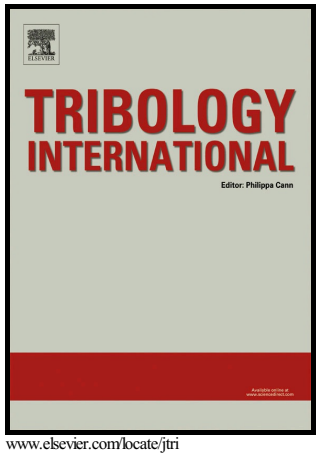
Sliding friction and wear behaviour of Titanium-Zirconium-Molybdenum (TZM) alloy against Al_2O_3 and Si_3N_4 balls under several environments and temperatures

Zhang, Zhenxue; Li, Xiaoying; Almandoz, Eluxka; Fuentes, Gonzalo Garcia; Dong, Hanshan

DOI:
10.1016/j.triboint.2016.10.049

Document Version
Peer reviewed version

Citation for published version (Harvard):
Zhang, Z, Li, X, Almandoz, E, Fuentes, GG & Dong, H 2017, 'Sliding friction and wear behaviour of Titanium-Zirconium-Molybdenum (TZM) alloy against Al_2O_3 and Si_3N_4 balls under several environments and temperatures', *Tribology International*, vol. 110, pp. 348-357. https://doi.org/10.1016/j.triboint.2016.10.049



www.elsevier.com/locate/jtri

Sliding Friction and Wear Behaviour of Titanium-Zirconium-Molybdenum (TZM) Alloy against Al_2O_3 and Si_3N_4 Balls under Several Environments and Temperatures

Zhenxue Zhang, Xiaoying Li, Eluxka Almandoz, Gonzalo García Fuentes, Hanshan Dong

PII: S0301-679X(16)30403-0
DOI: http://dx.doi.org/10.1016/j.triboint.2016.10.049
Reference: JTRI4448

To appear in: *Tribiology International*

Received date: 15 September 2016
Revised date: 21 October 2016
Accepted date: 26 October 2016

Cite this article as: Zhenxue Zhang, Xiaoying Li, Eluxka Almandoz, Gonzalo García Fuentes and Hanshan Dong, Sliding Friction and Wear Behaviour of Titanium-Zirconium-Molybdenum (TZM) Alloy against Al_2O_3 and Si_3N_4 Balls under Several Environments and Temperatures, *Tribiology International*, http://dx.doi.org/10.1016/j.triboint.2016.10.049

Sliding Friction and Wear Behaviour of Titanium-Zirconium-Molybdenum (TZM) Alloy against Al_2O_3 and Si_3N_4 Balls under Several Environments and Temperatures

Zhenxue Zhang[1,a], Xiaoying Li[1], Eluxka Almandoz[2] and Gonzalo García Fuentes[2], Hanshan Dong[1]

1. The University of Birmingham, Birmingham B15 2TT UK
2. AIN, Cordovilla (Navarra) 31191 SPAIN

Abstract:

Due to its resistant to thermal shock and strength at elevated temperature, Titanium-Zirconium-Molybdenum (TZM) alloy is used for hot-work tooling up to 1500°C. The friction and wear behaviour of the TZM alloy reciprocating against Al_2O_3 and Si_3N_4 in different conditions were investigated. It has an adhesion and/or oxidation character with a high coefficient of friction when dry sliding against an alumina ceramic ball. It is characterised with reduced wear in an abrasion mode when reciprocally sliding against a Si_3N_4 ceramic ball. In addition, the friction and wear between TZM and an Al_2O_3 ball under unidirectional sliding conditions can be reduced when lubricating molybdenum oxides was formed at higher temperature i.e. 600°C. Finally, the friction and wear mechanisms involved are discussed.

Keywords: Molybdenum, TZM, Al_2O_3, Si_3N_4, friction and wear.

1. Introduction

Plasma sintering or electric-field-activated sintering technology (FAST) enables binder-free, rapid sintering of high-performance components with nano-structured micro-powders[1]. It is particularly suitable for mass-production of miniature or micro-parts (i.e. Micro-FAST) due to its rapid heating nature. However, the micro-tools need to withstand not only high temperature but also cyclic high heating/cooling rates. Although graphite is the most widely used material for FAST tools (dies/punches) mainly due to its high electric conductivity, however, it is characterised by low load bearing capacity with a maximum pressure capability of 80-150 MPa[1]. When sintering ceramic materials such as Al_2O_3 and Si_3N_4 at high-temperature for micro-parts, tools must be able to withstand the higher load, but the graphite tools can only be used for a few times due to the limited strength and the

shrunk dimension. Therefore, tools must be made from stronger materials such as superalloys, refractory metal alloys or even ceramics because of the high pressure essential for plasma sintering of ceramics [2].

Titanium-Zirconium-Molybdenum (TZM) alloy can retain its strength at an elevated temperature up to 1500°C. In addition, TZM exhibits high thermal and electrical conductivities and low coefficient of thermal expansion. The combination of these desirable properties makes the TZM alloy a material of choice for high-temperature (up to 1500°C) hot-work tooling and a potential candidate material for Micro-FAST tooling with high resistance to thermal shock and cracking arising from high cycles of rapid heating and cooling [3].

After Micro_FAST sintering, the ceramic micro-parts need to be pushed to slide out the mould off-site or on-site depending on the production system setup and throughput. However, when the size of the tools and components is scaled down to mm-scale, soldering due to severe adhesion between the mould and the working material would occur and thus demoulding becomes a major challenge for Micro-FAST process. As the TZM tools are designed to replace the relatively vulnerable graphite tools for a much-increased cycle life, the sliding friction and wear behaviour of the ceramic materials (i.e. Al_2O_3 and Si_3N_4) and the proposed TZM tool material is critical for a smooth demoulding. It has been reported that the coefficient of friction (CoF) of an arc-cast Mo rider sliding against a dense Mo disk was 0.8 at 25 °C and 1.15 at 900 °C, however the CoFs was 0.27 at 25 °C and 0.5 at 900 °C when the counterpart was changed to a dense Co-25Mo in the unlubricated condition [4]. It was found that TZM–TZM pair has a lower coefficient of friction than that of the molybdenum–molybdenum pair in a friction welding but no value of CoF was reported [5]. TZM alloy was used as a brake material with high friction and low wear under high speed and high load conditions[6]. The friction behaviour of the Al_2O_3/Mo composite (up to 10% of Mo) disc against an Al_2O_3 ball in a ball-on-disk tribometer at 25 °C and 400 °C were investigated by Cura and colleagues [7]. Mo coatings on steel can greatly enhance its wear resistance sliding against bearing steel specimen under boundary lubrication conditions [8]. However, little work has been conducted to systematically investigate the friction and wear properties of the Titanium-Zirconium-Molybdenum (TZM) alloy sliding against ceramics.

Molybdenum-based alloys are susceptible to oxidation at a temperature of 371°C and above and during sliding it forms a soft and lubricious tribo layer at the surface [7].

Elevated temperature or generated heat during dry sliding at room temperature may lead to the formation of the lubricious layer mostly in the form of MoO_3. The CoF of a sample of 40 vol% Mo in a matrix of yttria stabilized zirconia and alumina mixture (Y-TZP/ Al_2O_3) was reduced from 0.86 at 25 °C to 0.48 at 800 °C [9]. Normally, another solid lubricant like silver needs to be combined with MoO_3 oxide to cover a broader temperature range [10]. Therefore, an oxygen-deficient environment (gas protected or vacuum) is necessary for the micro_FAST process to reduce the catastrophic oxidation of molybdenum as MoO_3 is volatile at 795°C and above. On the other hand, lubricative molybdenum oxides could reduce friction at higher temperature, and thus enable on-site demoulding easier.

In this paper, for a possible replacement of graphite tool set in a newly developed high-throughput FAST production system for miniaturised components made of ceramic materials, the friction and wear behaviour of the TZM alloy reciprocating against Al_2O_3 and Si_3N_4 in different mediums (air, nitrogen) under different loads were investigated at room temperature. In addition, the friction and wear behaviour of the TZM alloy unidirectionally sliding against Al_2O_3 at elevated temperature was also evaluated for a possible demoulding at higher temperature on site. The coefficient of friction under different conditions was recorded, the wear tracks were profiled by a 3D profilometer to quantitatively calculate the wear volume and the tribo-products formed in the wear tracks were identified by SEM/EDX. Finally, the friction and wear mechanisms involved were discussed to study the tribological behaviour sliding against ceramics. To advance scientific understanding, the tribological properties of the counterparts in lubricated conditions (water and salted water) are also reported.

2. Experimental

A molybdenum-based TZM alloy bar of 25mm in diameter purchased from EDFAGAN EUROPE Inc. was used in this study. The chemical compositions of the TZM alloy (in wt%) are 0.50% titanium, 0.08% zirconium and 0.02% carbon with the balance molybdenum. Coupons of Φ25×4.5mm were sectioned from the bar and wet ground to a surface roughness of about 0.072 μm (R_a) using SiC paper down to 1200 grit. After ultrasonic cleaning in an acetone bath, the coupons were used for tribo-tests.

A TE79 multi-axis tribology machine (Compend 2000 Version 2.3.1) was used to assess the friction and wear of the material in reciprocating mode at room temperature with a 8 mm in diameter Al_2O_3 or Si_3N_4 ball as the counterpart under a load of 1, 2 and 4 N.

Samples were mounted in a container on a movable table. The whole tribo-tester was enclosed in a chamber with transparent walls to avoid dust and reduce air turbulence. The reciprocating sliding wear tests were conducted in air, in nitrogen by nitrogen purging, in distilled water and in simulated seawater containing 3% NaCl by filling the liquid into the container. The reciprocating sliding distance was set to be 5 mm, the sliding speed was 10 mm/s, and the coefficient of friction (CoF) was recorded for 1000 or 2000 cycles. As the value of CoF is symmetrical, only the positive side (one direction) is shown in the figures. Each reciprocating test was repeated 2-3 times.

In addition to reciprocating sliding, unidirectional sliding wear tests were also conducted using the CSM HT pin-on-disc tribo-tester. The pin-on-disc wear tests were carried out under a load of 2 N with an Al_2O_3 ball of 6 mm in diameter at a unidirectional sliding speed of 10 cm/s for 5000 cycles at three different temperatures: room temperature (21-25°C), 300 ºC and 600 ºC.

The friction and wear test conditions and the corresponding test codes are listed in Table 1. The 1st group of the tests were designed to study the load effect without lubrication in reciprocation whilst the third group was used to study the temperature effect in unidirectional sliding. The combination of the tests from the 2nd group and from the 1st can be used to study the effect of the test medium and counterpart materials. The surface roughness (R_a) and the wear tracks of the tested samples were measured utilising a XP-Plus Stylus Profilometer and the wear volumes were calculated accordingly by integrating the wear track areas. The wear morphology of the wear tracks was observed under SEM and the composition of the tracks was analysed by EDX.

Table 1. Test code and corresponding friction and wear test conditions

Test code	Counterpart	Medium	Load (N)	Temperature	Motion	Cycles
AA1	Al_2O_3	Air	1	RT	Reciprocating	1000
AA2	Al_2O_3	Air	2	RT	Reciprocating	1000
AA4	Al_2O_3	Air	4	RT	Reciprocating	1000
AA22	Al_2O_3	Air	2	RT	Reciprocating	2000
AN1	Al_2O_3	Nitrogen	1	RT	Reciprocating	1000
AN2	Al_2O_3	Nitrogen	2	RT	Reciprocating	1000
AW	Al_2O_3	Water	2	RT	Reciprocating	1000
ASW	Al_2O_3	Sea water	2	RT	Reciprocating	1000
SA1	Si_3N_4	Air	1	RT	Reciprocating	1000
SA2	Si_3N_4	Air	2	RT	Reciprocating	1000
SN2	Si_3N_4	Nitrogen	2	RT	Reciprocating	1000
UA	Al_2O_3	Air	2	RT	Unidirectional sliding	5000
UA300	Al_2O_3	Air	2	300°C	Unidirectional sliding	5000
UA600	Al_2O_3	Air	2	600°C	Unidirectional sliding	5000

3. Results

3.1 Friction and wear in air

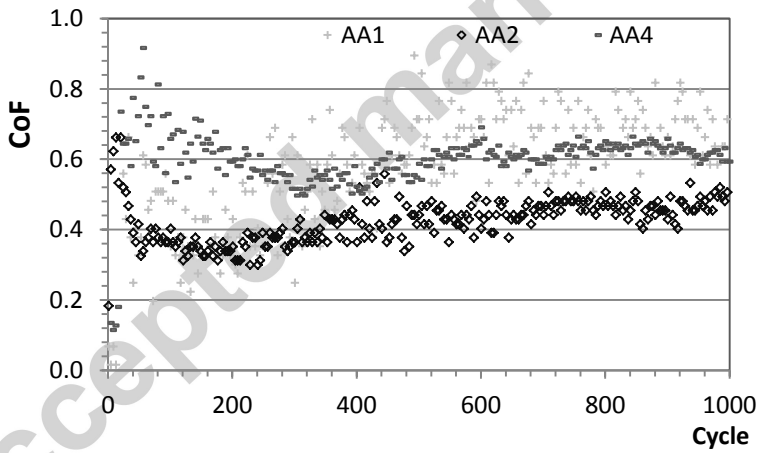
Figure 1 shows the change of coefficient of friction (CoF) of TZM sample against reciprocating cycles in the air as a function of counterpart balls (Al_2O_3 and Si_3N_4) and loads (1N, 2 N and 4N). As seen in Figure 1a, under a load of 1 N with an Al_2O_3 counterpart ball (AA1), the CoF of the TZM sample climbed up to as high as 0.8 at the beginning and then gradually reduced to about 0.5 till about 200 cycles; this value was slightly up and scattered in a big range between 0.5 and 0.9. When a load of 2 N (AA2) was used, the CoF developed similarly as AA1 but the values (0.3-0.5) were generally lower than that tested under 1 N load (AA1) and less scattered in the whole test. The CoF (AA2) remained between 0.35 and 0.5 after 500 cycles even in an extended test (AA22, 2000 cycles). When a load of 4 N (AA4) was used, the CoF of the TZM sample climbed up to as high as 0.94 at the beginning and then gradually reduced to about 0.5 after about 300 cycles; this value was slightly up and fluctuated around 0.62.

When changing the counterpart ball to Si_3N_4 (Figure 1b), the CoF of the low-load (1 N) SA1 sample increased gradually to a value around 0.4 after about 100 cycles. When changing the load to 2 N, the CoF of SA2 increased rapidly to 0.52 within about 65 cycles before reducing to a similar average value around 0.4 with relatively small fluctuation range in comparison with that tested under a load of 1 N (SA1).

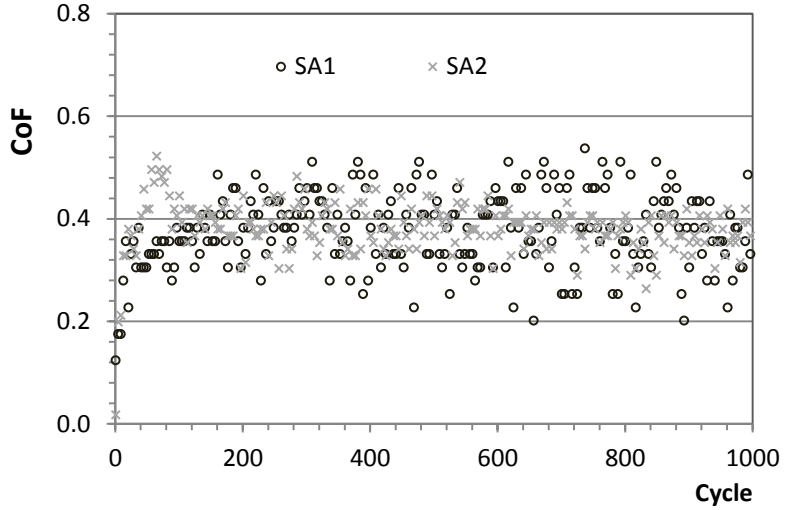
The effect of counterpart materials can be studied by comparing the CoF of TZM samples reciprocating against Al_2O_3 and Si_3N_4 balls when tested under the same load and in the

same medium like air. As displayed in Figure 1c, when tested under 1N, although the friction fluctuated greatly for both counterparts, except for the initial 200 cycles the average CoF is much higher when against the Al_2O_3 ball (~0.6) than against the Si_3N_4 ball (~0.4). However, when tested under 2 N, the initial CoF was higher when against the Al_2O_3 ball (AA2) than against the Si_3N_4 ball (SA2) but they were gradually levelled after about 100 cycles to around 0.4 and the CoF of AA2 was slightly higher after 500 cycles as seen in Figure 1d.

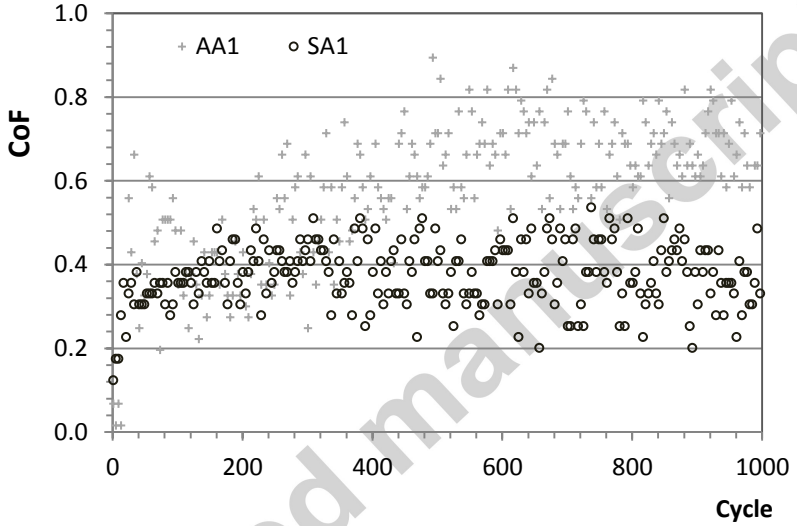
After the test, the wear tracks were measured by a 3D profilometer and plotted in 2-D profiles across the wear track (Figure 2). It can be clearly seen that a clear, deep concave wear track was produced by an Al_2O_3 counterpart ball under a load of 4 N (AA4); but a prominent plateau wear track was found after tests under loads of 1 N and 2 N against the same Al_2O_3 counterpart ball (only AA2 presented). However, when the track was cleaned by a plastic brush, a concave wear track was revealed (see Figure 2, AA2_track cleaned). After being rubbed against a Si_3N_4 counterpart ball under a load of 2 N, the wear track was hardly measurable even after cleaning (SA2 in Figure 2).



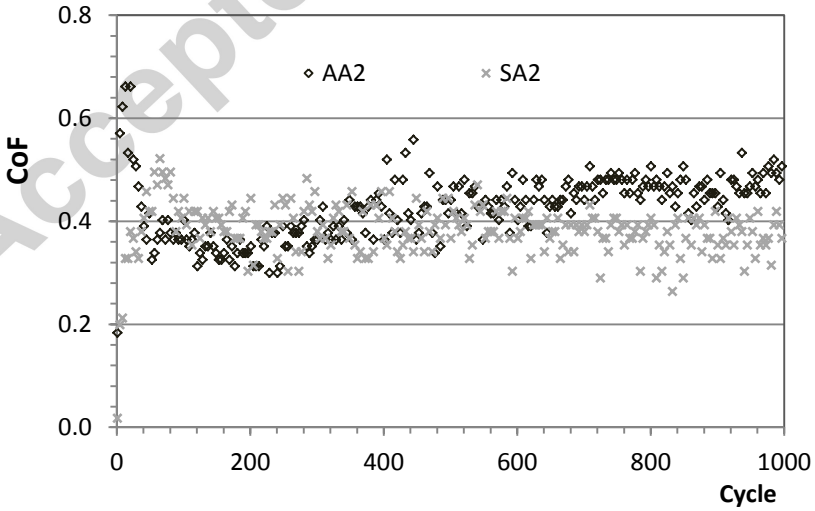
(a)



(b)



(c)



(d)

Figure 1. The coefficient of friction of TZM against moving cycles in air: (a) alumina ball under 1, 2 and 4 N, (b) Si_3N_4 ball under 1 N and 2 N, (c) alumina and Si_3N_4 ball under 1 N and (d) alumina and Si_3N_4 ball under 2 N.

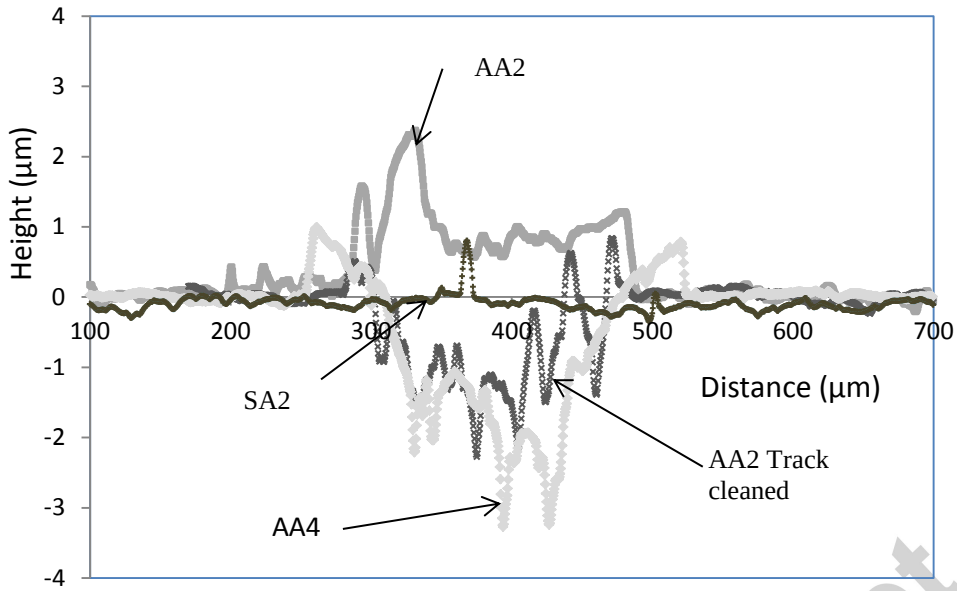
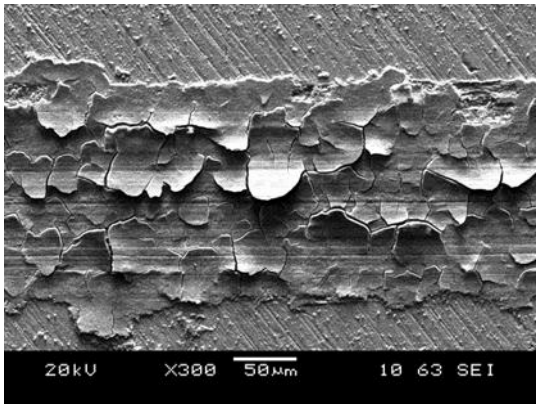


Figure 2. The wear tracks on TZM sample plotted by a 3-D profilometer after friction test of 1000 cycles in the air with different balls.

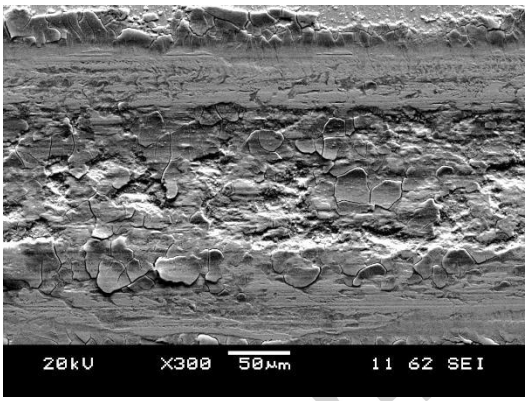
SEM observations revealed flake featured wear track surfaces for AA1 and AA2 tested samples (Figure 3a). However, when tested under 4N, the wear track formed on the AA4 tested sample was only partially covered by the flake-like feature (Figure 3b) together with some wear craters and grooves. EDX analysis at different spots of the wear tracks and the substrate was conducted and the results are shown in Figures 3a, b&d. As expected, the substrate (Spot 1) is dominated by Mo with 0.48% Ti. However, although the flake (Spot 2) formed on the wear track of AA2 tested sample was still dominated by Mo, it contained a high amount (10.53%) of oxygen and a small amount of aluminium. This indicated that the flake formed on the wear track surface was likely to be a product of molybdenum oxides with a little aluminium-containing debris from the counterpart Al_2O_3 ball. The flakes observed from the wear track of AA4 tested sample (spot 4 in Figure 3b) had a similar composition as for Spot 2, while Spot 3 taken from the crater had less oxygen (5.28%) than Spot 2 (10.53%).

These observations implied that when tested in air, severe oxidation occurred to the surface of TZM samples and the wear track was fully covered by the flake-like wear debris when tested under 2N. When increasing the test load to 4N, most of the flakes were removed from the track as wear debris accumulated along the wear track. SEM observations on the AA4 tested counterpart Al_2O_3 ball identified a patch of debris stuck on the wear surface of

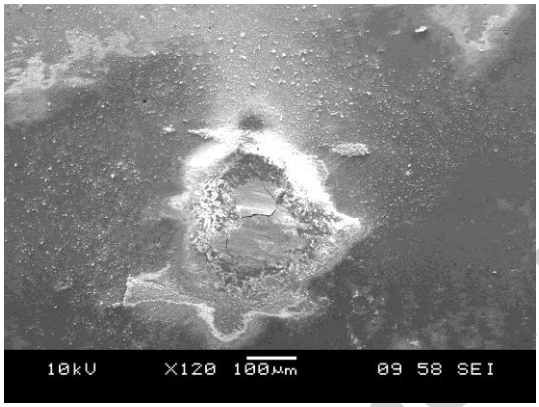
the Al_2O_3 ball, and EDX analysis (Spot 5 in Figure 3c) revealed a high amount of molybdenum (75.47%) and oxygen (22.44%) but a low content of aluminium (2.10%). This evidenced that very mild wear occurred to the Al_2O_3 ball but the TZM sample was worn by Al_2O_3 ball severely and the wear debris was transferred to the Al_2O_3 ball during the wear tests.



(a)



(b)



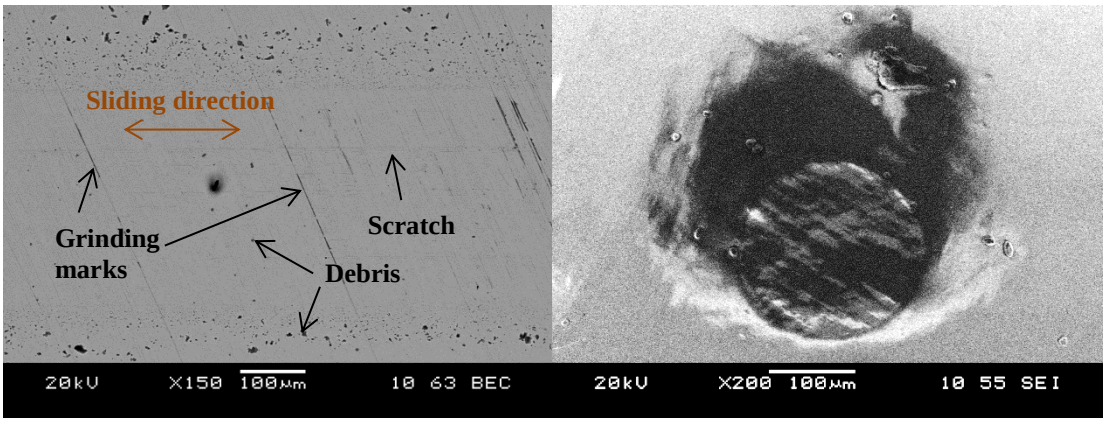
(c)

Spot	O	Al	Ti	Mo
1	-	-	0.48	99.52
2	10.53	0.23	0.35	88.89
3	5.28	0.59	0.64	93.50
4	8.37	0.43	0.47	90.73
5	22.44	2.10	-	75.47

(d)

Figure 3 Wear tracks after friction test: (a) AA2, (b) AA4, (c) crater on AA4 counterpart Al_2O_3 ball and (d) EDX analysis

In contrast, the wear track formed on TZM surface by sliding against a Si_3N_4 ball in the air was barely visible and only some minor scratches were found regardless of the loads applied as indicated in Figure 4a. Indeed, some of the grinding marks produced during sample preparation remained after the test. This indicated very mild wear, which is in line with the 2D profile across the wear track formed on the SA2 tested surface (see Figure 2). Some wear debris was in clear contrast with the base material in a backscattering electron image and EDX analysis identified high silicon content in the debris. A relative flat wear surface was observed on the Si_3N_4 ball, indicating clearly material lost from the ball during the tribo-tests (Figure 4b).



(a) (b)

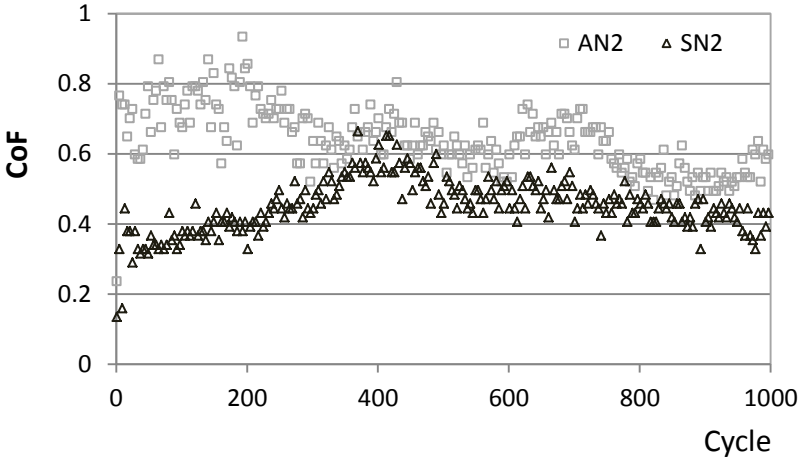
Figure 4. Wear tracks after friction test: (a) SA2, (b) Crater on counterpart Si_3N_4 ball

3.2 Friction and wear in a nitrogen gas atmosphere

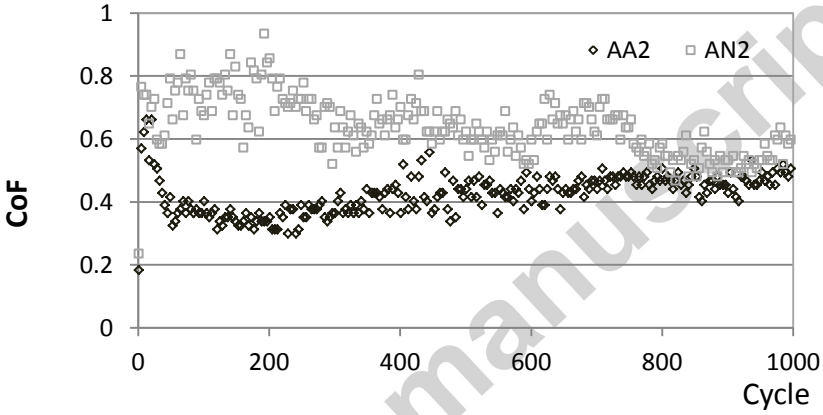
In order to study the effect of oxygen in the air on the tribological behaviour of TZM alloy, the wear test chamber was purged by a high flow of nitrogen gas for 10 minutes, followed by a low and constant flow of nitrogen to expel the air between the tribo-pair. The typical frictional curves are given in Figure 2a for the TZM samples reciprocating against an Al_2O_3 ball (AN2) and a Si_3N_4 ball (SN2) in nitrogen under 2 N. In general, the CoFs of TZM samples were lower when reciprocating against a Si_3N_4 ball (SN2) than against an alumina ball (AN2) in nitrogen gas atmosphere as displayed in Figure 5a.

The CoF of the AN2 tested TZM sample started at around 0.8 and then declined gradually but periodically with the tests cycles to about 0.5-0.6 after 1000 cycles (Figure 5a). The CoFs for AN2 were generally higher than those tested in air (AA2) especially in the first half of the tribo-test process (Figure 5b).

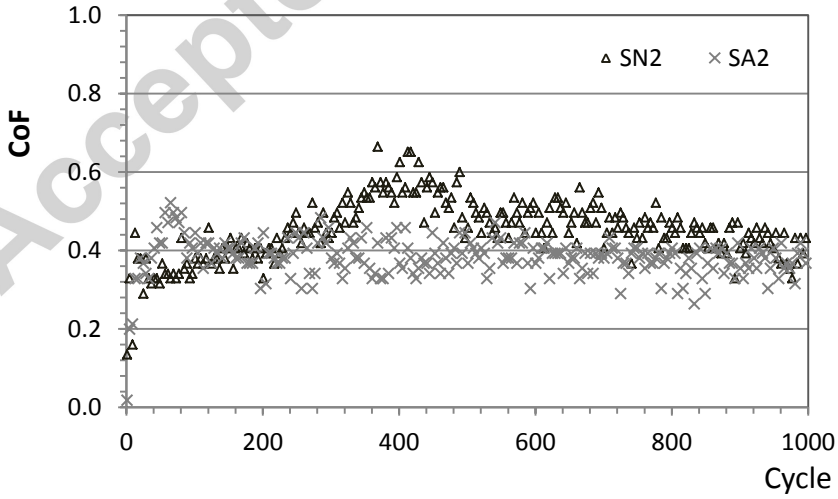
The friction between a Si_3N_4 ball and the TZM in nitrogen (SN2) was quite similar to that tested in air (SA2) under otherwise same conditions (Figure 5c). For both tests, the CoFs increased with the cycles to a peak before it decreased to a similar level. It was noted that the CoF peaked after about 65 cycles when tested in the air but after 400 cycles when tested in nitrogen.



(a)



(b)



(c)

Figure 5. The CoF against cycle between TZM and (a) different counterpart balls in nitrogen (AN2 vs SN2), (b) Al_2O_3 ball in air (AA2) and in nitrogen (AN2) and (c) Si_3N_4 ball in air (SA2) and in nitrogen (SN2).

As shown in Figure 6, the profiles of the wear tracks for AN2 and SN2 tested TZM surfaces are in big contrast: two deep grooves produced by an Al_2O_3 ball (AN2) verse multiple shallow-grooves produced by a Si_3N_4 ball (SN2). SEM observations (Figure 7) of these two wear tracks revealed different features: deep and wide grooves with side loose flakes for the formal and shallow and narrow abrasive multi-grooves for the latter. EDX analysis of the oxygen content detected was much lower in the deep groove than in the flake along the wear track (Figure 7a). This is similar to the results shown in Figure 3d under AA4 conditions. In the meantime, a much bigger wear scar on the counterpart alumina ball was observed by optical microscopy. This means that severe wear also occurred to the counterpart ball. Some silicon information can be picked up in the multi-grooves (Figure 7b point 1) suggesting some Si_3N_4 particles from the ball was transferred into the track and contributing to the wear of the grooves.

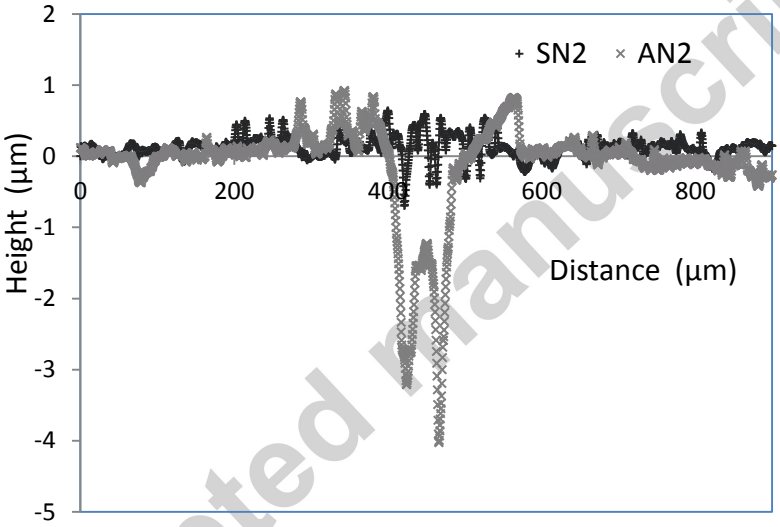
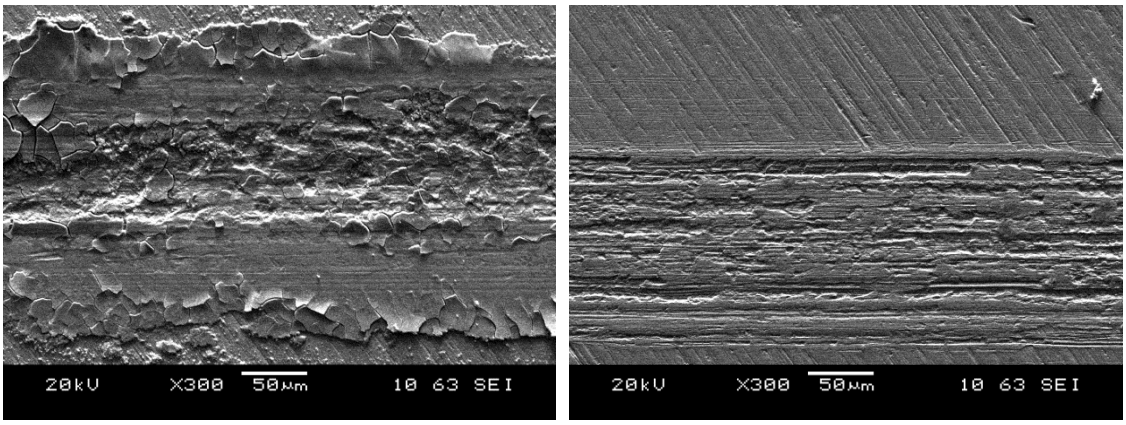


Figure 6. The wear tracks on TZM sample after tribo-test against different counterpart balls in a nitrogen gas atmosphere.



(a) (b)

Wt%	O	Si	Ti	Mo
1	12.48	6.60		80.92
2				100.00
3			0.55	99.45

(c)

Figure 7. Wear tracks of (a) AN2 and (b) SN2 after friction test in nitrogen (c) EDX analysis.

3.3 Friction and wear in distilled water and salted water

Figure 8 shows the CoFs of the TZM alloy reciprocating against an Al_2O_3 counterpart ball in distilled and salted water. The initial CoFs were low when the friction counterparts were submerged in distilled or salted water. The CoF in distilled water (AW) increased steadily to about 0.58 after about one hundred cycles, and then gradually reduced to about 0.4 after 1000 cycles (Figure 8). After an initial low value, the CoF in salted water (ASW) gradually climbed up and remained quite stable at around 0.4 untill the end of the tribo-test. Overall, they are quite similar except for a heap for AW between 100-250 cycles.

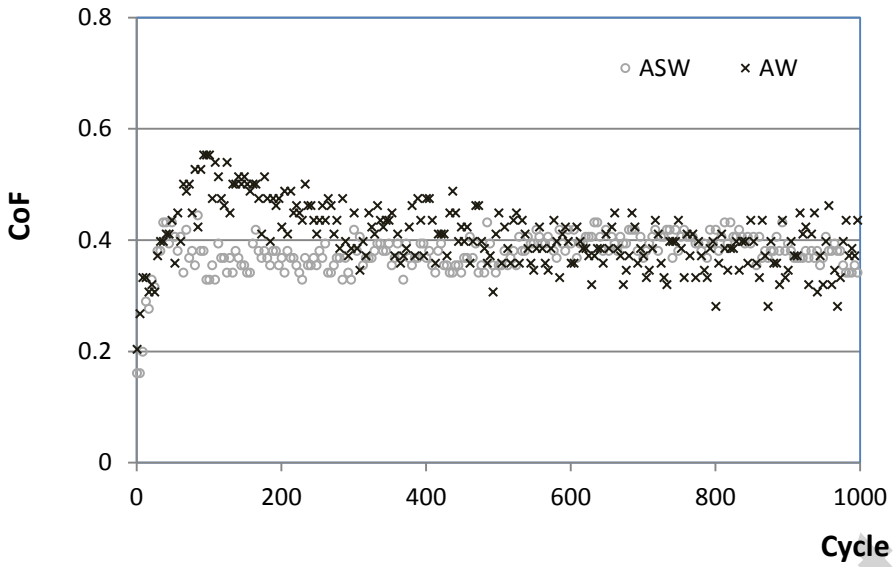
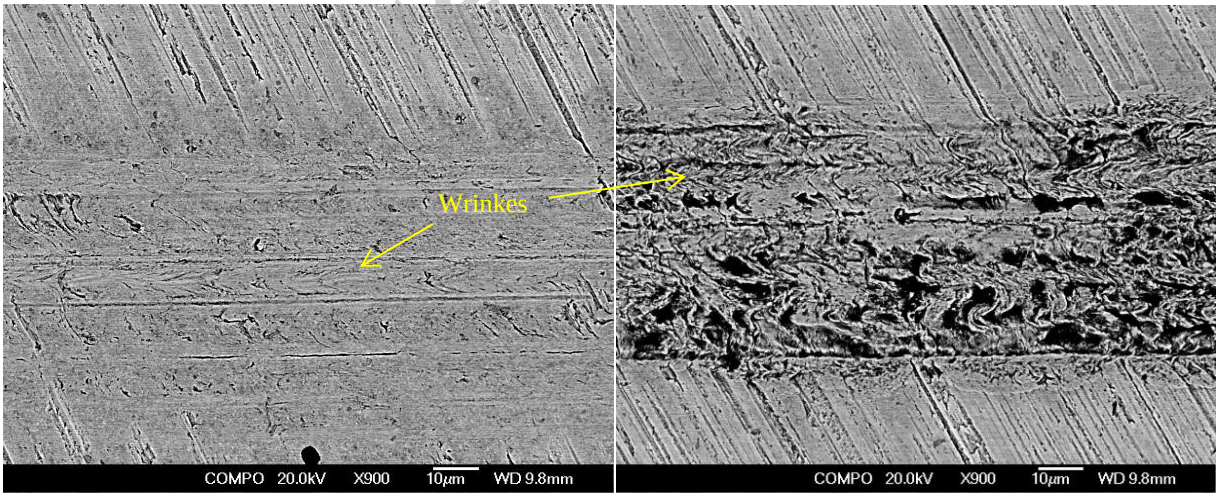


Figure 8. The CoFs of TZM reciprocating against an Al_2O_3 counterpart ball in distilled water and salted water.

No measurable wear could be detected by a 3D profilometer for the ASW and AW samples after reciprocating against an alumina counterpart ball in distilled water and salted water. However, SEM observations revealed different features for these two tested samples. As can be seen in Figure 9a, the wear track of AW tested sample shows polished trace with very fine scratch lines and ripples. In contrast, although no measurable wear as for AW tested sample, the wear track of the ASW tested sample developed severe ripples and corrosion pits (Figure 9b), indicating poor corrosion resistance of TZM alloy to NaCl.



(a) (b)

Figure 9. Wear tracks after tribo-test under lubricant of: (a) distilled water (AW), (b) 3.5% NaCl water (ASW)

3.4 Friction and wear at different temperatures under unidirectional test conditions.

Unidirectional pin-on-disc friction and wear tests of TZM alloy against an alumina ball at room temperature (UA), 300°C (UA300) and 600°C (UA600) in the air were conducted. The CoFs of these three systems are compared in Figure 10. It can be seen that at room temperature, the CoF of UA was very high in the first 400 cycles, and then it decreased to about 0.76 for about 2000 cycles before slightly increased to around 0.8 with a few jerks in the test process (Figure 10). When tested at 300 ºC, after a few run-in cycles with high friction, the CoF of UA300 decreased to about 0.65 at cycle 20 and then increased gradually to above 0.9 at 2400 cycles and kept constant but with a fluctuation from 0.9 to 1.0 until the end of the test. Interestingly, when tested at 600 ºC, apart from the short running-in process, the CoF of UA600 showed a constant low value of 0.5 for the whole tribo-test cycles.

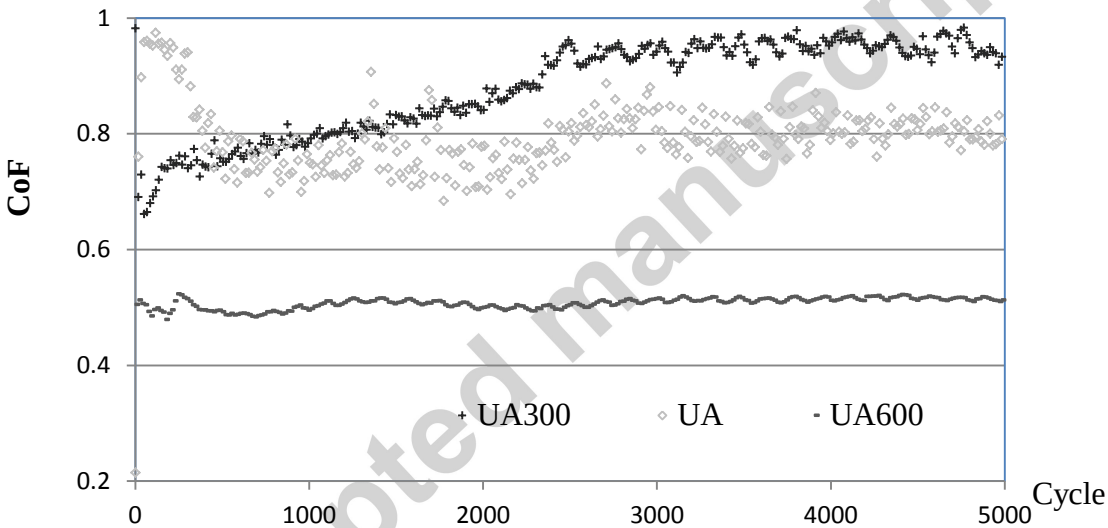
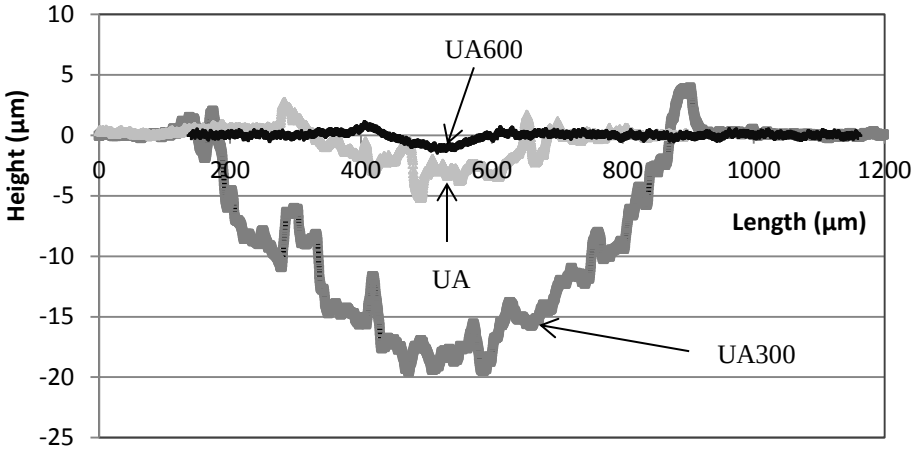
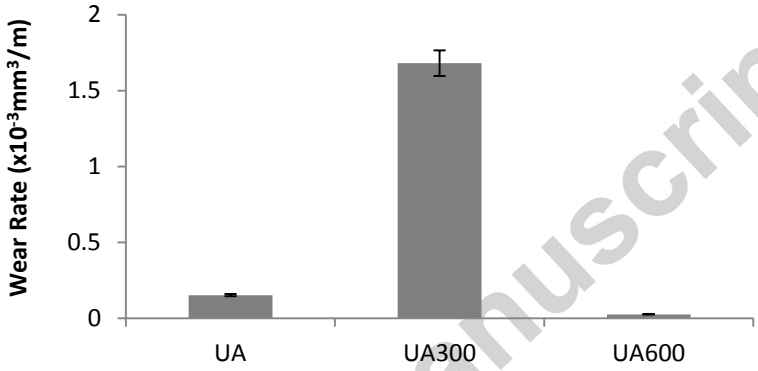


Figure 10. The coefficient of friction between Al_2O_3 ball and TZM sample as a function of the testing temperature.

As shown in Figure 11a, when tested at room temperature, the wear track of UA is shallow (about 2.5-5.0µm) with a rough surface. When tested at elevated temperatures, the wear track of UA300 showed severe material removal with a much wider and deeper wear track (18-20 µm) as compared with that formed at room temperature. However, the wear track of UA600 revealed a large contrast to that of UA300 with only a fraction of the wear loss comparing to UA300. The wear rates at different temperatures were calculated and plotted in Figure 11b, and it was found that the wear rates were 0.152, 1.68 and $0.0258 \times 10^{-3} mm^3/m$ for UA, UA300 and UA600 respectively, and the UA600 achieved best wear resistance under the unidirectional test conditions.



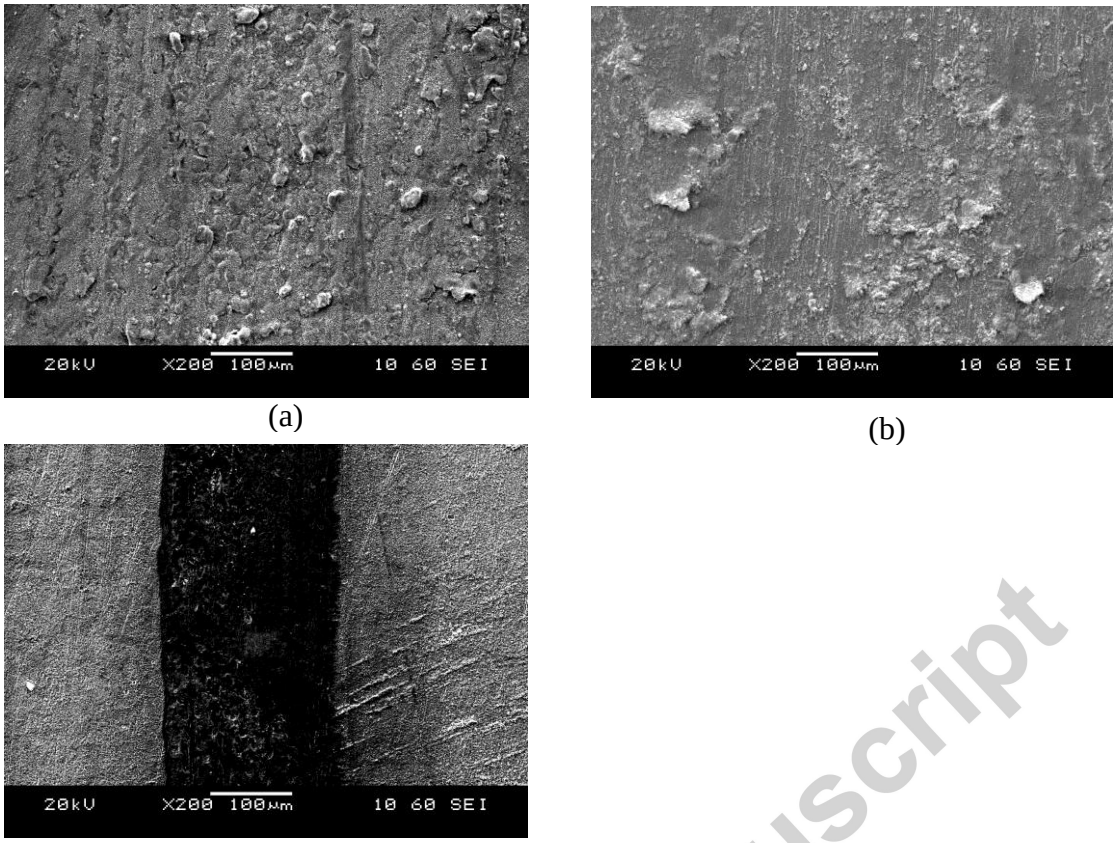
(a)



(b)

Figure 11. The wear tracks on TZM sample after unidirectional tribo-test at different temperatures: (a) track profile and (b) wear rate.

SEM observations on the wear tracks formed in the tested samples revealed that, when tested at room temperature, there were some flakes left on the wear tracks which were similar to that formed on the reciprocating tested sample (Figure 12a). When tested at 300 °C, the worn surface was covered by a lot of bulged lumps (Figure 12b). In contrast, after a test at 600 °C, the wear track became dark and relatively smooth with only some scattered bumps were left on the track (Figure 12c).



(a) (b) (c)

Figure 12. Wear tracks after unidirectional friction test at different temperatures: (a) at room temperature (UA), (b) 300°C (UA300) and (c) 600°C (UA600).

4 Discussion

Molybdenum-based TZM alloy has been a promising candidate material for dies/punches in hot working of ceramic materials. However, it is interesting to find that TZM alloy responds differently to alumina and Si_3N_4 counterparts in the same tribological setting. Therefore in this part, the different tribological behaviours of these two tribo-pairs are discussed.

4.1. Tribological behaviour of Al_2O_3 /TZM tribosystem

As reported in Section 3, the friction and wear behaviour of TZM sample sliding against an Al_2O_3 counterpart ball changed with the load, temperature and lubrication conditions. As summarised in Figure 13, the average coefficient of friction (CoF) was much higher when tested in nitrogen than tested in air and under lubrication. In the meantime, the wear rate of TZM when tested in water (AW) and in sea water (ASW) were much lower in comparison with those when tested in air (AA2) and in nitrogen atmosphere (AN2) with the wear rate

in nitrogen (AN2) being the highest for all the test conditions. In this part, the mechanism of friction and wear between TZM sample and Al_2O_3 counterpart ball in different conditions is discussed.

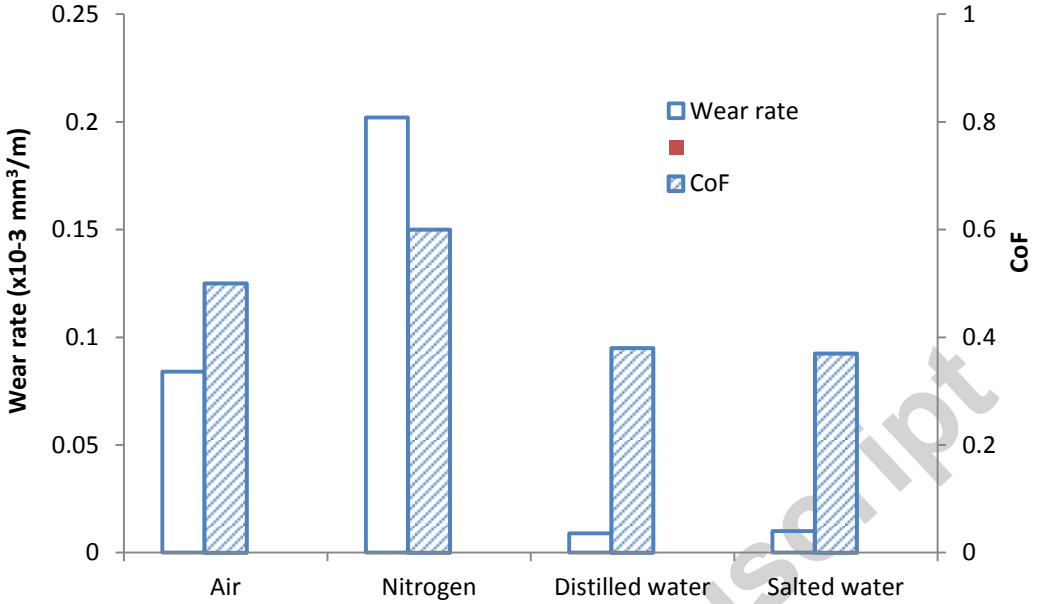


Figure 13. Wear rate and average CoF (shaded) after friction test utilising a Φ8 mm Al_2O_3 ball under a load of 2 N for 1000 cycles in different mediums.

4.1.1 Tribological behaviour in air

As shown in Figure 1a, under a load of 1 N (AA1), the CoF of the TZM sample remained high and scattered largely throughout the whole tribotest. The CoF became lower and less scattered when the load was increased to 2 N (AA2). When increasing the load to 4 N (AA4), initially the CoF of TZM sample against an Al_2O_3 ball was higher than that tested under the lower loads (1N and 2N); however, at a later stage, it remained higher than that test under 2 N (AA2) but lower than that tested under 1 N (AA1).

In the beginning of the tribo-test under 4N (AA4), the moving Al_2O_3 ball torn some material apart from the surface of TZM sample to form flaky pieces, which strongly hindered the movement between the Al_2O_3 ball and the TZM surface. In the meantime, some flaky pieces of TZM were transferred to the surface of the counterpart ball (Point 5 in Figure 3c) as schematically shown in Figure 14a. This is because molybdenum is well known for its adhesive character as it has a strong bond to glasses, polymers, ceramics and other materials [11, 12]. For example, molybdenum has been added into Al_2O_3 ceramic as a

binding phase or forming a laminate structure to improve the fracture toughness of the ceramics used in cutting tools [13, 14], solar selective absorbing coatings [15] and catalysts [16] etc. This could be explained by the fact that even though TZM is not very hard (280 $HV_{0.05}$), its elastic modulus (320 GPa) [3] is higher than most of the other metals. This results in a high E/H ratio of 116.5 and thus makes the material susceptible to plastic deformation and adhesion.

Further sliding and rubbing between the Al_2O_3 ball and the TZM sample led to the oxidation of the flaky molybdenum pieces in some local points. As evidenced in Figure 3d, oxygen content varied at different locations in the wear track produced, which implies that different oxides might have been formed. Oxides like MoO_3 and Mo_4O_{11} are Magnéli phases, which has a similar structure like graphite, and they have lubrication effect at elevated temperature but lose it at room temperature [7, 10, 17]. The friction was slightly reduced (AA4) after the initial high friction period. This might be due to the lubricating effect of the molybdenum oxides formed in certain areas where severe rubbing raised the local temperature, which is in agreement with Portu's findings [13]. After certain reciprocating cycles, the oxidised flaky pieces were peeled off from the surface and some of the particles would stay between the tribo-pair acting as third-body objects (Figure 14b). The mixed milled oxides and wear particles increased the wear of TZM and thus a deep concave wear track was formed (Figure 14c). The wear mechanism is dominated partially by oxidation wear and partially by adhesive wear. Similarly, Lucchini [18] found molybdenum tended to adhere to aluminium and easily peeled off from the Mo/Al_2O_3 cutting tool during machining Al/Al_2O_3 composite.

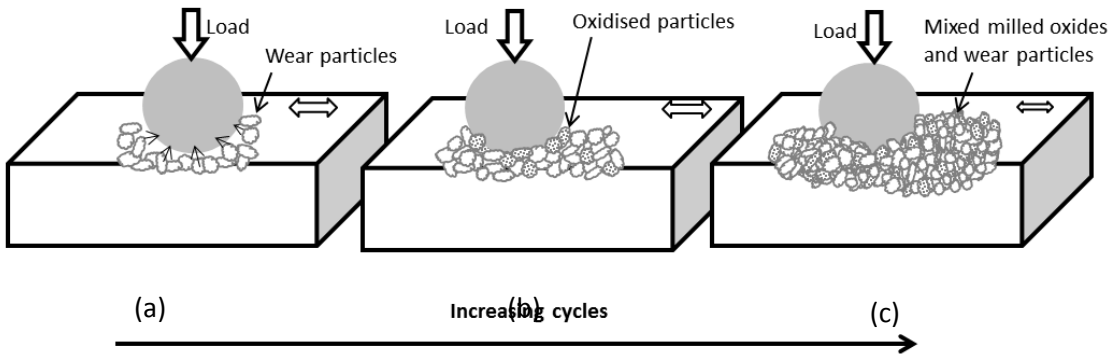


Figure 14. Schematics of tribological interaction between an Al_2O_3 ball and TZM sample

Under a load of 2N (AA2), most of the oxidised flaky pieces were not removed due to reduced shear force. Therefore a mild tribo-oxidative friction prevailed, and overall, the

CoF was lower than that tested under a load of 4 N (Figure 1a). When the load was reduced to 1 N (AA1), the rubbing force between the tribo-pair decreased further and thus less frictional heat generated to oxidise the flaky pieces of metals. Therefore severe galling or adhesive wear dominated thus causing large and widely scattered friction between the tribo-pair (Figure 1). Comparably, Portu found that the lower the load, the higher the friction between Al_2O_3/Mo and WC ball [13].

4.1.2 Effect of nitrogen gas and lubricants

It can be seen by comparing Figure 1a with Figure 5a that, when tested under the same load of 2N, the CoF of the Al_2O_3/TZM was increased from about 0.4 when tested in air (AA2) to about 0.6 when tested in nitrogen atmosphere (AN2). This is mainly because oxides were difficult to form in a nitrogen atmosphere due to the lack of oxygen after initial galling, thus reducing the potential lubrication effect of oxides. Once the material was torn apart, more galling occurred in the tribo-test, which led to a very high CoF as shown in Figure 5a. Elemental information collected by EDX revealed that the oxygen content detected in the wear groove was much lower than that in the flakes. This could be due to the deficient of oxygen during tribo-test at the contact area or the removal of the flakes (Figure 7). In this case, some metal particles rather than oxide pieces were peeled off and acted as abrasive particles between the ball and the substrate thus increasing the friction and wear. However, it is not clear why the friction was then gradually reduced with the progress of the tribo-test. One possibility would be the effect of wear debris, which changed high-friction two-body abrasive wear to low-friction three-body abrasive wear due to the rotation of the wear particles. In the meantime, it was reported that molybdenum oxide film was easily formed on top of aluminium/molybdenum film in a low vacuum annealing at a temperature of 450°C [19], therefore, some molybdenum oxides might be formed with the help of oxygen from Al_2O_3 ball with the progress of tribo-test.

In liquid lubrication, a low CoF was observed in the beginning of tribo-test and the CoF increased gradually and then stabilised at around 0.4. The track formed during the tribo-test in sea water (ASW) showed severe ripples and corrosion pits. However, no such features were observed in the wear track produced by the tribo-tests in water (AW). Such tribological behaviour should be attributed to the liquid used in the test. The liquid used could prevent the adhesion of the rubbing surfaces to some extent and facilitate the removal of the flakes (i.e. wear debris) from the wear track. Therefore, a relatively low and stable CoF is expected.

However, when tested in salted water (ASW), the sodium chloride could attack the substrate as evidenced by some small pits formed in the TZM substrate away from the wear track. However, the wear track was characterised by ripple-like wear morphology with some black areas (Figure 9b). This implies that tribo-corrosion wear occurred to the TZM surface when rubbing against an alumina ball in salted water under the combined attack of sodium chloride induced corrosion and rubbing by the alumina ball.

4.1.3 Effect of temperature

Due to the technical limitation of the reciprocating tribometer used, the effect of testing temperature was investigated using a unidirectional pin-on-disc tribometer. As reported in Section 3.4, temperature played an important role in determining the tribological behaviour of TZM alloy sliding against an alumina ball. It is of interest to find that the medium temperature (300°) tested UA300 sample exhibited the highest CoF and wear when compared with the room temperature (RT) tested UA and high-temperature (600°) tested UA600 samples.

As shown in Figure 10, when tested at RT the initial CoF of UA reached about 0.9 before it reduced to about 0.7-0.8 after about 500 cycles. The initial CoF of the UA (Figure 10) is much higher than that of the AA2 (Figure 1a) when both tested in air and under the same normal load of 2N. This could be explained by the difference in the applied contact stress and in the mode of movement. Firstly, the diameter of the alumina ball used in the unidirectional UA test (6 mm) was smaller than that (8 mm) used in reciprocating AA2 test, which led to a higher contact stress and larger plastic deformation at the interface. Secondly, in unidirectional sliding, the formation and growth of adhesion junctions could continue with the one direction sliding; on the other, hand, the formation and growth of adhesion junctions could be intermittently stopped by the reciprocating action in the AA test. Hence, the extremely high initial CoF observed from the unidirectional sliding UA test could be the consequence of severe adhesion and rapid growth of adhesion junctions at the beginning. Then the CoF gradually reduced to 0.7-0.8 mainly due to friction-induced mild oxidation; however, it remained high and sometimes jogging due to the fragments trapped in the wear track, thus causing abrasion. This is evidenced by the very rough wear track surface (Figures 11a and 12a).

When tested at 300°C, the initial CoF was about 0.7. The relatively low initial CoF could be attributed to the oxide film formed during the heating stage prior to the test. Then the

CoF increased gradually to about 0.95 at 2400 cycle largely because of the gradual removal of the oxide film by wear. Although the in-situ formation of the oxide film may also occur, the fragments in the wear debris formed in the first half of the tribotest could act as abrasives to rub off the in-situ formed oxide film. Consequently, strong adhesion /galling between the exposed TZM and alumina ball occurred. This is evidenced by the large prow-like ridges (Figure 12b) and very rough wear track (Figure 11a) formed during the tribo-test and the very high wear rate (Figure 11b). The high CoF of UA300 could also be due to the poor lubrication of oxides formed at a medium and lower temperature [7].

The lowest CoF about 0.5 was observed when TZM was tested at 600 °C (Figure 10). This may be attributed to the formation of lubricious oxides (MoO_3 and/or Mo_4O_{11}) thin film on the surface at high temperature although $Al_2(MoO_4)_3$ compound might also be formed at this temperature range which has been reported elsewhere[16, 20]. In the tribo-test, due to the high test temperature the formation of the oxide film is most probably faster than the wear, thus maintaining the self-lubrication of the oxide film on the surface in the whole process. This is clearly supported by the black (Figure 12c) and smooth (Figure 11a), the low friction (Figure 10) and the very low wear rate (Figure 11b).

4.2. Tribological behaviour of TZM / Si_3N_4 tribosystem

The tribological behaviour (especially wear) of TZM alloy reciprocating against a Si_3N_4 ball differs greatly from against an Al_2O_3 ball. For example, when tested in air under the same normal load of 2N, whilst a deep wear track was produced in TZM surface by reciprocating against an Al_2O_3 ball, no measurable wear to TZM surface was observed after reciprocating against a Si_3N_4 ball (Figure 2). The corresponding surface wear morphologies are also different. As shown in Figure 3a, the wear track produced by reciprocating against an Al_2O_3 ball were covered by flaky wear debris while there were only a few minor scratches appearing in the wear track produced by reciprocating against a Si_3N_4 ball (Figure 4a). In addition, a clear flat wear surface was formed on Si_3N_4 ball (Figure 4b) but very mild wear occurred to the Al_2O_3 ball.

The larger wear of a silicon nitride ball compared with an alumina ball after reciprocating against TZM could be partially explained based on abrasive wear mechanism by the difference in their hardness because Si_3N_4 ball is not so hard ($HV_{0.1}$1676) as Al_2O_3 ball ($HV_{0.1}$2055) [21]. However the silicon nitride ball is still much harder than TZM, and hence the severe wear of the hard Si_3N_4 ball by the relatively soft TZM alloy could not be

explained by abrasive wear mechanism alone. Clearly, there must be some other mechanisms behind the observed severe wear of the silicon nitride ball.

It has been reported that $MoSi_2$ can be produced by ball milling of Mo and Si_3N_4 powders, and the impact energy typically in the range of 0.145–0.173 J can reduce the pyrolysis temperature significantly [22]. Hence, there is a reason to believe that tribo-chemical reaction between the silicon nitride ball and the molybdenum-based TZM during the reciprocating sliding might happen although further evidence is needed. This might have been promoted by the rubbing between the silicon nitride ball and molybdenum-based TZM surface and the resulting high flashing temperature at the real contact points.

It is known that $MoSi_2$ is brittle (1-2 MPa $m^{1/2}$) with a hardness about 12-14 GPa at temperatures below 1000°C. Therefore, some wear particles came off from the Si_3N_4 ball as schematically shown in Figure 15a. A small flat surface would be created, the contact area increased and thus the contact stress reduced. Due to the brittleness and relatively low hardness, the wear particles were milled into fine particles, which polished the TZM surface (Figure 15b) and created localised scratches (Figure 15c). This is supported by the wear track morphologies shown in Figure 4a and the large flat wear scar formed on the silicon nitride ball (Figure 4b). Therefore, unlike the test against Al_2O_3 ball, chemical and abrasive wear rather than adhesive wear dominated the tribo-test against a Si_3N_4 ball.

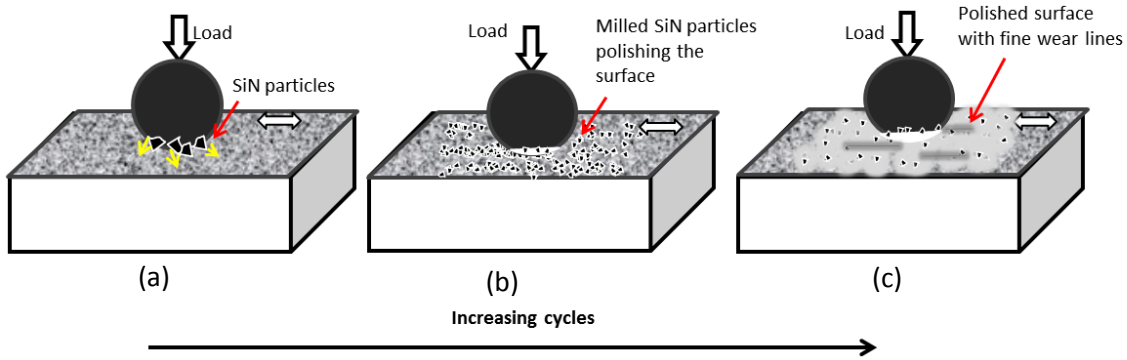


Figure 15. Schematic of friction between a Si_3N_4 ball and TZM sample

5 Conclusions

The friction and wear behaviour of the molybdenum-based TZM alloy against different counterparts (Al_2O_3 and Si_3N_4) in different mediums (air, nitrogen, distilled water and salted water) under different loads were investigated at room temperature. The behaviour of

the alloy against Al_2O_3 at elevated temperature was also evaluated. Based on the results, some conclusions can be drawn as follows:

1) The reciprocating friction and wear of TZM against an alumina ceramic ball in the air has an adhesion character with a high coefficient of friction (CoF) and a very low wear rate when under a low load, i.e. 1N. The friction and wear mechanisms change to adhesion/oxidation with reduced CoF but significantly increased wear when increasing the applied load to 2N and 4N. When tested in a nitrogen gas atmosphere, both the CoF and the wear rate of TZM alloy increased as adhesion wear prevailed at the cost of the reduction of oxidation. Lubrication can reduce the friction and wear of the tribo-pair but severe ripples and many corrosion pits are formed in the wear track when tested in salted water.

2) When reciprocating against a Si_3N_4 ceramic ball in the air, the friction and wear of TZM are predominated by a mild abrasion mode but severe tribo-chemical wear occurred to the Si_3N_4 ceramic ball. The average coefficient of friction for this tribo-pair is about 0.4. The wear of the TZM sample surface is much lower when reciprocating against a Si_3N_4 ceramic ball than against an alumina ball, but the wear of the Si_3N_4 ceramic ball is much more severe than that of the alumina ball.

3) The friction and wear between TZM and an Al_2O_3 ball under unidirectional sliding conditions can be reduced when lubricating molybdenum oxides was formed at higher temperature .i.e. 600°C, but they would increase before a lubricating layer is formed at a medium temperature of 300 °C.

Acknowledgement

The research was funded by the EU FP7 Micro-FAST project (Contract No GA608720).

Reference:

[1] Munir ZA, Quach DV, Ohyanagi M. Electric Current Activation of Sintering: A Review of the Pulsed Electric Current Sintering Process. J Am Ceram So 2011;94:1-19

[2] Chakraborty SP. Studies on the development of TZM alloy by aluminothermic coreduction process and formation of protective coating over the alloy by plasma spray technique. Int J Refract Met H 2011;29:623-30.

[3] Shields JA. Applications of Molybdenum Metal and Its Alloys. 2013 ed. www.imoa.info: International Molybdenum Association (IMOA); 2013.

[4] Sliney HE, Fnsaro RL. Friction and wear of sintered tungsten, molybdenum, and cobalt-molybdenum impregnated with a fluoride eutectic. Cleveland, Ohio 44135 NASA Lewis Research Center 1971. p. 23.

[5] Ambroziak A. Friction welding of molybdenum to molybdenum and to other metals. Int J Refract Met H 2011;29:462-9.

[6] Thompson MS, Beals JT, McCluskey PH, McKee DW, Lang MC, Lussier FJ, et al. Molybdenum alloy elevator safety brakes. USA: Google Patents; 2002.

[7] Cura ME, Liu XW, Kanerva U, Varjus S, Kivioja A, Söderberg O. Friction behavior of alumina/molybdenum composites and formation of MoO_{3-x} phase at 400 °C. Tribol Int 2015;87 23-31.

[8] Liu Z, Hua M. Wear transitions and mechanisms in lubricated sliding of a molybdenum coating. Tribol Inter 1999;32:499-506.

[9] Zhang Y-S, Hu L-T, Chen J-M, Liu W-M. Lubrication behavior of Y-TZP/Al_2O_3/Mo nanocomposites at high temperature. Wear 2010;268:1091-4.

[10] Zhang Z, Dong H. A State-of-the-art overview: Recent development in low friction and wear-resistant coatings and surfaces for high-temperature forming tools. Manuf Review 2015;1.

[11] Cha J-H, Ashok K, Kissinger NJS, Ra Y-H, Sim J-K, Kim J-S, et al. Effect of Thermal Annealing on the Structure, Morphology, and Electrical Properties of Mo Bottom Electrodes for Solar Cell Applications. J Korean Phys Soc 2011;59:2280-5.

[12] Aryal K, Khatri H, Collins RW, Marsillac S. In Situ and Ex Situ Studies of Molybdenum Thin Films Deposited by rf and dc Magnetron Sputtering as a Back Contact for CIGS Solar Cells. Inter J Photoenergy 2012;2012:1-7.

[13] Portu Gd, Guicciardi S, Melandri C, Monteverde F. Wear behaviour of Al_2O_3-Mo and Al_2O_3-Nb composites. Wear 2007;262:1346-52.

[14] Broniszewski K, Wozniak J, Czechowski K, Jaworska L, Olszyna A. Al_2O_3–Mo cutting tools for machining hardened stainless steel. Wear 2013;303:87-91.

[15] Cheng J, Wang C, Wang W, Du X, Liu Y, Xue Y, et al. Improvement of thermal stability in the solar selective absorbing Mo–Al_2O_3 coating. Sol Energ Mat Sol C 2013;109:204-8.

[16] Kouachi K, Lafaye G, Pronier S, Bennini L, S. Menad. Mo/γ-Al_2O_3 catalysts for the Biginelli reaction: Effect of Mo loading. J Mol Catal A: Chem 2014;395:210-6.

[17] Gulbiński W, Suszko T, Sienicki W, Warcholiński B. Tribological properties of silver- and copper-doped transition metal oxide coatings. Wear 2003;254:129-35.

[18] Lucchini E, Lo Casto S, Sbaizero O. The performance of molybdenum toughened alumina cutting tools in turning a particulate metal matrix composite. Mater Sci Eng: A 2003;357:369-75.

[19] Kitada M, Shimizu N. Reaction of Al/Mo thin films. J Mater Sci 1984;19:1339-42.

[20] Hu P, Hu B-l, Wang K-S, Yang F, Song R, Yu Z-T, et al. Arc erosion behavior of La-doping titanium-zirconium-molybdenum alloy. J Alloy Compd 2016;685:465-70.

[21] Li CX, Xia J, Dong H. Sliding wear of TiAl intermetallics against steel and ceramics of Al_2O_3, Si_3N_4 and WC/Co. Wear 2006;261:693-701.

[22] Singh S, Godkhindi MM, Krishnarao RV, Murty BS. Effect of milling energy on mechanical activation of (Mo + Si_3N_4) powders during the synthesis of Si_3N_4–$MoSi_2$ in situ composites. J Eur Ceram Soc 2009;29:2069-77.

Highlights

1. The tribological properties of Titanium-Zirconium-Molybdenum (TZM) alloy are investigated at room temperature and elevated temperature.
2. TZM alloy has adhesive character when sliding against the Al_2O_3 ball.
3. A mild abrasion mode is predominated when reciprocating against the Si_3N_4 ball.