

Effect of temperature on friction and wear behaviour of CuO–zirconia composites

Mahdiar Valefi^{a,*}, Matthijn de Rooij^a, Dirk J. Schipper^a, Louis Winnubst^b

^a University of Twente, Faculty of Engineering Technology, Surface Technology and Tribology, P.O. Box 217, 7500 AE Enschede, The Netherlands

^b University of Twente, Faculty of Science and Technology, Inorganic Membranes, MESA⁺ Institute for Nanotechnology, P.O. Box 217, 7500 AE Enschede, The Netherlands

Received 8 September 2011; received in revised form 26 December 2011; accepted 7 February 2012

Available online 3 March 2012

Abstract

Results of wear tests using an alumina ball sliding against 5 wt% copper oxide doped tetragonal zirconia polycrystalline (CuO-TZP) ceramics are reported as a function of temperature up to 700 °C. The specific wear rate and friction coefficient are strongly dependent on temperature. Below a critical temperature ($T < 600$ °C), CuO-TZP showed a high coefficient of friction as well as a high wear rate. This was ascribed to the formation of a rough surface, caused by brittle fracture and abrasive wear, based on observations by scanning electron microscopy (SEM), laser scanning microscopy (LSM) and X-ray photoelectron spectroscopy (XPS). However, above 600 °C a self-healing layer is formed at the interface and results in low friction and wear. The mechanism of layer formation and restoration is discussed and rationalized by onset of plastic deformation caused by a reduction reaction of CuO to Cu₂O at high temperatures.

© 2012 Elsevier Ltd. All rights reserved.

Keywords: Composites; Wear resistance; Self-lubricating; Wear parts; Zirconia

1. Introduction

The surface of a component can undergo degradation due to interaction with the environment or by a countersurface. Surface-healing materials are a special class of novel smart materials, which have the ability of repairing damage imposed by friction and wear.^{1,2} Several research efforts have been made to understand the different healing mechanisms of biological systems and it is tried to mimic these techniques in state-of-the-art material systems. For instance, bone healing is an example showing that, after significant damage, not only the human biological systems can return to full functionality, but also the initial structure is completely restored.³ Contrary to healing mechanisms in other tissues, which are repaired by producing scar tissue, bone has the ability to regenerate itself and therefore returns to its pre-fracture state.

Structural ceramics are used in several tribological applications since they possess unique properties, like resistance to wear and corrosion under high temperature conditions. Among them, yttria stabilized zirconia (3Y-TZP) has the highest fracture toughness. Basically, microfracture is the dominant wear mechanism when ceramic components operate under sliding contact conditions.^{4–6} Thus, in principle, it is expected that a higher fracture toughness enhances the wear resistance of ceramics. Despite the outstanding mechanical properties of 3Y-TZP, investigations of wear and friction of this material have revealed that it has a high friction coefficient under dry sliding conditions at high temperatures.^{7–10} Since liquid lubricants are not stable at higher temperatures, solid lubricants are currently used to reduce friction and wear when two ceramic surfaces are brought into contact. If the interface between two contacting ceramics contains a solid lubricant, the material can resist the stresses imposed by sliding motion. Although a solid lubricant film can reduce the friction coefficient and wear rate, removal of the layer itself by wear can be a problem. To increase the life time of the component and to avoid surface damage, a self-lubricating ceramic composite material consisting of a hard ceramic matrix and a supply of a solid lubricant embedded into the ceramic matrix is desirable.

* Corresponding author. Tel.: +31 534894325; fax: +31 53489 4784.

E-mail addresses: mahdiyar59@yahoo.com,
m.valefi@utwente.nl (M. Valefi).

Table 1
Mechanical properties of materials used.¹⁶

Material	Hardness (GPa)	Elastic modulus (GPa)	Fracture toughness (MPa m ^{1/2})	Grain size (μm)
Alumina	19.5 ± 0.9	320	3.3 ± 0.4	5 ± 0.5
CuO-TZP	9.3 ± 0.7	205	3.4 ± 0.3	2 ± 0.2

It is expected that stresses associated with sliding contact trigger the deformation of the solid lubricant and the formation of a friction reducing layer at the interface between the ceramic and the counter surface. This layer can be worn away during further sliding but it is regenerated by the composite material in the sliding contact.

There is an ongoing demand for developing high-temperature self-lubricating materials that satisfy the requirement of mechanical systems functioning under severe conditions, such as advanced engines that require increasingly high working temperatures (at 600 °C or even 1000 °C) and a long lifetime.^{11–14} In a previous paper a mechanical model has been described predicting the thickness of a lubricant layer in a self-lubricating ceramic composite materials during dry sliding tests.¹⁵ Further, it has been shown that the wear behaviour of CuO-TZP sliding against alumina depends on load and temperature.¹⁶ At room temperature the formation of an aluminium hydroxide layer results in reduced friction and wear rate.¹⁷ At intermediate temperatures (25 °C < *T* < 600 °C), CuO-TZP shows a rather high coefficient of friction, while at 600 °C it exhibits a friction coefficient of 0.35 and the specific wear rate of a value less than 10^{−6} mm³/N m. A detailed SEM/EDS and XPS analysis have been performed on the wear track to elucidate the wear mechanism at 600 °C for Y-TZP and CuO-TZP.¹⁶ The results reveal that CuO-TZP has a lower friction and wear rate below a critical load at 600 °C as compared to Y-TZP. However, investigation of the wear mechanisms of CuO-TZP at intermediate temperatures and temperature higher than 600 °C have not been reported yet.

In the work, described in this paper, wear of CuO-TZP at intermediate temperatures as well as 600 °C and 700 °C are investigated by using laser scanning microscopy (LSM), SEM/EDS and XPS. The main objective of this paper is to acquire a better understanding of the copper-rich phase and its influence on wear behaviour of CuO-TZP at intermediate temperatures as well as above 600 °C. Eventually the following questions will be addressed: Is a self-healing layer formed at all temperatures and is a low friction and wear rate obtained when CuO is added to TZP sliding against alumina?

2. Experimental

2.1. Material preparation

3Y-TZP (3 mol% yttria-doped tetragonal zirconia polycrystals: TZ3Y, Tosoh, Tokyo, Japan) and CuO (Aldrich, Steinheim, Germany) have been used as starting materials. Details on preparation are described elsewhere.¹⁸ In short to obtain 5 wt% CuO-TZP, appropriate amounts of CuO and 3Y-TZP were mixed and ball milled in ethanol for 24 h using high purity

zirconia balls. The milled slurry was dried at 120 °C for 24 h. The dried cake was ground in a mortar and sieved through a 180 μm sieve. The powder was uniaxially pressed into discs and subsequently cold isostatically pressed at 400 MPa. Samples were then sintered at 1500 °C for 8 h with a heating and cooling rate of 2 °C/min.

The sintered density was measured by immersion in mercury using the Archimedes method. The sintered discs were polished to a surface roughness (*R_a*) of <100 nm using a diamond paste. To remove the contaminants and to release residual surface stresses, all the polished discs were annealed at 850 °C for 2 h.

2.2. High temperature tribological experiments and characterization

High temperature tribological experiments were conducted using the ball on disc configuration on a pin-on-disc tribometer (CSEM, Neuchatel, Switzerland) capable of heating to 800 °C. Commercial high purity alumina balls with mirror-polished surfaces (GIMEX Technische Keramiek B.V., Geldermalsen, The Netherlands) and diameter of 10 mm were used as a counter surface. Before the sliding tests, both ball and disc were ultrasonically cleaned with isopropanol, rinsed with deionized water

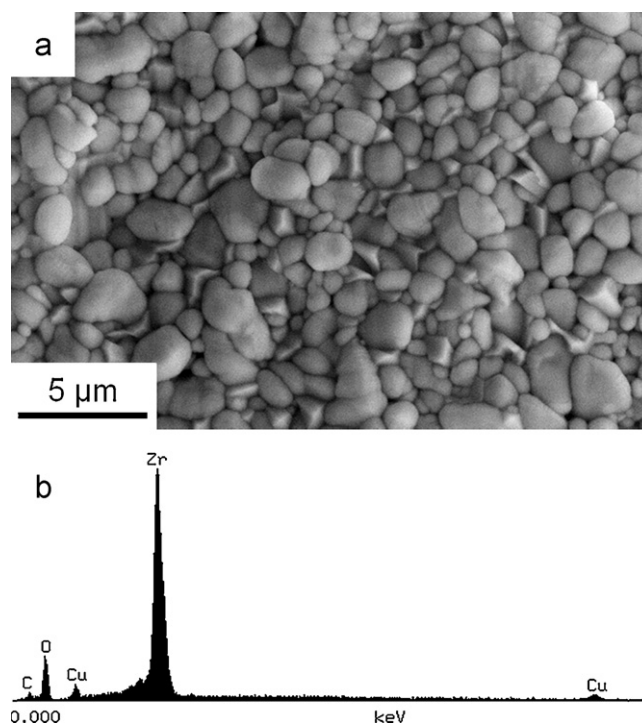


Fig. 1. (a) SEM micrograph of polished and thermally etched sintered CuO-TZP and (b) the corresponding EDS.

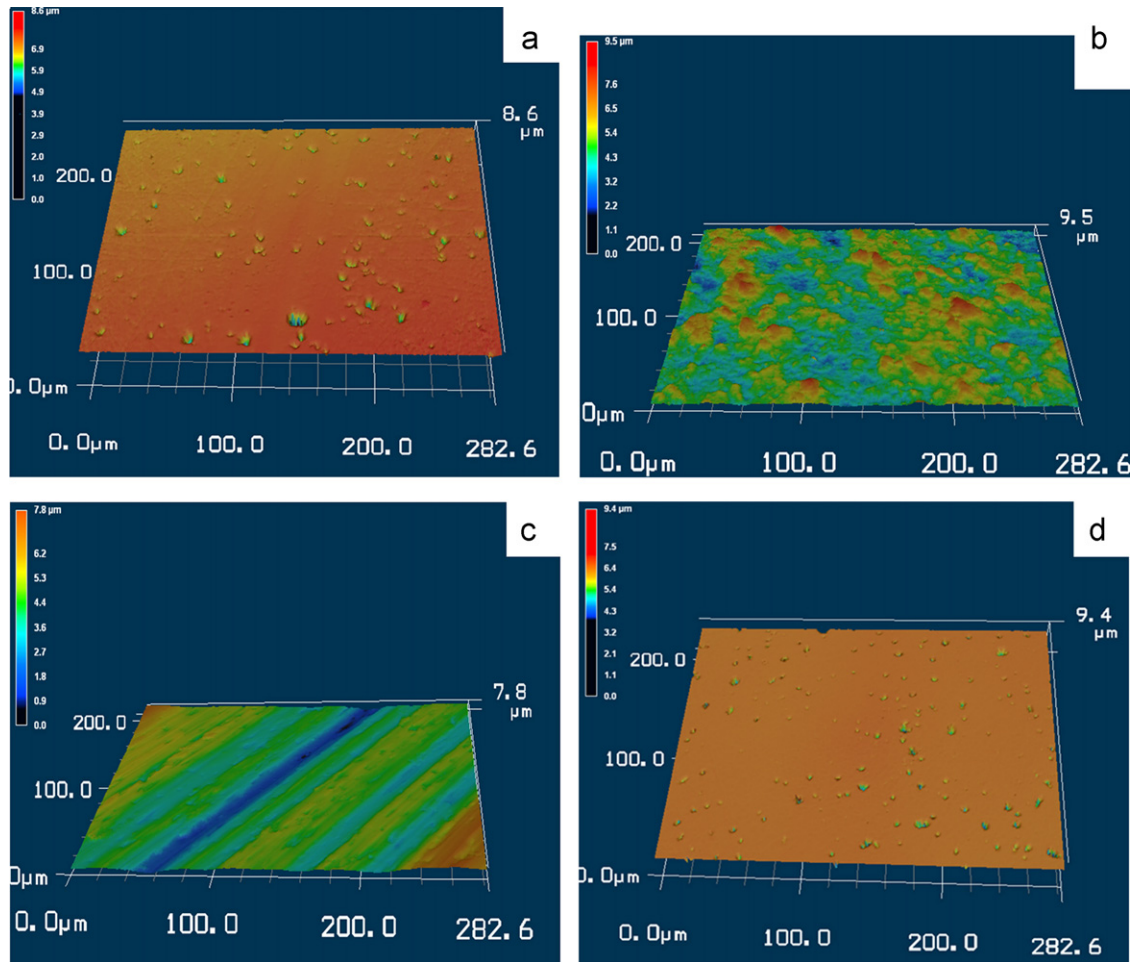


Fig. 2. 3D surface topography of CuO-TZP sliding against alumina using laser scanning microscopy; (a) before wear test and wear tracks, (b) at 200 °C, (c) at 400 °C and (d) at 600 °C ($F = 1$ N, $v = 0.05$ m/s).

and oven dried at 120 °C for 24 h. All tests were done with 1 N load (corresponding to an initial maximum Hertzian contact pressure of 0.52 GPa), a velocity of 0.05 m/s, a radius of the wear track 10–12 mm, a sliding distance of 1 km and test temperatures of 200, 400, 600 and 700 °C. All tests were performed three times. The amount of wear from the discs was determined by measuring the mass of the samples before and after the tests on a balance with a resolution of 0.01 mg. For a sample with negligible mass loss, interference microscopy has been used to determine the wear volume. The mass difference was then normalized by dividing the volume loss by the applied load and the sliding distance to gain the specific wear rate.

The Vickers hardness of the disc material was determined by a microindentation test at a load of 10 N and an indentation time of 10 s. Ten indentations were made and the average was taken. The fracture toughness was obtained using an indentation-strength method using the formula given by¹⁹:

$$K_{Ic} = \frac{0.016(E/H)^{1/2}P}{c^{3/2}} \quad (1)$$

where E is the elastic modulus, H is the Vickers hardness, P the load and c is the crack length measured from the centre of indent to the crack tip. The applied load was 98 N with an

indentation time of 10 s. An elastic modulus value of 205 GPa was calculated using the rule of mixture for CuO-TZP ($E_{TZP} = 210$,⁸ $E_{CuO} = 125$ ²⁰).

Since indentation fracture toughness is not an absolute value, this method gives relative information about fracture toughness of the two materials investigated in this work. Some mechanical properties of the materials used are summarized in Table 1.

Worn surfaces were examined by scanning electron microscopy (JEOL, JSM6400, Japan) equipped with an energy dispersive spectroscope (EDS). The surface topography was analysed by laser scanning microscopy (LSM), (Keyence VK-9700K, Japan) while chemical changes were detected by XPS (Model Quantera SXM, Physical Electronics, USA, using Al K_{α} (1486.6 eV) excitation source with monochromator).

3. Results

Fig. 1a shows the microstructure of a polished and thermally etched surface of 5 wt% CuO-TZP disc sintered at 1500 °C. The material shows an average grain size of 2 μm using the Mendelson method.²¹ Furthermore, EDS analysis (Fig. 1b) revealed that both zirconium and copper are present in the material. Ran et al.,¹⁸ who prepared identical ceramics in the same way as

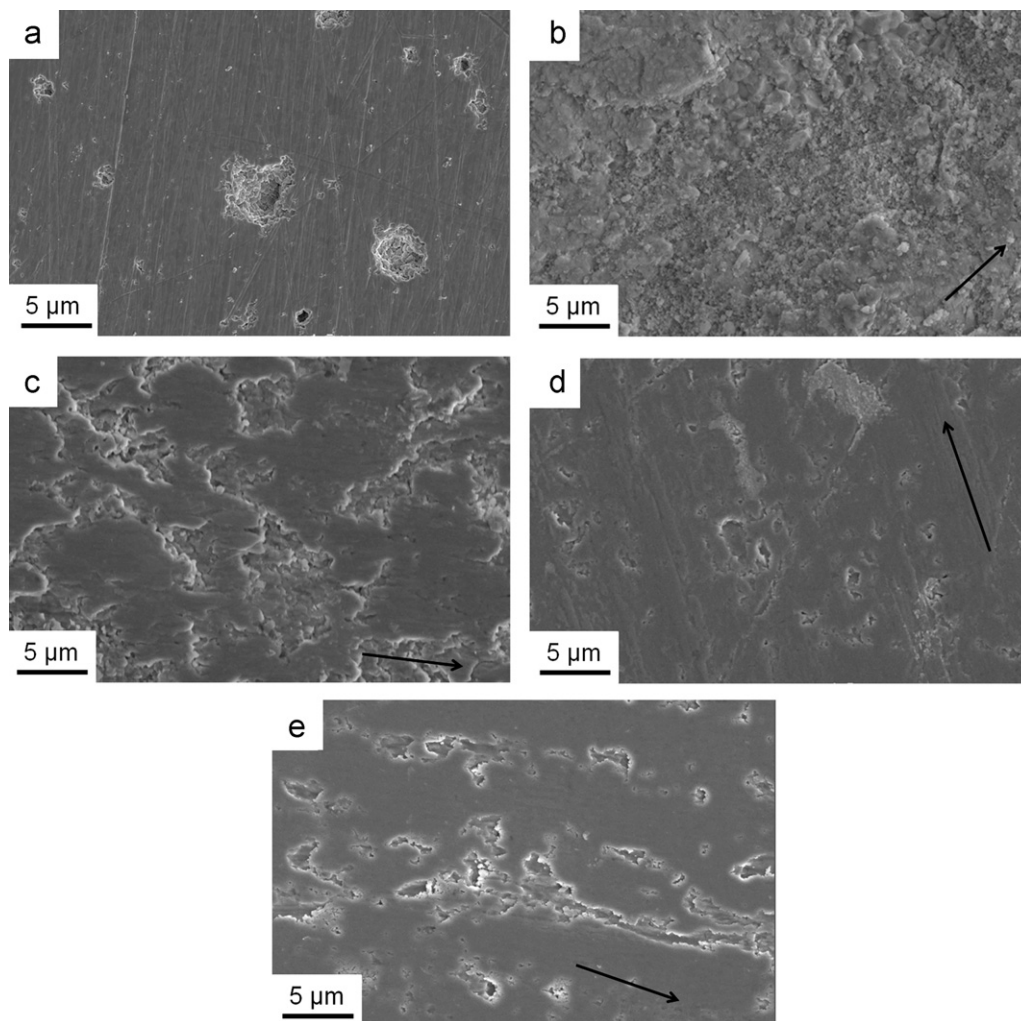


Fig. 3. SEM micrographs of CuO-TZP sliding against alumina ($F = 1$ N, $v = 0.05$ m/s). (a) The unworn surface and worn surfaces; (b) at 200 °C, (c) at 400 °C, (d) at 600 °C, and (e) at 700 °C (arrows indicate the sliding direction).

Table 2
Specific wear rate of CuO-TZP as a function of temperature.

Temperature (°C)	Coefficient of friction ^a	Specific wear rate ($\times 10^{-6}$ mm ³ /N m)
200	0.85 ± 0.02	1100 ± 20
400	0.71 ± 0.01	1900 ± 36
600	0.35 ± 0.05	0.43 ± 0.005^a
700	0.39 ± 0.01	0.18 ± 0.009

^a Data taken from Valefi et al.¹⁶

described in this paper, observed by TEM that copper oxide is present in CuO-TZP system. The sintered CuO-TZP has a relative density $>97\%$ and an average Vickers hardness of 9.3 ± 0.7 GPa.

Table 2 shows the coefficient of friction as well as specific wear rate data of CuO-TZP at different temperatures under an applied load of 1 N at a sliding speed of 0.05 m/s. The CuO-TZP composite reveals a high friction coefficient at 200 and 400 °C; however beyond 600 °C the composite shows a significantly lower coefficient of friction. At 200 °C, the wear rate of CuO-TZP is 1100×10^{-6} mm³/N m. At 600 °C, the wear

rate (0.43×10^{-6} mm³/N m) is 3–4 orders of magnitude lower than at 200 °C and 400 °C. This clearly indicates that the temperature has a strong influence on the wear behaviour of the CuO-TZP disc material. Although a few studies have shown low wear rates for self-lubricating zirconia composites at high temperatures (e.g. 800 °C),^{7,22} CuO-TZP results in a lower wear rate at relatively lower temperatures.

The 3D profile images of the disc material before and after sliding tests against an alumina ball at different temperatures are shown in Fig. 2. The CuO-TZP disc shows a smooth surface after polishing (Fig. 2a). Analysis of the measurement reveals that the roughness of the disc before wear test was $R_a = 0.08$ μm. After wear test at 200 and 400 °C the wear tracks become significantly rough (Fig. 2b and c). The measured surface roughness of CuO-TZP disc increased to 0.68 and 0.79 μm, respectively. Careful investigation on the wear track using laser scanning microscopy (Fig. 2b and c) indicates that the wear mechanism of CuO-TZP at 200 °C differs from 400 °C. It is clear from Fig. 2c that abrasive wear is the dominant wear mechanism at 400 °C. Similar observations of the wear mechanism have been reported for several ceramics at 200 and 400 °C.^{23–25} However, in this work at

600 °C the wear track shows a very smooth surface which is similar to that of the polished disc (Fig. 2d). The measured surface roughness of CuO-TZP disc only increased slightly from 0.08 to 0.095 μm after a wear test against an alumina ball at 600 °C.

To elucidate the wear mechanism, SEM analyses have been performed on the CuO-TZP wear tracks. Fig. 3 shows the micrographs of unworn and worn CuO-TZP discs at different temperatures. The unworn surface (Fig. 3a) shows a smooth surface with polishing lines. SEM images of Fig. 3b and c reveal severe wear at 200 °C and 400 °C resulting in a high roughness of the wear tracks. Moreover, Fig. 3b indicates that brittle fracture is the dominant wear mechanism at 200 °C and compaction of wear debris and plastic deformation does not take place. However, when the temperature increases to 400 °C, the wear track shows the formation of discontinuous smooth island-like (patchy) films in addition to a rough surface. When the temperature approaches 600 °C (Fig. 3d) a smooth layer (film) covers the wear track and causes low friction and low wear rate. The surface morphology after the wear tests at 600 °C is significantly different from that observed at 200 °C and 400 °C.

Fig. 4 shows the EDS analysis of wear track of CuO-TZP sliding against alumina at different temperatures. EDS analysis confirms the presence of Zr, Cu and Al in the wear track at 200 °C and 400 °C. However, on the wear track at 600 °C, Al was below the detection limit of EDS, indicating at that testing temperature no Al from the counterface was present on the wear track. The

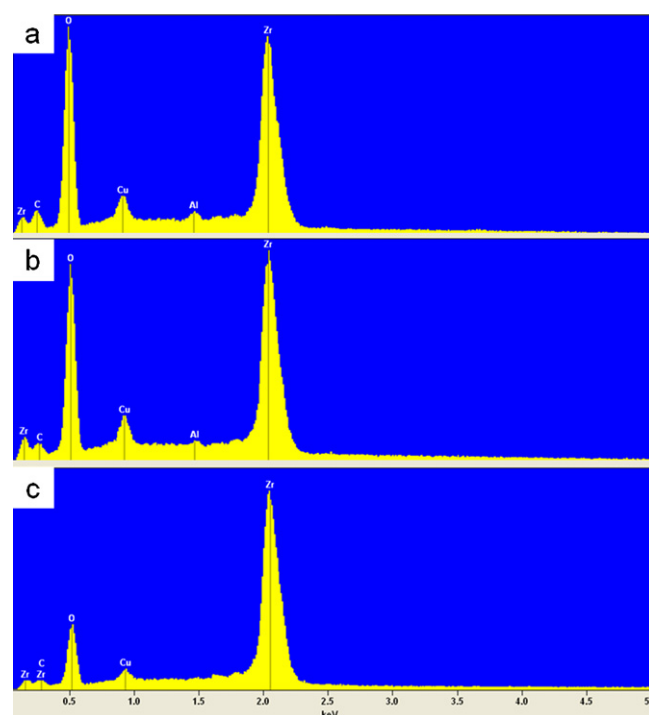


Fig. 4. EDS analysis of wear track of CuO-TZP sliding against alumina at different temperatures: (a) at 200 °C, (b) at 400 °C and (c) at 600 °C.

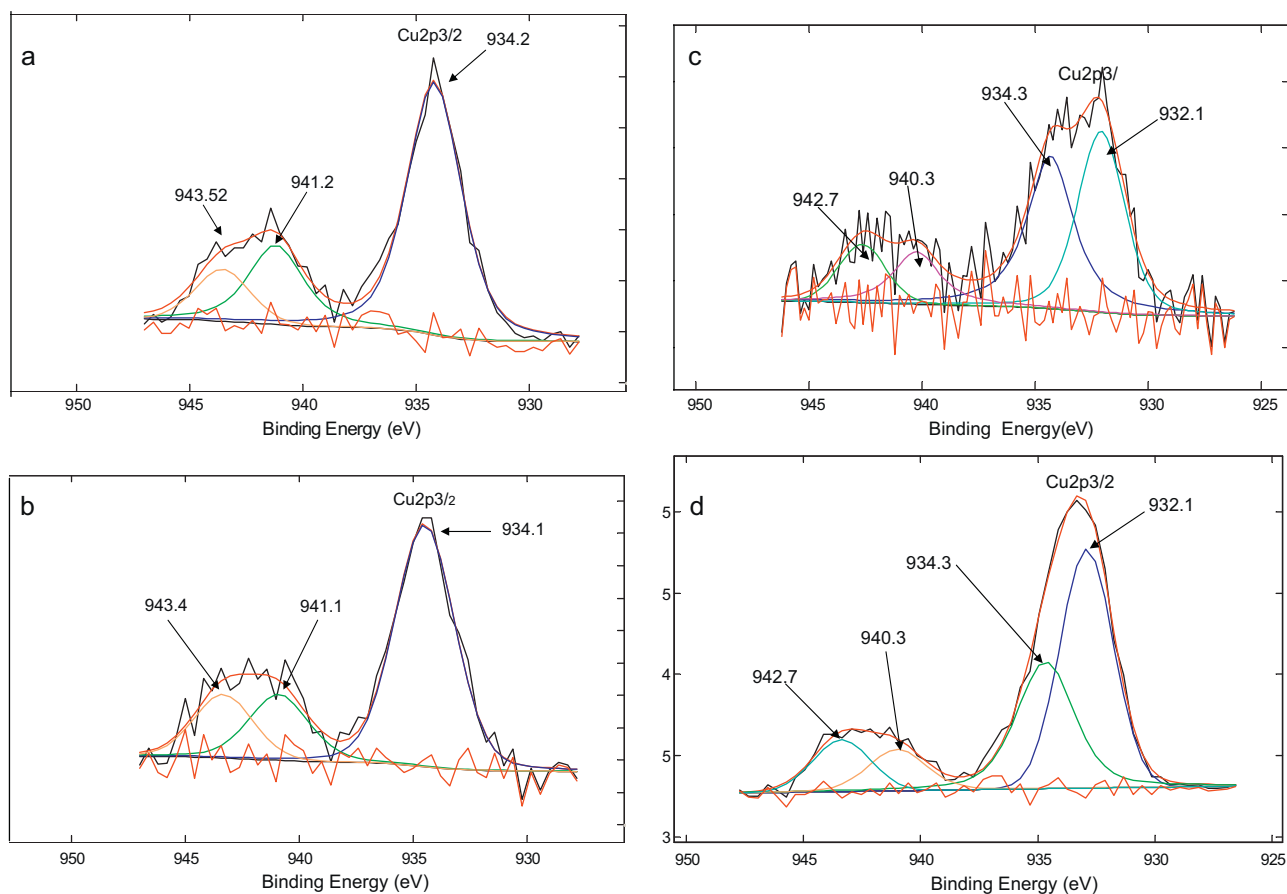


Fig. 5. Cu 2p XPS spectra of worn surface of CuO-TZP disc sliding against alumina ball (a) at 200 °C, (b) at 400 °C, (c) at 600 °C and (d) at 700 °C.

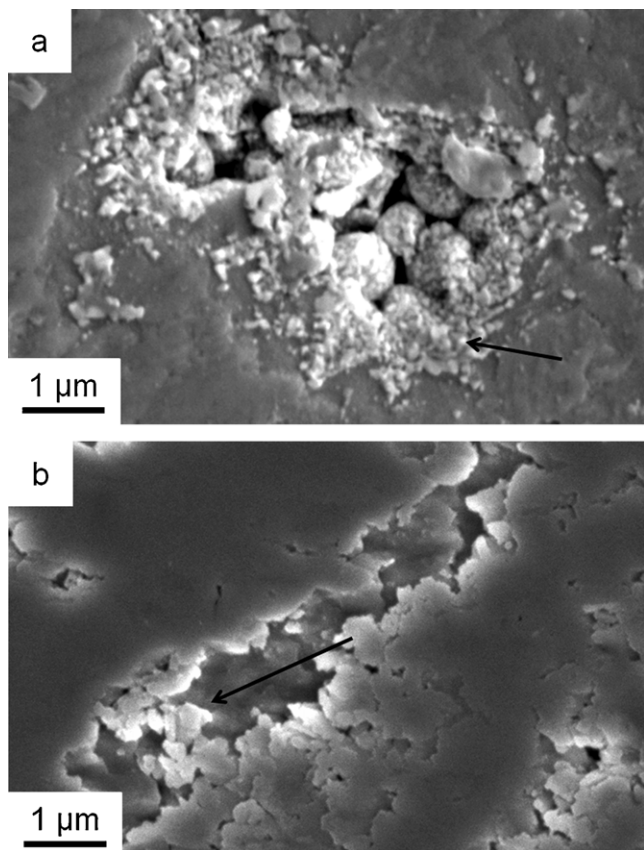


Fig. 6. SEM image of wear track of CuO-TZP (a) at 600 °C and (b) at 700 °C (arrow indicating clusters of wear debris).

presence of Al and Cu at 200 °C and 400 °C suggests that at these temperatures, in addition to ZrO₂ and CuO, the wear track is covered with aluminium oxide from the counterface.

The XPS spectra of copper on the wear track at 200 °C, 400 °C, 600 °C and 700 °C are given in Fig. 5. The core level Cu 2p_{3/2} XPS at ~934 eV and satellite peaks at a higher binding energy of ~941 and 943.5 eV as given in Fig. 5a and b are in good agreement with the data of the Handbook of X-ray Photoelectron Spectroscopy indicating the presence of CuO in the wear track.²⁶ However careful inspection on the XPS spectra of copper at 600 °C and 700 °C (Fig. 5c and d) reveal that both Cu²⁺ and Cu¹⁺ (with peaks at BE = 932.1 eV) are formed while alumina is sliding against CuO-TZP. The influence of Cu₂O on friction and wear of CuO-TZP will be discussed later.

4. Discussion

The tribological results obtained at different temperatures reveal that below a critical temperature CuO-TZP shows a higher friction and wear rate at the same load and sliding velocity while it is sliding against alumina under dry conditions. It is well-known that wear debris plays a crucial role in friction and wear of ceramics.^{27–30} A higher coefficient of friction can be caused by the presence of loose wear debris which acts abrasively during sliding tests. In the current study, the formation of a smooth layer and its stability is dependent on the temperature during the tribological experiment. XPS analysis shows that above a

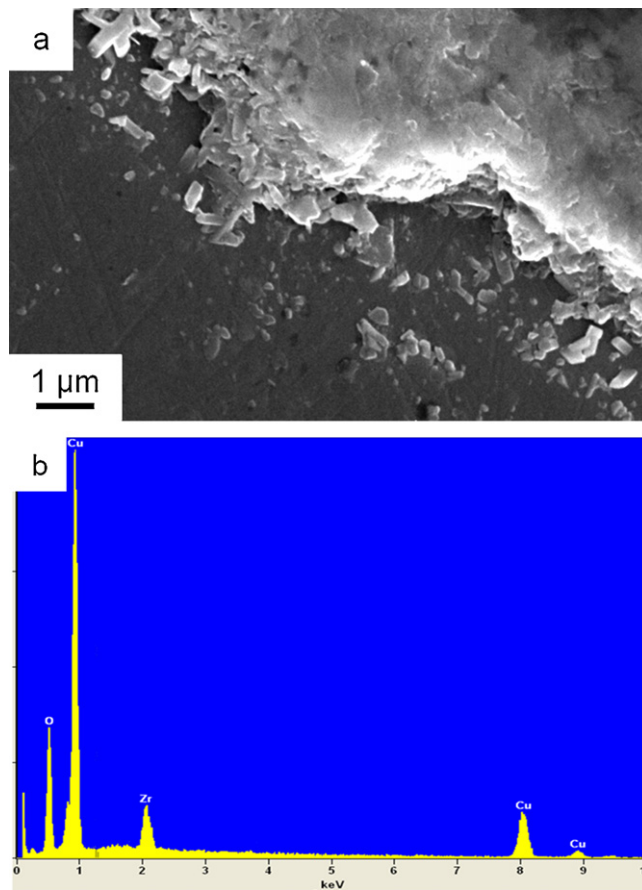


Fig. 7. (a) SEM image of the transfer layer of wear debris formed on alumina ball sliding against CuO-TZP at 600 °C, (b) corresponding EDS ($F = 1$ N, $v = 0.05$ m/s).

critical temperature T_c ($400^\circ\text{C} < T_c < 600^\circ\text{C}$) copper is present in the wear track both in the form of Cu²⁺ and Cu¹⁺. This has been confirmed by XPS analysis on the 600 and 700 °C tested samples.

Copper oxide has two phases: Cu₂O (cuprite or cuprous oxide) and CuO (tenorite or cupric oxide). The former is cubic and the latter has a monoclinic crystal structure. CuO is dissociated into Cu₂O above 1000 °C by the following reaction^{31,32}:



The standard Gibbs energy (in kJ) for this reaction is as follows³³:

$$\Delta G_T^\circ = 146.32 + 25.54T \log T - 185.47T \quad (298\text{--}1300 \text{ K}) \quad (2)$$

At 600 °C (873 K) one can calculate from Eq. (2) that the Gibbs energy is: −97.6 kJ. Based on thermodynamics, it is therefore possible that CuO dissociates at 600 °C. However, a kinetic barrier impedes the dissociation reaction below 1000 °C. Beside, it has been reported that CuO can be reduced by mechanical activation in the presence of carbon at room temperature since the standard free energy formation of Cu₂O in the presence of carbon was estimated −88 kJ.³⁵ Based on our XPS observation and assuming low frictional heating,³⁴ it is suggested that the

copper oxide wear debris undergoes mechanical activation which enhances the dissociating reaction of CuO to Cu_2O at 600°C . Furthermore it has been reported that this Cu_2O phase shows extensive plastic deformation above 600°C .³⁵ This formation of Cu_2O at 600°C is associated with onset of enormous plastic deformation.

The generated wear debris has a dualistic role; either as abrasive particles at lower temperatures or as a part of a patchy layer undergoing plastic deformation around 600°C . The mechanical properties of this third body are important for the tribological behaviour.^{28,38} The presence of a soft ‘third body’ will lower the stresses in the material and will, in turn, reduce wear.^{36,37} On the contrary, since oxide ceramics show poor plastic deformation at low temperatures, the third body produces severe damage on the wear track as shown in Fig. 3b and c. At 200°C the entrapped debris, generated by brittle fracture (Fig. 3b), is responsible for the higher coefficient of friction as compared to 400°C . However above 600°C , this submicron wear debris, shown in Fig. 6, reattached (together) and is smeared out over the surface by opposing asperities and forms the smooth third body. Further sliding induced shear by friction and removes the third body and transfers it to the alumina counterface at the edge of contact area as shown in our recent work.¹⁶ A careful look at Fig. 7a and corresponding EDS indicates accumulation of debris at the edge of the wear scar with a substantial amount of copper. This may be a further evidence that a copper rich layer is formed on the wear track which is consistent with the XPS results.

As can be seen in Fig. 3c, islands consisting of wear debris are formed when the temperature is 400°C . It has been reported that these islands can increase the load-carrying capacity at the wear track and consequently decreases the wear rate.²⁸ Although there are few islands formed at 400°C , CuO -TZP still shows a high friction and wear rate. This can be attributed to the presence of harder wear particles which promote abrasive wear of the disc material as shown in Fig. 2c. When the temperature is increased to 600°C , the area of the islands drastically increases and the surface becomes smoother which results in a lower contact pressure at the asperities and a lower friction and wear of the material couple.

Based on XPS analysis of the wear tracks at 600°C and 700°C , it is obvious that the smooth third body consisted of a mixture of Cu^+ and Cu^{2+} rich phase. As mentioned earlier, Cu_2O shows enhanced plastic deformation at a temperature of 600°C .³⁵ Therefore, at 600°C , the low friction is ascribed to plastic deformation, squeezing out and smearing of copper oxide under formation of a ‘smooth third body’ on the wear track. Although this smooth third body is plastically deformed, removed and transferred to the alumina counterface (Fig. 7), it can be regenerated by the copper rich phase at the surface and grain boundary. This process can be regarded as self-healing since the layer is continuously reformed and regenerated due to mechanical stresses in the contact itself. Below 600°C , the smooth third body is not formed and the presence of harder wear debris demolishes the formation of a compacted debris layer.

Zhang et al.,²² studied high temperature tribological properties of Mo -TZP nanocomposite. They found low friction at 800°C and ascribed this to the formation of MoO_3 , which shows

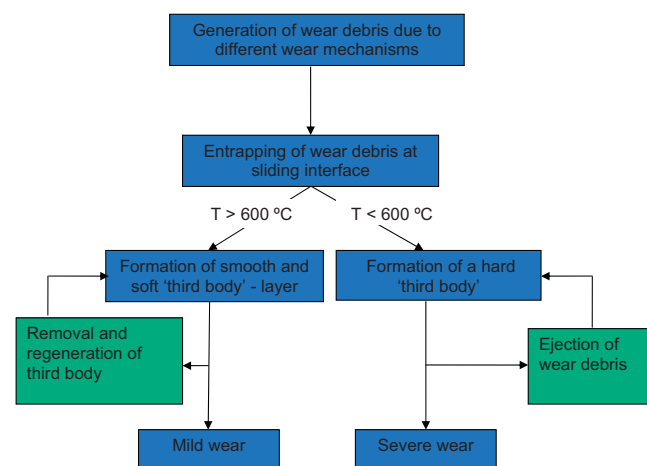


Fig. 8. Diagram showing the wear processes, taking place at the contact area between ball and plate.

plastic deformation at high temperatures and functions as a self-lubricant layer. Although our results show good consistency with their results, it emerges from this study that copper oxide triggers a self-healing layer at lower temperatures.

Based on results in the present research a wear process is proposed in Fig. 8, which results in a self-healing ceramic surface. According to this diagram, the design of a ceramic composite with a soft second phase can enhance the formation of a smooth third body (layer) which can later protect the material from further damage and increase the lifetime of the ceramic component. It is also noteworthy to mention that formation of a self-healing layer is influenced not only by material but also by system conditions (temperature, load, sliding velocity, etc.). Further work on modelling of a stable third body using a contact mechanics approach is ongoing and the results will need to be compared with the experimental results.

5. Conclusion

1. CuO -TZP exhibits a coefficient of friction of 0.85, 0.7, 0.35 and 0.4 at 200, 400, 600 and 700°C respectively.
2. The low friction at 600 and 700°C is attributed to the formation of a smooth third body (layer) which is generated by plastic deformation of copper-rich wear debris. The third body, containing the soft Cu_2O phase, is deformed and removed from interface while it is regenerated and healed by the sliding contact. The formation of this stable third body is likely to be load dependent and beyond a critical load this smooth third body will be removed during further sliding.
3. The lower friction at 400°C as compared to 200°C is ascribed to the formation of small islands of wear debris on the wear track. However, at both temperatures the wear rate is of the same order, since the load-carrying capacity of third body is insufficient.
4. CuO is a promising solid lubricant for designing a self-lubricating ceramic matrix composite at high temperatures. It is found that simultaneous plastic deformation and dissociation of CuO at $T \geq 600^\circ\text{C}$ may enhance smooth third body

formation and eventually resulting in low friction and wear rate of CuO-TZP.

Acknowledgments

The authors thank to L. Vargas, E.G. de Vries and W. Lette for assistance with SEM, hardness and confocal microscopy measurements respectively. G. Kip is appreciated for his XPS analysis. Funding of this work was supported by the Dutch governmental program “IOP Self Healing Materials”.

References

1. Van der Zwaag S, Van Dijk NH, Jonkers HM, Mookhoek SD, Sloof WG. Self-healing behaviour in man-made engineering materials: bioinspired but taking into account their intrinsic character. *Philos Trans R Soc A* 2009;**367**(1894):1689–704.
2. Nosonovsky M, Bhushan B. Surface self-organization: from wear to self-healing in biological and technical surfaces. *Appl Surf Sci* 2010;**256**(12):3982–7.
3. Fratzl P, Weinkamer R. Nature's hierarchical materials. *Prog Mater Sci* 2007;**52**:1263–334.
4. Lee SW, Hsu SM, Shen MC. Ceramic wear maps: zirconia. *J Am Ceram Soc* 1993;**76**(8):1937–47.
5. Hsu SM, Shen MC. Ceramic wear maps. *Wear* 1996;**200**(1–2):154–75.
6. Kerkwijk B, Winnubst AJA, Verweij H, Mulder EJ, Metselaar HSC, Schipper DJ. Tribological properties of nanoscale alumina–zirconia composites. *Wear* 1999;**225–229**:1293–302.
7. Ouyang JH, Li YF, Wang YM, Zhou Y, Murakami T, Sasaki S. Microstructure and tribological properties of $ZrO_2(Y_2O_3)$ matrix composites doped with different solid lubricants from room temperature to 800 °C. *Wear* 2009;**267**:1353–60.
8. Bundschuh W, Gahr KH. Effect of temperature on friction and oscillating sliding wear of dense and porous 3Y-TZP zirconia ceramics. *Tribol Int* 1994;**27**:97–103.
9. Murakami T, Umeda K, Sasaki S, Ouyang J. High-temperature tribological properties of strontium sulfate films formed on zirconia–alumina, alumina and silicon nitride substrates. *Tribol Int* 2006;**39**:1576–83.
10. Pasaribu HR, Reuver KM, Schipper DJ, Ran S, Wiratha KW, Winnubst AJA, et al. Environmental effects on friction and wear of dry sliding zirconia and alumina ceramics doped with copper oxide. *Int J Refract Met Hard Mater* 2005;**23**:386–90.
11. Zhu S, Bi Q, Wu H, Yang J, Liu W. NiAl matrix high-temperature self-lubricating composite. *Tribol Lett* 2011;**41**:535–40.
12. Zhu S, Bi Q, Yang J, Liu W, Xue Q. Ni3Al matrix high temperature self-lubricating composites. *Tribol Int* 2011;**44**:445–53.
13. Pasaribu HR, Sloetjes JW, Schipper DJ. Friction reduction by adding copper oxide into alumina and zirconia ceramics. *Wear* 2003;**255**:699–707.
14. Jin Y, Kato K, Umehara N. Further investigation on the tribological behaviour of Al_2O_3 –20Ag20 CaF₂ composite at 650 °C. *Tribol Lett* 1999;**6**:225–32.
15. Song J, Valefi M, de Rooij M, Schipper DJ. A mechanical model for surface layer formation on self-lubricating ceramic composites. *Wear* 2010;**268**:1072–9.
16. Valefi M, de Rooij MB, Schipper DJ, Winnubst L. High temperature tribological and self-lubricating behaviour of copper oxide-doped Y-TZP composite sliding against alumina. *J Am Ceram Soc* 2011;**94**:4426–34.
17. Song J, Valefi M, de Rooij MB, Schipper DJ. The effect of alumina counterface on the friction reduction of CuO/3Y-TZP composite at room temperature. *Wear* 2012;**274–275**:75–83.
18. Ran S, Winnubst AJA, Blank DHA, Pasaribu HR, Sloetjes J-W, Schipper DJ. Effect of microstructure on the tribological and mechanical properties of CuO-doped 3Y-TZP ceramics. *J Am Ceram Soc* 2007;**90**:2747–52.
19. Anstis G, Chantikul P, Lawn B, Marshall D. A critical evaluation of indentation techniques for measuring fracture toughness: I, direct crack measurements. *Journal of the American Ceramic Society* 1981;**64**:533–8.
20. Lump JK, Chen N, Gorreta KC, Herro HM. Mechanical properties of CuO. *High Temp Mater Process* 1990:1–5.
21. Mendelson MI. Average grain size in polycrystalline ceramics. *J Am Ceram Soc* 1969;**52**:443–6.
22. Zhang Y-S, Hu L-T, Chen J-M, Liu W-M. Lubrication behaviour of Y-TZP/ Al_2O_3 /Mo nanocomposites at high temperature. *Wear* 2010;**26**:1091–4.
23. Melandri C, Gee MG, de Portu G, Guicciardi S. High temperature friction and wear testing of silicon nitride ceramics. *Tribol Int* 1995;**28**:403–13.
24. Yust CS, Carignan FJ. Observations on the sliding wear of ceramics. *ASLE Trans* 1985;**28**:245–52.
25. Dong X, Jahanmir S, Ives LK. Wear transition diagram for silicon carbide. *Tribol Int* 1995;**28**:559–72.
26. Moulder JF, Stickle WF, Sobol PE, Bomben KD, editors. *Handbook of X-ray photoelectron spectroscopy*. 1992.
27. Fischer TE, Zhu Z, Kim H, Shin DS. Genesis and role of wear debris in sliding wear of ceramics. *Wear* 2000;**245**:53–60.
28. Denape J, Lamon J. Sliding friction of ceramics: mechanical action of the wear debris. *J Mater Sci* 1990;**25**:3592–604.
29. Kato K, Adachi K. Wear of advanced ceramics. *Wear* 2002;**253**:1097–104.
30. Ajayi OO, Erdemir A, Lee RH, Nichols FA. Sliding wear of silicon carbide–titanium boride ceramic–matrix composite. *J Am Ceram Soc* 1993;**76**:511–7.
31. Ran S, Winnubst AJA, Wiratha W, Blank DHA. Sintering behaviour of 0.8 mol%-CuO-doped 3Y-TZP ceramics. *J Am Ceram Soc* 2006;**89**:151–5.
32. Seidensticker JR, Mayo MJ. Thermal analysis of 3-mol%-yttria-stabilized tetragonal zirconia powder doped with copper oxide. *J Am Ceram Soc* 1996;**79**:401–6.
33. Kubashewski O. Metallurgical. *Thermochemistry* 1967:423.
34. Tokumitsu K. Reduction of metal oxides by mechanical alloying method. *Solid State Ionics* 1997;**101–103**:25–31.
35. Vagnard G, Washburn J. Plastic deformation of cuprous oxide. *J Am Ceram Soc* 1968;**51**:88–94.
36. Godet M. The third-body approach: a mechanical view of wear. *Wear* 1984;**100**:437–52.
37. Fillot N, Iordanoff I, Berthier Y. Wear modeling and the third body concept. *Wear* 2007;**262**:949–57.
38. Singer IL. How third-body processes affect friction and wear. *MRS Bull* 1998;**23**:37–40.