volume (0.0026 mm^3). Overall, the experimental alloys displayed very similar wear resistance to Ti-6Al-4V, making them promising commercial alloys that can replace Ti-6Al-4V in bioimplant applications.

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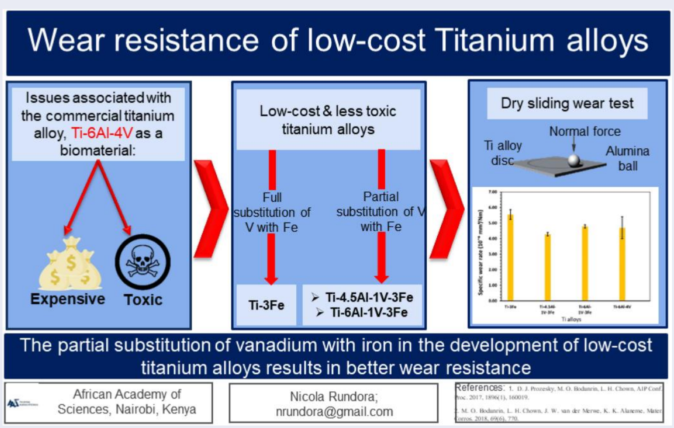
GRAPHICAL ABSTRACT



Abbreviations: COF: Coefficient of Friction; EDS: Energy Dispersive X-ray Spectroscopy; FEG-SEM: Field Emission Gun Scanning Electron Microscopy

Introduction

The attractive properties of titanium and its alloys have led to their extensive utilization across various industries. (*1*,*2*) The aerospace industry benefits from their high specific strength, using them in making aircraft components such as airframes and engine parts. (*1*,*3*–*5*) One of the main advantages of lighter aircrafts is their consumption of less fuel. (*5*,*6*) The marine sector finds use for titanium alloys in ship equipment, as well as offshore structures, as they have exceptional resistance to corrosion in saltwater environment. (*7*,*8*) The sports industry has also exploited the high specific strength of titanium alloys for years. This industry incorporates them into the manufacturing of bicycles, golf clubs, and tennis rackets to

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enhance performance while minimizing weight. (9) The automotive industry, one of the biggest industries using titanium alloys today, incorporates them in various components, such as valves and exhaust systems, because of their excellent specific strength, which improves fuel efficiency and reduces carbon dioxide emissions. (5,6) Furthermore, the oil and gas industry, the desalination sector, and the jewelry industry also find significant benefits in utilizing titanium and its alloys. (10) Titanium alloys have gained significant importance in the biomedical field as they are commonly employed in joint replacements, dental implants, and surgical instruments due to their excellent biocompatibility and ability to integrate with the human bone. (5,11,12)

Wear is an inevitable issue in any joint replacement implant, no matter the type of material used due to the joint movements and subsequent rubbing of materials within the joint that occurs. (13) Because wear has been identified as the leading cause of implant failure, one of the main requirements for biomaterials is to have high resistance to wear. (2) Wear leads to bioimplants' failure due to implant loosening. (2,14) Additionally, the resulting wear particles can cause inflammation that destroys the bone supporting the implant, ultimately resulting in revision surgery. (15) Despite the preference given to titanium alloys in the biomedical industry, their poor wear resistance poses significant challenges. (5,16) Their poor wear resistance ultimately disqualifies them from being utilized as articulating components/bearing surfaces materials in joint replacement biomedical implants. (17,18) Instead, titanium alloys find their niche in orthopedics as a material choice for load-bearing components within joint implants. For example, in hip replacements, titanium is often used for the production of the femoral stem and the acetabular cup. These load-bearing components provide stability and support, transferring the mechanical load from the implant to the surrounding bone. (18) Titanium alloys are exceptional for this application as their unique combination of flexibility, strength, and light weight is particularly advantageous in these applications. This enables the implant to withstand physiological loads without compromising the structural integrity of the implant–bone interface. (18) Currently, the common materials for bearing surfaces, particularly the acetabular liners, in joint replacement implants is the Ultra-High Molecular Weight Polyethylene (UHMWPE). (19) Ceramics or metals, which is usually the CoCr alloy, are typically used for the femoral head components. (19)

Although these materials have a wear resistance more acceptable for articulating components in comparison to titanium alloys, wear and subsequently osteolysis are still reported as problems associated with polyethylene bearings which are associated with ceramic or metal heads (metal-on-polyethylene or ceramic-on-polyethylene). (20) The wear particles generated from the polyethylene in particular lead to periprosthetic inflammation and the activation of phagocytosis. (19,20) This may eventually lead to periprosthetic osteolysis that affects the longevity of the implant as it may result in late revision surgery. (20) Cross-linked Ultra-High Molecular Weight Polyethylene (XLPE) was then introduced to improve the wear resistance of the conventional polyethylene. (19) The development of this generation of PE resulted in a reduction in the wear, however, the mechanical properties of the material have been found to be compromised as issues of fracture and dislocation have been reported in some clinical studies. (21) Further research is being conducted and PE still remains the superior material for joint implant bearing surfaces. However, titanium alloys possess far more attractive properties for bioimplant use in general. These include excellent resistance to corrosion, a good strength-to-weight ratio, and they are generally biocompatible. The development of new and better titanium alloys for biomedical use opens an avenue for the possible use of these new titanium alloys as biomedical implants across the whole human body, which includes joint replacement implants, without limiting them only to load-bearing applications. The newly developed experimental titanium alloys can potentially be utilized for articulating components if they pass the necessary tests. One of these tests being wear tests. This is the basis of this study.

Titanium's poor wear resistance can be attributed to several factors. First, the low hardness of titanium and its alloys, particularly the common commercial titanium alloy, Ti-6Al-4V, compared to some cobalt-based alloys (CoCrMo alloys). (5,22) Hardness plays a crucial role in wear resistance as it determines the material's ability to resist plastic deformation and surface damage. Therefore, the low hardness of titanium alloys contributes to their poor wear resistance as it makes them more susceptible to wear when subjected to abrasive and/or erosive forces. (5,23) Second, depending on the properties of the counterface material and other operating conditions, titanium and its alloys can experience adhesive wear due to their capacity to develop an oxide layer on their surface, which can promote adhesion between the titanium alloy and the mating surface, resulting in increased wear. (5,24) A few researchers have reported that the main reasons for titanium alloys' poor resistance to wear is their low resistance to plastic shearing and work hardening. (25–27) The poor resistance to plastic shearing reduces thermal conductivity, bringing about poor tribological properties. (5) Additionally, studies have indicated that the inadequate wear resistance of titanium alloys can be attributed to the minimal protection provided by the surface oxides that form due to the high flash temperatures generated by friction during dry sliding. (25,26,28,29)

Several researchers have examined the wear behavior and characteristics of titanium alloys, particularly Ti-6Al-4V. Most of these investigations focused on the wear mechanisms of these alloys under different loads and sliding speeds to establish the wear behavior of Ti-6Al-4V in diverse operational conditions. Molinari et al. (25) investigated the wear mechanisms of Ti-6Al-4V sliding against itself and found that the primary wear mechanisms were adhesion, abrasion, and tribochemical reactions (oxidative wear). Wear rates and wear mechanisms were sensitive to the applied load and sliding velocity. For example, oxidative wear dominated at low-speed sliding. Oxides are protective, and the development of oxides within the tribo-layer generally improves the wear resistance of the alloy. (11) Molinari et al. (25) observed that the tribo-oxides formed on the surface of Ti-6Al-4V were susceptible to spalling and microfragmentation, thus removing them easily and exposing the bare metal to further damage. Moreover, increasing the load and sliding velocity decreased the wear resistance of Ti-6Al-4V. Oxidative wear was also observed in the study by Straffelini and Molinari. (*28*) According to reports, the tribo-layer's effectiveness in providing protection is compromised when the oxides lack adequate support from the underlying material that has undergone strain hardening. In addition, they do not sufficiently adhere to the substrate and can be brittle, thus leading to continuous fragmentation and spalling. (*28*) In contrast to the studies mentioned thus far, Kumar et al. (*16*) found that a protective oxide layer formed under heavier loads and increased sliding velocities, improving the common commercial alloy's wear resistance. This difference in results is due to the differences in the counter material used (alumina), as well as in the testing parameters employed. (*5*) Higher sliding velocities have been reported to raise the sliding temperatures, resulting in the formation of oxides. (*11*)

A direct relationship between titanium alloy's hardness and wear resistance has been indicated in previous works. Alam and Haseeb (*29*) demonstrated the influence of hardness on titanium alloys' wear resistance. They discovered that Ti-24Al-11Nb exhibited significantly higher wear resistance (approximately 48 times higher) compared to Ti-6Al-4V, which is attributed to its superior hardness. In addition to the high hardness, a stable and protective oxide layer contributed to the good wear resistance of Ti-24Al-11Nb. Gain et al. (*2*) confirmed the poor wear resistance of Ti-6Al-4V when they found severe loose fragments and delamination on the surface following the dry sliding wear tests, the severity of which escalated with higher applied loads.

In most cases, the wear rates of titanium alloys, particularly Ti-6Al-4V, exceed the upper limit typically associated with mild wear of materials (10^{-3} mm^3/Nm). (*28*,*30*) This is quite a challenge as titanium alloys have numerous advantageous and attractive properties that are beneficial for many industries, but the poor wear resistance makes it challenging to exploit them fully. Researchers have explored various strategies to address and overcome the poor wear resistance of titanium alloys. (*11*,*31–33*) These mainly include surface modifications, such as coatings, ion implantation, and surface treatments aiming to enhance the hardness and lubricity of the materials. (*11*,*34*) Additionally, alloying elements and heat treatments can be employed to modify the microstructure and improve wear resistance. (*35*) These approaches aim to improve the tribological performance of titanium alloys by reducing friction, minimizing wear rates, and increasing the lifespan of bioimplants. The current research activities have focused on developing advanced titanium alloys and exploring novel surface engineering techniques to address the wear limitations and expand the range of applications for these materials.

Bodunrin et al. (*8*) developed a group of low-cost titanium alloys as possible alternatives for the expensive and potentially toxic common titanium alloy, Ti-6Al-4V. To this point, these low-cost experimental titanium alloys have proven to compete with Ti-6Al-4V alloy as they exhibit higher hardness than it. (*36*) In addition, the corrosion resistance of these alloys in various environments, including acidic and simulated marine environments, as well as simulated body fluids, is comparable to that of the Ti-6Al-4V and is, in some cases, better. (*8*,*37*) Because these alloys have potential applicability in the bioimplant industry, it is imperative to understand their wear properties and compare them to the common titanium alloy, Ti-6Al-4V. These alloys are under investigation in this study.

Due to the wear and mechanical issues associated with polyethylene as mentioned above as well as the poor wear resistance of the commercially available titanium alloys, (*38*,*39*) it is important to get full insight into the properties of the newly developed alloys. This will give insight into whether the alloys can be utilized for a wide range of biomedical applications or not. This study examined the dry sliding wear properties of the new experimental alloys developed by Bodunrin et al. (*8*) by looking at their coefficient of friction (COF), wear volume, wear rates and analyzing their wear mechanisms by studying their respective wear scars.

Materials and methods

Materials

Table 1 presents the composition of the titanium alloys employed in this study. These alloys were previously produced using vacuum induction melting and underwent hot isostatic pressing. (*8*) In preparation for the dry sliding tests, small disks with a diameter of 14 mm and a thickness of 3 mm were cut from the alloy samples using a Gold San computer numerical controls wire-cutting electrical discharge machine. Alumina (Al_2O_3) ceramic balls with a 6 mm diameter and a hardness of around 780.4 HV were used as the articulating counter material. Alumina was used since it has a much higher hardness than the titanium alloys, so it was expected that the deformation process during sliding would primarily occur within the titanium alloys. Additionally, using a much harder material allows the performance of the experimental titanium alloys to be assessed under extreme conditions.

Microstructural characterization

After the wear tests, surface analysis of the samples was conducted using a Zeiss Sigma Field Emission Gun Scanning Electron Microscopy (FEG-SEM) equipped with back-scattered electron, secondary electron, and Oxford energy dispersive X-ray detectors. The FEG-SEM was operated at 15 kV in back-scattered electron and secondary electron imaging modes to observe the microstructural characteristics. Stereoscopic images of the wear scar were taken to

Table 1. Alloy compositions.

Titanium alloys
Ti-3Fe
Ti-4.5Al-1V-3Fe
Ti-6Al-1V-3Fe
Ti-6Al-4V

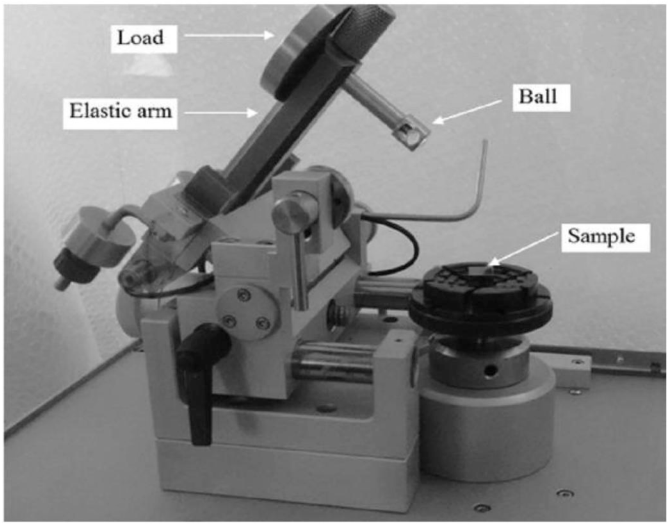

Figure 1. Image showing the ball-on-disk tribometer setup. (*47*)

measure the area of the alloys' wear tracks. The MarSurf PS 10 roughness measuring device was employed to assess the alloys' wear track profiles after the wear tests, as well as the maximum penetration depth of the wear tracks.

Sliding wear tests

Dry sliding wear tests were conducted using a CSM ball-on-disk tribometer operating under the following conditions: ambient temperature of 25 °C, normal load of 2 N, sliding velocity of 0.08 m/s, and a sliding distance of 300 m. The ball-on-disk configuration was employed mainly because it is one of the commonly and readily available wear testing configuration on a laboratory scale. The ball-on-disk configuration closely conforms to the ASTM G99 standard. A visual representation of the test setup can be seen in Fig. 1. During the duration of the sliding test, the normal force of 2 N was constantly exerted on the titanium surface with an alumina ball of a diameter of 6 mm. The normal load of 2 N which was employed falls under low loading conditions (from ~1.8 N to 5 N) which have been investigated by several researchers. (*2*,*40–42*) The loads exerted by the human body on the implant at any given moment vary greatly depending on the activities of daily living. Therefore, a wide range of loads can be used for dry sliding wear tests. (*43–45*) The sliding speed of 0.08 m/s lies in the low sliding speed range and was chosen mainly due to the testing constraints of the available tribometer. The duration of each test was one hour and two minutes. The testing parameters are given in Table 2. Prior to the tests, the titanium alloy disks underwent grinding using silicon-carbide paper with various grit sizes. Subsequently, the samples were polished using a colloidal silica suspension until a mirror-like surface finish was achieved. Finally, the samples were cleansed with distilled water and air-dried in preparation for the tests. The tests were performed at least twice to check for reproducibility of the results. Friction coefficients were recorded during the tests. The penetration depth of the alloys' wear tracks was found by analyzing their wear scar profiles, using a

Table 2. Sliding wear test testing parameters.

Testing parameters	Value
Sliding speed	0.08 m/s
Sliding distance	300 m
Nominal load	2.00 N
Acquisition radius	2 mm
Acquisition rate	4 Hz
Humidity	40%
Testing temperature	20 ± 5 °C

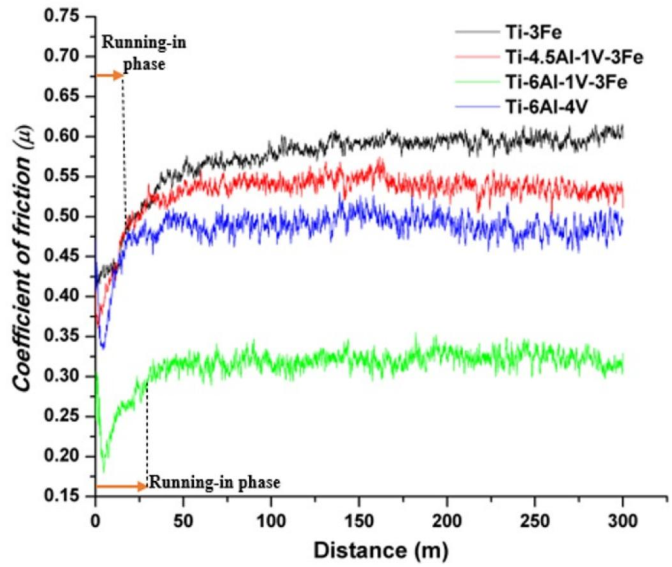

Figure 2. Coefficient of friction behavior of experimental alloys and Ti-6Al-4V against an alumina ball over a 300 m sliding distance.

surface roughness tester (profilometer) to measure the cross-sectional area of the wear scars by moving the stylus across the wear scar from the edge. The wear rates of the alloys were then calculated according to Archard's theory for sliding wear of homogenous materials, where the wear volume is assumed to be proportional to the normal load and the sliding distance. (*35*,*46*,*47*)

Results

Coefficient of friction of the tested alloys under dry sliding

The COF versus sliding distance curve is presented in Fig. 2. The COF varied with sliding distance for all the alloys. A running-in/break-in phase was observed for a distance of about 35 m from the beginning of the test for Ti-6Al-1V-3Fe and about 20 m for the rest of the alloys. In this region, the COF of all the alloys was between 0.18 and 0.43. After the running-in phase, a gradual increase in the alloys' COF was observed. The highest COF was attained by the experimental alloy Ti-3Fe from the initial point until the completion of the 300 m sliding distance. The highest COF reached by this alloy was approximately 0.62. Ti-6Al-1V-3Fe had the lowest COF from the initial point until the completion of the 300 m sliding distance. The highest COF reached by this alloy was approximately 0.35, which is much lower than that of Ti-3Fe. The COF of all the alloys reached a plateau (steady state) at about 50 m, where the COF began fluctuating within a close range. The fluctuation or

Table 3. Average coefficient of friction of experimental alloys and Ti-6Al-4V.

Titanium alloys	Coefficient of friction (μ)
Ti-3Fe	0.55 ± 0.035
Ti-4.5Al-1V-3Fe	0.51 ± 0.029
Ti-6Al-1V-3Fe	0.37 ± 0.078
Ti-6Al-4V	0.49 ± 0.000

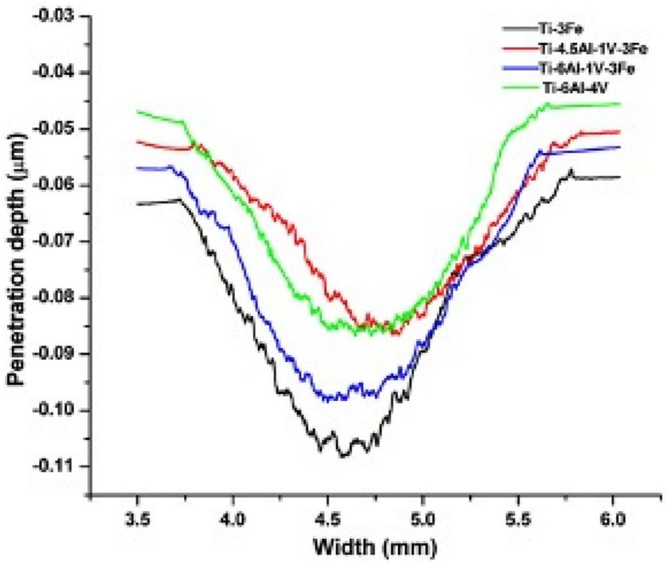

Figure 3. Penetration depth versus wear track width of experimental alloys and Ti-6Al-4V.

oscillations in the COF can be explained by the third body effect (*11*); the stick-slip behavior that occurs under applied load leading to the periodic accumulation and removal of wear debris between the alumina ball and the titanium alloy surface. (*46,48*) Table 3 displays the alloy's average COF. The COF of Ti-4.5Al-1V-3Fe and Ti-6Al-4V were quite close and not too far off that of Ti-3Fe. The average COF of Ti-4.5Al-1V-3Fe was 0.51, while that of Ti-6Al-4V was 0.49. This result correlates with a study conducted by Jozwik, (*42*) who performed a similar dry wear test on Ti-6Al-4V alloy with alumina as the counter material under a load of 5 N and found the COF of Ti-6Al-4V to be 0.52 at room temperature.

Worn wear volume and wear rates

Four areas of the wear track were analyzed and recorded using the profilometer after the total sliding distance of the test, i.e., at the end of the test. These four profile measurements were then averaged and plotted as a single profile (Penetration depth versus wear track width; Fig. 3). The alloys had similar wear tracks, suggesting their wear mechanism could be comparable. Ti-3Fe displayed a deeper wear scar than the rest of the alloys. This supports its high COF as a deeper wear track indicates a strong resistance to motion between the alloy and the alumina ball, which resulted in more abrasion between the two surfaces, thus deepening the wear scar on this alloy. This suggests that a greater level of wear took place. (*22*) Although it had the deepest wear scar, the maximum penetration depth values in Table 4 show that the penetration depths of the alloys were quite similar as the values lie in a very similar and close range (between −0.11 and −0.09). In addition to the deepest wear track, Ti-3Fe displayed the widest wear track among all alloys, while Ti-4.5Al-1V-3Fe had the narrowest and shallowest wear track compared to the rest of the alloys. The penetration depth and the track width of Ti-6Al-4V were very close to that of Ti-4.5Al-1V-3Fe.

The worn wear volume graph shown in Fig. 4, supported by the data in Table 4, shows that Ti-3Fe experienced the most material loss of 0.0033 mm^3 compared to the rest of the alloys, while Ti-4.5Al-1V-3Fe had the least amount of material loss of 0.0026 mm^3 for the entire duration of the wear tests. Once again, the alloys' material losses were within a very similar range, further supporting the observation that these alloys have very similar wear resistance.

It is quite important to note that the third body concept plays a role in this tribosystem as the two solids sliding against each other resulted in the generation of a third body. This third body was composed of particles detached from the alloy and alumina surfaces and it possesses several functions. First, the third body somewhat releases the pressure from the alloy surface as it supports the load, it accommodates the sliding velocity, and lastly, it separates the sliding surfaces thus avoiding direct interactions. (*49*) All of this leads to a reduction in all of the stresses and displacements imposed by the system on the contact. The third body has the ability to act as a solid lubricant that ultimately protects the materials rubbing against each other from further degradation. (*49*) Ideally, the ejection of the third body from the contact has to be prevented as much as possible to maintain the lubrication role of the third body thus avoiding the detachment of further particles. (*49*) Wear is generally one to two orders of magnitude smaller in three body abrasion than in two body abrasion as a result of this. (*50*) Therefore, based on this, the worn wear volume should rather be considered as the loss of the third body particles from the contact as opposed to the whole area of the wear scar. In this study however, because the alumina ball experienced negligible wear, the third body phenomena was not necessarily considered in this work. It would however be of interest to explore it in further studies.

Finally, the wear rates of Ti-4.5Al-1V-3Fe, Ti-6Al-1V-3Fe, and Ti-6Al-4V were in a very similar range, with the experimental alloy Ti-3Fe having the highest wear rate (Table 4). This high wear rate is supported by a combination of different parameters: deeper maximum penetration depth, greater worn volume, and higher COF. Despite Ti-4.5Al-1V-3Fe having a COF value quite close to that of Ti-3Fe, it had the lowest wear rate, which is supported by its shallow and narrow wear track, as well as its minimal worn volume. This shows that this alloy has the best resistance to wear compared to the popular commercial alloy and the other alloys under investigation. (*22*) A clearer representation of the wear rates is presented in Fig. 5.

Surface morphology: wear tracks and sliding wear mechanisms

The scanning electron images of the wear tracks of Ti-6Al-4V and the experimental alloys under investigation are presented in Fig. 6. In sliding contact, wear can occur due to

Table 4. Sliding wear parameters of experimental alloys and Ti-6Al-4V.

Ti alloy	Worn surface area (mm^2)	Penetration depth (μm)	Worn volume (mm^3)	Wear rate (10^{-6} mm^3/Nm)	Wear track width (mm)
Ti-3Fe	29.2850	−0.1137 ± 0.0075	0.0033 ± 0.0002	5.5471 ± 0.3194	1.9825 ± 0.1025
Ti-4.5Al-1V-3Fe	29.6750	−0.0864 ± 0.0003	0.0026 ± 0.0001	4.2721 ± 0.1108	1.7975 ± 0.3429
Ti-6Al-1V-3Fe	29.4100	−0.0977 ± 0.0013	0.0029 ± 0.0001	4.7876 ± 0.1098	1.8600 ± 0.1980
Ti-6Al-4V	29.6250	−0.0950 ± 0.0117	0.0028 ± 0.0004	4.6899 ± 0.7019	1.9040 ± 0.0212

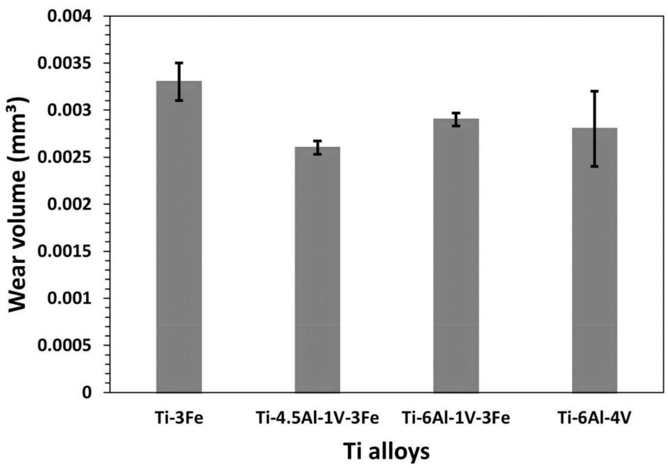

Figure 4. Worn wear volume of titanium alloys after sliding wear tests.

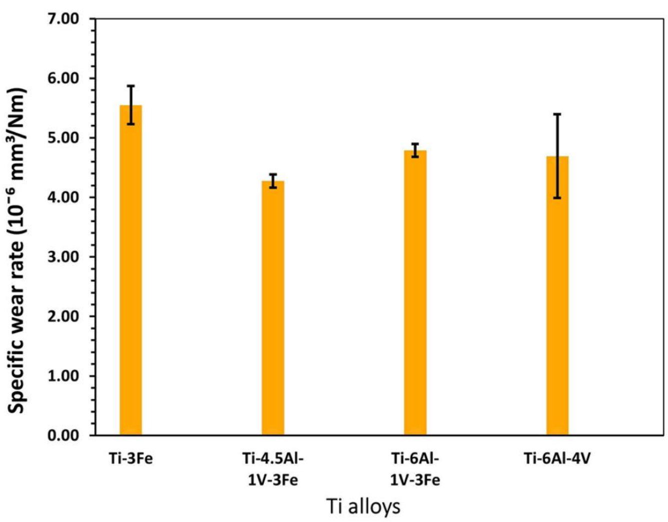

Figure 5. Specific wear rate (10^{-6} mm^3/Nm) of titanium alloys after sliding wear tests.

any of the four main wear mechanisms which include abrasion, adhesion, surface fatigue, and tribochemical reactions, together with their respective sub mechanisms. (*51*) To understand the tribological behavior of a particular material, it is important to understand its exact acting wear mechanisms and their sub-mechanisms. (*50*) Insight into the acting wear mechanisms can be given through the determination of the sub-mechanisms. In this study, all the alloys' wear tracks were made of parallel wear scars caused by the plowing and crushing action of the hard alumina ball sliding against the alloys. These parallel wear scars are indicative of micro plowing which is a sub-mechanism of abrasion. Therefore abrasion is one of the main acting wear mechanisms for these alloys. (*22*) Minimal differences are observed in the wear tracks of these alloys, which indicates that their wear mechanisms were the same, with slight differences in the intensity of the wear. The depth of the wear grooves on the wear tracks was quite shallow, suggesting that the abrasive wear taking place was quite mild. (*52*) The depth of the wear grooves on Ti-6Al-4V was slightly deeper than those on the rest of the alloys, indicating higher abrasive wear in Ti-6Al-4V.

Plastic deformation is not considered a wear mechanism but it plays a very important role in many wear processes. (*51*) Plastic deformation generally occurs as a result of the surface fatigue wear mechanism. A few researchers have reported having observed plastic deformation on the titanium alloys after dry sliding wear tests. (*28*,*42*) Plastic deformation is generally characterized by smooth compacted layers lying on top of many abrasive grooves aligned in the sliding direction. (*28*,*42*) Plastic deformation, usually accompanied by delamination, indicates severe wear and is thus undesirable for biomaterials. (*53*) After analyses of the experimental alloys under investigation in this study, it was found that the alloys did not display any plastic deformation. However, sub-surface plastic deformation could have occurred, and this would have to be confirmed by performing an analysis of longitudinal cross-sections of the alloys in order to obtain information on the sub-surface damage. No distinct gray or dark (black) patches were found on these wear tracks. This suggests there was possibly no active tribo-oxidation (tribochemical reactions wear mechanism) in this tribosystem. As a result, the tribochemical reactions wear mechanism did not form part of the alloys' wear mechanisms, as it is possible not to have the formation of an oxide layer. (*30*) The EDS (energy dispersive X-ray spectroscopy) images in Fig. 7 confirm this, as no oxygen peaks were observed in the EDS spectra of any of the alloys. Analysis of the wear debris using X-ray diffraction was not performed as the debris was too small for this analysis. Only the EDS spectra of the Ti-3Fe and Ti-4.5Al-1V-3Fe alloys are shown here as all the alloys displayed no oxygen peaks and just metallic peaks.

The wear scars on the alumina balls were analyzed using the stereoscope. These are presented in Fig. 8. The wear scar on all the balls is very close to a round shape. A more irregular and elliptical shape would be observed if the wear was severe. (*42*) This was not the case here, as the scars are round-like, which is evidence of mild wear. Evidence of material transfer from the alloys to the alumina ball (counterbody) can be seen through the black/metallic marks on the wear scar of the alumina balls seen in Fig. 8. This is a sub-mechanism of adhesive wear. Therefore, adhesion was one of the acting wear mechanisms of this tribosystem. The wear rate of the counterbody was assumed to be negligible due to the very small wear scar observed on their surface. According to the ASTM G133-05 standard, if the ball tip remains significantly round with only light abrasion, a few scratches, and/or an adherent deposit of wear debris, after the wear tests, this is an indication that the flat alloy sample experienced the greatest amount of wear, therefore the ball (counterbody) exhibited no measurable

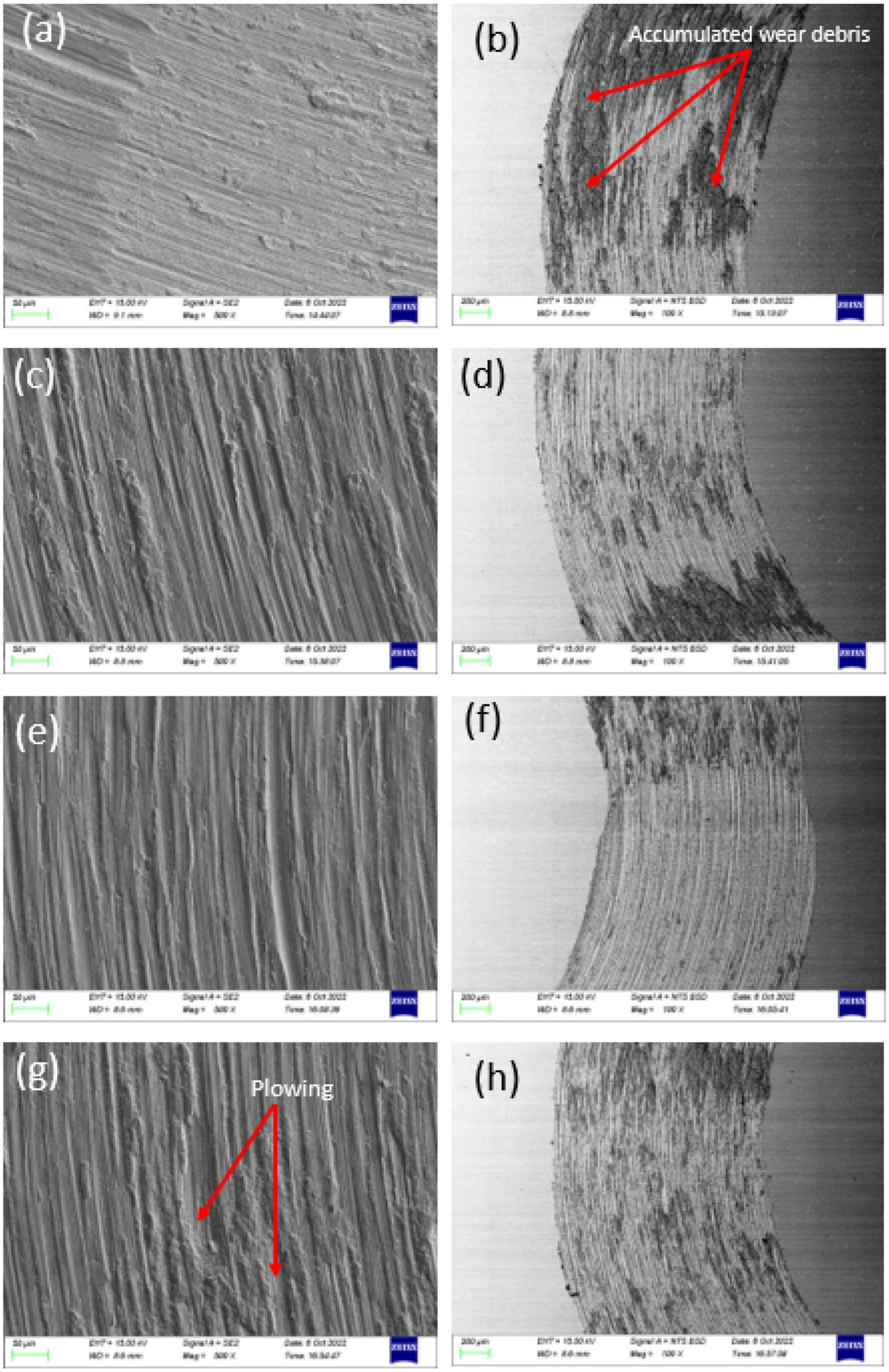

Figure 6. Secondary electron (a, c, e, and g) and back-scattered electron (b, d, f, and h) scanning electron micrographs of the experimental alloys and Ti-6Al-4V alloys wear tracks after dry sliding: (a) and (b) Ti-3Fe; (c) and (d) Ti-4.5Al-1V-3Fe; (e) and (f) Ti-6Al-1V-3Fe; (g) and (h) Ti-6Al-4V.

wear. (*54*) Therefore, no measure of wear shall be reported. The evolution of the 3D surface topographies can be seen in Fig. 9. Upon analysis of the 3D images, we observed that the valley depth of Ti-3Fe was bigger than the rest of the alloys. The valley of Ti-4.5Al-1V-3Fe was slightly shallower than Ti-3Fe and is closely comparable to that of Ti-6Al-4V.

Discussion

A material's wear characteristics are determined by a vast number of factors, including the material composition, hardness, friction coefficient, and elastic modulus. (*5*,*11*,*55*,*56*) The hardness of a material is crucial as a high hardness

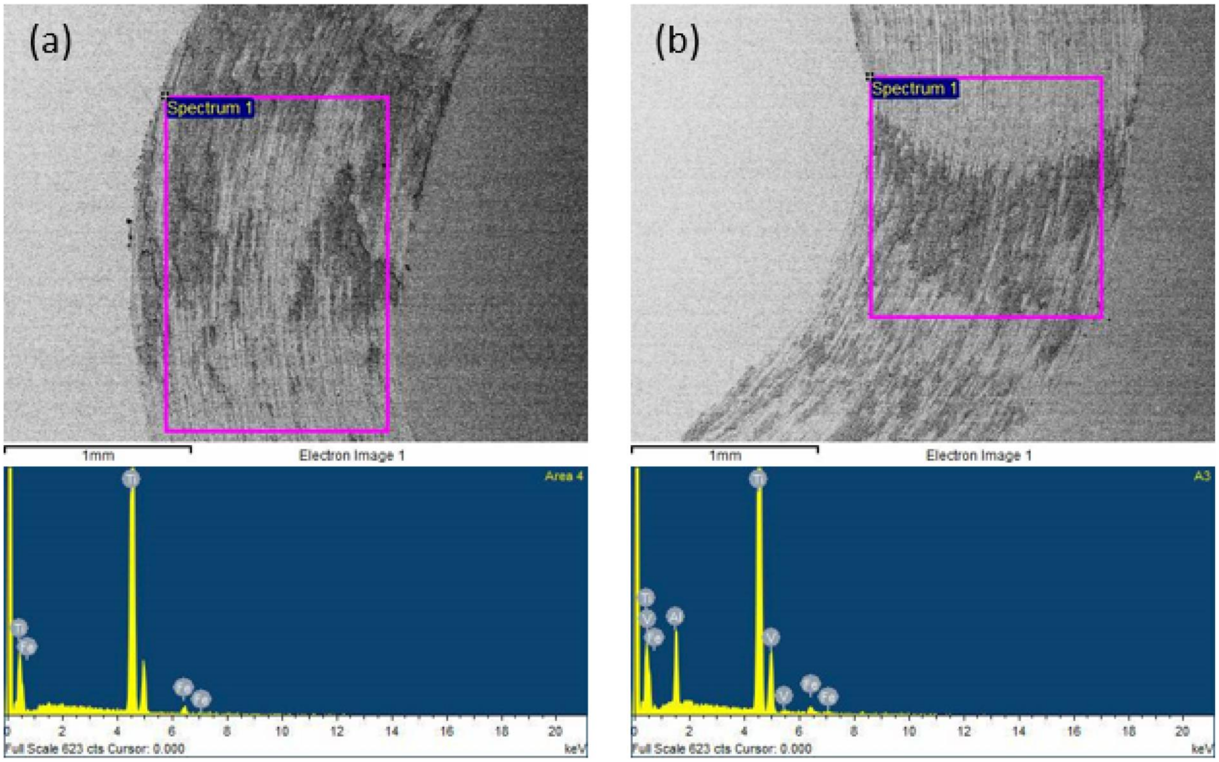

Figure 7. Energy dispersive X-ray images of the area analysis of experimental alloys and Ti-6Al-4V wear tracks: (a) Ti-3Fe and (b) Ti-4.5Al-1V-3Fe.

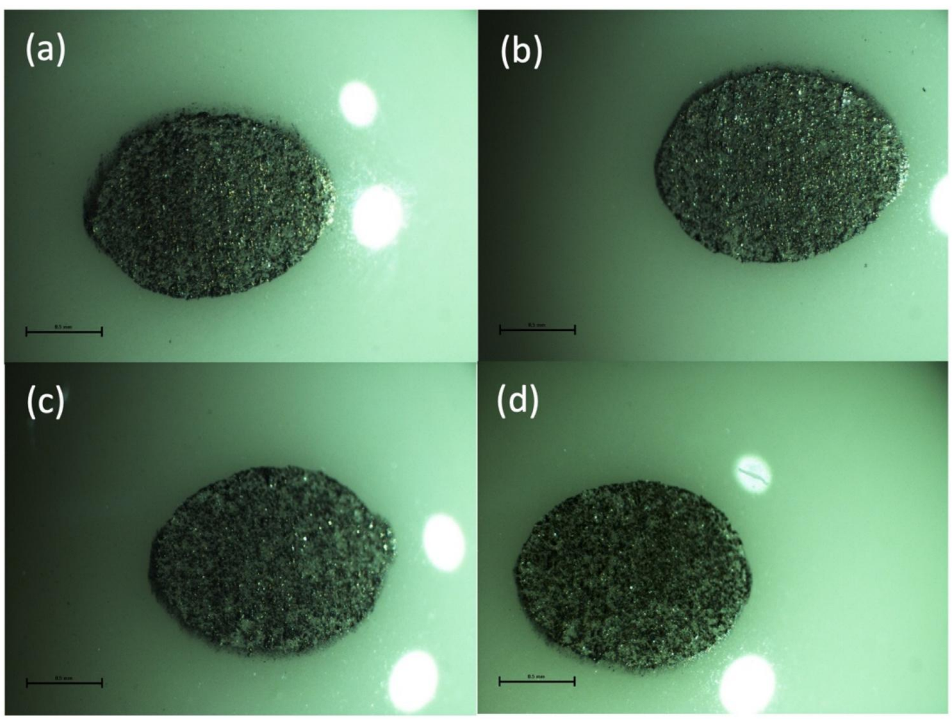

Figure 8. Stereoscope images of the alumina balls after the dry sliding wear tests with experimental alloys and Ti-6Al-4V (a) Ti-3Fe; (b) Ti-4.5Al-1V-3Fe; (c) Ti-6Al-1V-3Fe; (d) Ti-6Al-4V.

enables the material to resist abrasion and deformation, particularly plastic deformation, quite significantly. (*5*,*22*) High resistance to plastic deformation will ultimately reduce the risk of delamination, which is a wear type commonly seen in metallic alloys with very poor wear resistance and quite detrimental to the material's life. (*2*) The importance of hardness can also be seen through the tribo-layers that form on the alloys' surface during the dry sliding test. A compacted, continuous, and hard tribo-layer has high load-bearing capabilities, inhibiting the applied force from being transferred to the matrix underneath the tribo-layer, potentially damaging the alloy. (*57*) The material's frictional

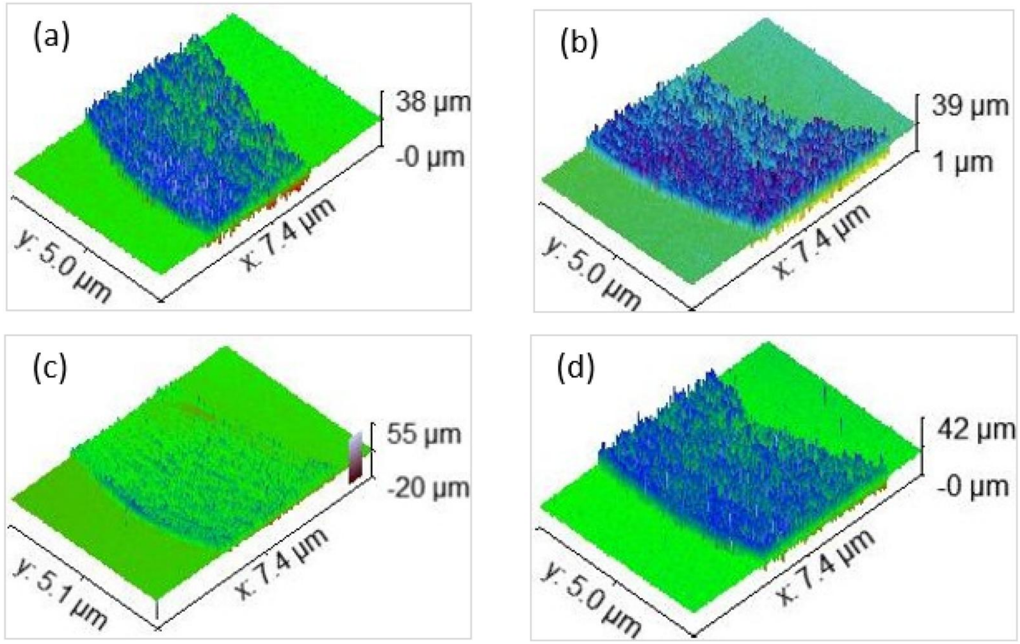

Figure 9. 3D Surface topography images of the experimental alloys and Ti-6Al-4V wear tracks: (a) Ti-3Fe; (b) Ti-4.5Al-1V-3Fe; (c) Ti-6Al-1V-3Fe; (d) Ti-6Al-4V.

property is also of utmost importance as it plays a role in the alloy's wear behavior. A high COF can be beneficial or detrimental to a system depending on the material's field of application. For example, for braking systems or tires where increased friction is desired to enhance grip and control, a high COF is advantageous. (*58*) On the other hand, it can lead to wear in mechanical systems as it requires more energy to overcome resistance and can generate heat or cause unwanted abrasion between surfaces. (*5*,*59*) The latter applies to bioimplants and bioimplant materials. A very high COF is not desirable, as the friction between a biomedical implant and the bones and bone tissues in the human body should be minimized for various reasons. Excessive friction can cause inflammation, severe discomfort, and restricted mobility for the individual with the implant (*15*,*39*,*59*,*60*). In addition, friction generates wear and tear on both the implant and the bone tissue, gradually leading to the implant material's degradation and potential damage to the surrounding bone. (*39*) Minimizing friction would help to reduce the risk of implant failure and ensure its long-term durability, thus reducing the need for expensive and painful revision surgery. (*39*,*60*) It is important to note, however, that a considerable amount of friction, enough to bring about safe resistance against motion between the bone and implant, has been reported to be desirable. (*61*) This promotes bone ingrowth, reducing the risks of fibrous tissue formation at the implant interface, which results in implant loosening. (*61*) It is, therefore, important to have a COF that is high enough to reduce excessive relative motions but low enough to minimize material volume loss and wear rate.

The analysis of friction alone cannot determine a material's wear resistance. Often a combination of multiple parameters, including friction behavior, worn volume, penetration depth, and wear rate, should be considered to determine and optimize the material's wear resistance. According to Kato, (*56*) it should not be assumed that there is always a straightforward, conventional correlation between friction and wear, as the COF and wear are not inherent material properties but rather two types of responses within a tribosystem. Their relationship is reasonably established when the tribosystems' essential functions are adequately considered. (*56*)

Our study evaluated the wear resistance of the low-cost titanium alloys with partial or full substitution of V with Fe under dry conditions with alumina as the counterpart material. The aim was to understand how these alloys would behave when exposed to environments characterized by high levels of friction and wear, such as the human body. When biomedical implants such as joint replacement implants are inserted into the human body, they experience a combination of corrosion and wear because of the corrosive body fluids in the environment, and the various daily movement activities of the individual ultimately result in scratching against the implant. This not only applies to the biomedical industry, applications in the aerospace and automotive industries cause wear to the materials. It was, therefore, important to study the wear characteristics of these alloys as it will give valuable insights into their performance when subjected to tribocorrosion conditions. Tribocorrosion studies in simulated body fluids have been conducted on these alloys and the results are currently being analyzed. The tested alloys' friction behavior during the dry sliding wear test was quite different. Ti-3Fe had the highest average COF of 0.55, while Ti-6Al-1V-3Fe had the lowest average COF (0.37). The high COF indicates a high amount of friction between the alloy's surfaces and the counterpart alumina ball. This friction is attributed to a strong resistance of motion between the two surfaces, which could result from the differences in the material compositions. As mentioned previously, hardness influences the wear properties of a material. In this case, alumina is a ceramic with a greater hardness than the titanium alloys, allowing this material to dig into the titanium alloys with relative ease, thus generating great resistance to motion. As mentioned previously, this high friction is detrimental for bioimplant applications because of the discomfort and mobility restrictions experienced by the individual due to possible aseptic loosening caused by released wear debris. (39,57) The low COF of the Ti-6Al-1V-3Fe alloy enables smooth motion between this alloy and its counterpart. The lower COF and smoother motion, in this case, could be attributed to the hardness of the Ti-6Al-1V-3Fe alloy. This alloy was reported to have a hardness of approximately 405 VHN, (36) higher than that of the Ti-6Al-4V and the rest of the experimental alloys. From the frictional behavior of these alloys, it is quite clear that differences in material composition and varying intrinsic properties influence their wear resistance differently.

Ti-3Fe also displayed the deepest maximum penetration depth, as well as the widest wear track width, compared to the rest of the alloys. This further indicates that there was a greater amount of frictional force between this alloy and the alumina ball. The largest worn volume displayed by this alloy compared to the rest of the alloys under investigation further justifies the highest wear rate of this alloy (5.55E-06 mm^3/Nm) as it indicates that it was unable to resist wear adequately and subsequently resist material loss as much as the rest of the alloys. Ti-4.5Al-1V-3Fe had a high COF as well. It was the closest to that of Ti-3Fe. This suggests that the material exhibits a high frictional force. The ease of motion between its surface and the alumina ball was minimal compared to that of Ti-6Al-4V and Ti-6Al-1V-3Fe. However, this alloy displayed the shallowest and narrowest wear track with the smallest amount of worn volume. This suggests a great amount of friction between the two surfaces, but it can withstand and resist wear and material loss effectively. So, this alloy can essentially withstand mechanical forces and abrasion wear, minimizing its wear loss and wear rate (4.27E-06 mm^3/Nm). This alloy is quite resilient and can withstand friction despite the frictional forces involved compared to the other titanium alloys investigated. The wear rates of all the alloys under the specifically applied load were well below 10^{-5} mm^3/Nm, which is the proposed wear rate limit for the mild wear of metallic materials. (30) Additionally, the wear rates of the experimental alloys are very close to that of Ti-6Al-4V (4.69E-06 mm^3/Nm), with Ti-4.5Al-1V-3Fe having a wear rate lower than Ti-6Al-4V. Some researchers studied the wear behavior of Ti-6Al-4V against various material counter bodies that include 304 stainless steel and GCr 15 steel, and they also found that the wear rate lies in the range of 10^{-6} mm^3/Nm (62) Gain et al. (2) however, found the wear rate of Ti-6Al-4V alloy against 304 stainless steel to lie in the range of 10^{-5} mm^3/Nm. This indicates severe wear behavior and describes catastrophic behavior. (30) Jozwik (42) also found the wear rate of Ti-6Al-4V to be in the region of severe wear (4.51E-04 mm^3/Nm). This provides insight into how the testing conditions play a role in the wear rate of a material since the load and sliding speed employed by Jozwik (42) was higher (5 N and 0.3 m/s) than the ones used in this study (2 N and 0.08 m/s). Straffelini and Molinari (28) also found the wear rates of the alloys tested under 50 N, 100 N, and 200 N to lie within the severe wear region as they were higher than 10^{-3} mm^3/Nm. Load was also a factor in the wear of these alloys as an increase in the load resulted in an increase in the wear rates of the alloys. Raj and Kailas (63) also reported wear rates in the range of 10^{-5} mm^3/Nm. Although the wear rates of the titanium alloys under investigation in this study lie in the mild wear region, hip joints perform well under wear rates in the ultra-mild wear region. (50) As a result, wear rates in the mild wear region are not sufficient enough for biomedical use and are actually considered high, however, the experimental alloys are promising as their wear rates are lower than that of the popular titanium alloy, Ti-6Al-4V. To improve the wear rates of these alloys to bring them down to the ultra-mild wear region, optimization approaches such as surface modification through coatings and or heat treatment in accordance with Obadele et al. (64) will be considered for future works.

The process of sliding wear in metals and alloys can be characterized by the progression of the following phenomena: surface and sub-surface plastic deformation, generation of debris and material transfer, reaction with the surrounding environment, and mechanical mixing. These cumulative effects ultimately lead to the formation of a mechanically mixed layer, also referred to as the tribo-layer, on the alloy's surface. (30) In this case, plastic deformation could not be detected when we analyzed the wear scars of the alloys under investigation. According to several researchers, one of the factors influencing the wear resistance of Ti-6Al-4V is plastic deformation and delamination. (2,25,28,29,58,59,65) They also found that the applied load plays an important role in the wear and the subsequent wear mechanism. Mild wear will be observed at low loads, and severe wear, which is associated with plastic deformation, will be observed at higher loads. Our study and other similar investigations (2,40–42) conducted wear tests under low loading conditions (from ∼1.8 N to 5 N) while the investigations mentioned above operated at high loading conditions (15 N to 250 N). Noticeable plastic deformation and delamination were reported mostly for very high loading conditions. A wide range of loading can be used to investigate the wear resistance of biomaterials because the loads exerted by the human body on the implant at any given moment vary greatly depending on the different activities of daily living such as walking, walking upstairs or downstairs, sitting, lying, running, and exercising. (43–45) In addition, the loads applied on the implants vary significantly as different locations in the human bone apply different pressure levels on the implant, which all ultimately depend on the type of movement taking place (44,61,66) Although abrasive wear was the main wear mechanism observed for the alloys in this study, some adhesive wear also occurred, as upon analysis of the alumina balls in Fig. 8, some of the alloy material, the dark gray/black metallic patches, and agglomerated debris, was transferred onto the scar of the alumina balls. No gray or black patches, which are usually an indication of oxides, were observed on the titanium alloys' wear scars. No oxygen was detected from the EDS analysis as well.

Efforts to develop titanium alloys with reduced toxicity and cost have involved completely substituting vanadium, the expensive beta-stabilizing element in Ti-6Al-4V, with iron, a less expensive eutectoid beta-stabilizing element. These substitutions enhanced resistance to corrosion compared to Ti-6Al-4V. (*40*,*41*,*62*) However, the alloy's mechanical properties are often compromised due to the potential formation of brittle intermetallic phases. (*67*) In our investigation, Ti-3Fe exhibited the poorest wear resistance, which could be attributed to the weakened properties brought about by the complete substitution of vanadium with iron. (*67*,*68*) In contrast, alloys employing partial substitution of vanadium with iron, such as Ti-4.5Al-1V-3Fe and Ti-6Al-1V-3Fe, demonstrated superior wear resistance when compared to both Ti-6Al-4V and Ti-3Fe. Furthermore, reports indicate that these alloys (Ti-4.5Al-1Ve-3Fe and Ti-6Al-1V-3Fe) exhibit improved hardness and corrosion resistance. (*8*,*69*) Based on these findings, it is evident that incorporating both vanadium and iron as beta-stabilizing elements by retaining 1 wt.% of vanadium in Ti-6Al-4V and replacing the remaining portion with iron proves more advantageous than completely substituting with iron alone. This combined approach not only enhances corrosion resistance and hardness but also improves wear resistance, as observed in these alloys.

Conclusion

The findings of this study indicate that the low-cost experimental alloys are quite comparable to the popular commercial alloy as far as their dry wear properties are concerned. According to the COF, wear volume, and wear rate, Ti-3Fe displayed the least resistance to wear compared to the other alloys. Another experimental alloy, Ti-4.5Al-1V-3Fe, displayed the best resistance to wear, performing better than Ti-6Al-4V under the testing conditions. Although the wear rate of Ti-6Al-4V was higher than that of Ti-6Al-1V-3Fe, it was only by a very small margin, so these alloys' wear properties are comparable. Overall, the alloys' wear rates lie within the mild wear region. However, effort should be put in to get the wear rates of the titanium alloys in the ultra-mild wear region ($\leq 10^{-9}$ mm^3/Nm) as biomedical implants, particularly hip joints, work well in this region. This will allow the titanium alloys to potentially compete with other metal alloys as well as the polymers currently in use. To achieve such wear rates, the typical acting wear mechanisms should be tribochemical reactions and surface fatigue. Ti-6Al-4V, as well as the experimental alloys, displayed the same wear mechanism of abrasive wear and adhesive wear. The grooves within the wear scar were quite shallow, further reinforcing that the alloys displayed mild wear. This observation further confirms the superiority of the partial substitution of vanadium with iron over the complete substitution of vanadium with iron when developing low-cost and less toxic titanium alloys, as Ti-3Fe had poor wear resistance, whereas Ti-4.5Al-1V-3Fe and Ti-6Al-1V-3Fe displayed the best resistance to wear. These alloys could, therefore, potentially compete with Ti-6Al-4V for commercial applications. However, further alloy adjustments and potentially surface modifications should be explored to get these alloys to potentially be utilized for bioimplant applications where they would be subjected to rubbing.

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Data availability

The data that supports the findings of this study are available on request from the corresponding author, Nicola Ruvimbo Rundora.

Disclosure statement

No potential conflict of interest was reported by the author(s).

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