Wear 267 (2009) 1696–1701

Contents lists available at ScienceDirect

Wear

journal homepage: www.elsevier.com/locate/wear

Dry-sliding self-lubricating ceramics: CuO doped 3Y-TZP

Shen Ran[a], Louis Winnubst[a,*], Dave H.A. Blank[a], Henry R. Pasaribu[b], Jan-Willem Sloetjes[b], Dik J. Schipper[b]

[a] *Inorganic Materials Science, Faculty of Science and Technology and MESA+ Institute for Nanotechnology, University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands*
[b] *Surface Technology and Tribology Section, Faculty of Engineering Technology, University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands*

ARTICLE INFO

Article history:
Received 19 September 2007
Received in revised form 12 April 2009
Accepted 18 June 2009
Available online 26 June 2009

Keywords:
Ceramics
Solid lubrication
Zirconia
Dry sliding

ABSTRACT

Dense 8 mol% CuO doped 3Y-TZP ceramics prepared by pressureless sintering at 1500 °C exhibits a good wear-resistance (specific wear rate $k < 10^{-6}$ mm^3 N^{-1} m^{-1}) and promisingly low friction (coefficient of friction $f = 0.2$–0.3) when sliding against an alumina ball under unlubricated conditions. It was recognized that a self-lubricating mechanism is the most important contribution to the reduction of friction. During operation of the tribosystem, a soft interfacial patchy layer is generated in the contact area. As confirmed by calculations, based on a deterministic friction model, this soft interfacial patchy layer reduces friction. It was demonstrated that the presence of copper oxide is important for the formation of such an interfacial layer. The mechanism of the transition from mild to severe wear was also investigated. Detachment of a top layer in the wear track was proven to be the main reason for this tribological change.

1. Introduction

In engineering applications wear and friction need to be minimized to avoid energy losses and fast damage of machine components. At present liquid lubricants, which are mainly organic substances, are widely used to reduce wear and friction. However, due to economic and environmental reasons, the use of liquid lubricants is more and more unfavorable. Additionally, under some special circumstances, such as in high vacuum and at high temperatures, liquid lubricants cannot be used. Therefore it is increasingly interesting to develop new engineering materials, which can be used under dry contact sliding situations. It is now generally recognized that materials suitable for unlubricated tribo-applications should fulfill the following two criteria: the specific rate, k, is less than 10^{-6} mm^3 N^{-1} m^{-1}; and the coefficient of friction, f, is less than 0.2 [1].

Zirconia based ceramics are one of the promising materials for tribo-engineering applications. Good wear resistance combined with high bending strength and fracture toughness were obtained on these materials [2–6]. However, coefficient of friction of those dry sliding ceramic tribosystems generally varies in a range of 0.5–1.0, which is unacceptable for real applications. Recently it was reported that, under unlubricated (dry sliding) conditions, the coefficient of friction of yttria-doped tetragonal zirconia (3Y-TZP) ceramics can be reduced to a promisingly low value (0.25) by addition of CuO [7–9]. The reduction of coefficient of friction was expected to be caused by the self-lubricating effect [10] of a soft second phase in the hard matrix of the 3Y-TZP [7–9]. However details on the self-lubrication mechanism for reduction of friction have not been reported yet and will be treated in this paper. The wear tracks after the tribological tests were carefully analyzed by using SEM, EDX, XRD and nano-indentation. The mechanism of reduction in coefficient of friction will be discussed, based on a deterministic friction model as developed by Pasaribu [9].

2. Experimental

Dense ceramic discs of 8 mol% CuO doped 3Y-TZP were prepared from commercial submicron 3Y-TZP (3 mol% Yttria doped Tetragonal Zirconia Polycrystals: TZ3Y, Tosoh, Japan) and CuO (Aldrich, Germany) starting powders. Appropriate amounts of powders were mixed by wet-milling for 24 h in a polyethylene bottle, using ethanol and zirconia balls as milling media. After drying and grinding, the powder was sieved through a 180 μm sieve. Green compacts of the composite powder with a diameter of 50 mm and a thickness of around 5 mm were prepared by uniaxial pressing at 30 MPa followed by isostatic pressing at 400 MPa. The 8 mol% CuO doped 3Y-TZP discs were sintered in stagnant air at 1500 °C for 8 h, with a heating and a cooling rate both of 2 °C min^{-1}. After sintering the discs reached a relative density more than 95% (measured according to Archimedes principle in mercury). Undoped 3Y-TZP sample discs were prepared by the same compaction method as used for the CuO doped one, followed by sintering at 1400 °C for 2 h. The sintered undoped 3Y-TZP discs exhibits a relative density of 99%.

* Corresponding author. Tel.: +31 53 489 2994; fax: +31 53 489 4611.
E-mail address: a.j.a.winnubst@utwente.nl (L. Winnubst).

0043-1648/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.wear.2009.06.033

The sintered discs were polished to a surface roughness (R_a) of 0.1 μm using diamond paste. The polished discs were ultrasonically cleaned in ethanol and then annealed at 850 °C for 2 h to remove carbon contamination and release surface stresses.

Dry sliding tribological tests were performed on a pin-on-disc tribometer (CSEM, Switzerland), using the ball on disc geometry. The ceramic disc was mounted on a holder, which is driven by a motor for controlled sliding velocity and sliding distance. A commercial alumina ball (Gimex Technische Keramiek b.v., The Netherlands) of 10 mm in diameter was used as counter material. The normal load is applied by placing a corresponding mass on top of the pin. In order to obtain constant test conditions the tribometer was placed in a controlled environment with the temperature set at 23 °C and the relative humidity at 40%. For each test a normal load of 5 N (maximum Hertzian pressure = 0.9 GPa) and a sliding velocity of 0.1 m s^{-1} were applied. The sliding distance was at least 1 km.

Wear track morphologies were analyzed using SEM equipped with an Energy dispersive X-ray analyzer (EDX, Thermo Noran Instruments) was used to analyze chemical composition. X-ray diffraction (XRD, X'pert_APD, PANalytical) was performed to analyze phase composition inside and outside the wear tracks. Nano-indentation experiments were carried out inside and outside the wear tracks to determine hardness of the materials in the outermost region of the samples. The indentation process starts by loading a nano-indenter with an increased load at a constant rate to a certain value, held at the peak value for a preset amount of time and then unloaded to zero at the same rate as that for loading. By analyzing the loading–unloading curve hardness value was determined as a function of indentation depth. Details of the nano-indentation experiments are described elsewhere [9].

3. Results and discussion

3.1. Tribological test

Fig. 1 shows the coefficient of friction of undoped and 8 mol% CuO doped 3Y-TZP as a function of the sliding distance. The CuO doped disc shows a coefficient of friction of 0.25–0.35 within a sliding distance of 1.2 km, which is significantly lower than that of an undoped 3Y-TZP measured under the same conditions (f = 0.6–0.7 when a normal load of 5 N and a sliding velocity of 0.1 m s^{-1} was applied). The specific wear rate associated with this low friction region is much less than 10^{-6} mm^3 N^{-1} m^{-1}, indicating that mild wear is dominant in this region. After this low friction region

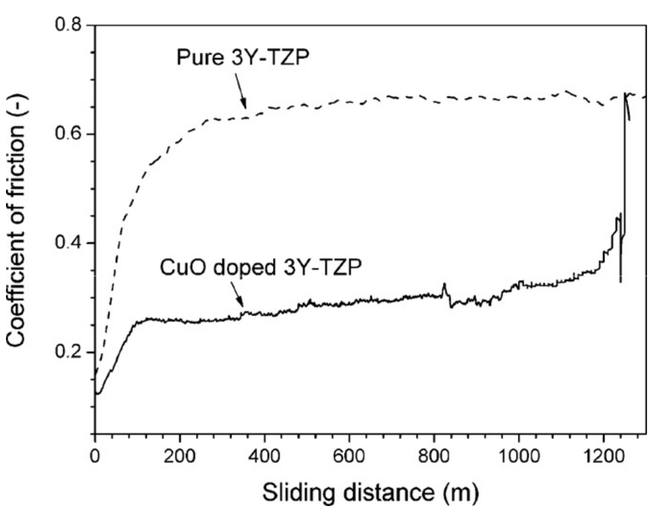

Fig. 1. Coefficient of friction of undoped and 8 mol% CuO doped 3Y-TZP ceramics, when sliding against an alumina ball, as a function of sliding distance.

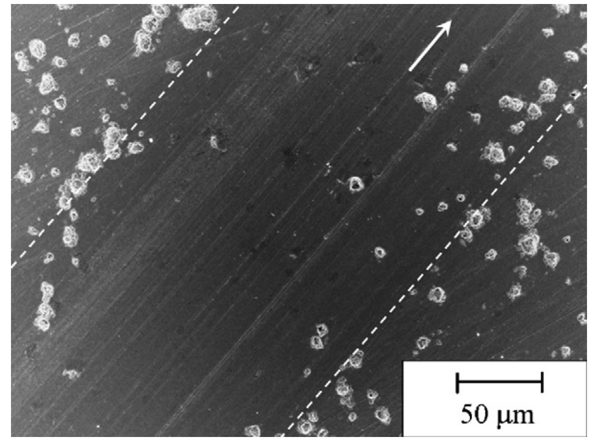

Fig. 2. SEM taken from a 3Y-TZP doped with 8 mol% CuO, after tribological test for around 0.2 km. The weak track is denoted within the two white dot lines and sliding direction is denoted by the white arrow.

(first 1.2 km sliding), the coefficient of friction of the CuO doped 3Y-TZP sample increases drastically up to a level higher than 0.6. Simultaneously the wear rate turned to be much higher than 10^{-6} mm^3 N^{-1} m^{-1}, which clearly indicates a transition from mild to severe wear. The coefficient of friction and specific wear rate of the undoped 3Y-TZP sample remain steady.

3.2. Wear track characterization

In order to reveal the mechanism of reduction in coefficient of friction, the wear tracks were analyzed in detail by various techniques. Fig. 2 compares general features of the surface inside and outside the wear track. After around 0.2 km the wear track had a width of approximately 250 μm. A coefficient of friction of 0.25 is corresponding to this sliding region. At the surface outside the wear track a large amount of voids with a typical size of several micrometres are present. These surface voids are formed by pull-out of clusters of grains during polishing. If more attention is paid to polishing (e.g. mild polishing) the surface voids are not visible. However mild polishing gives the same tribological results as discussed in this paper.

Inside the wear track only few pores can be observed, indicating elimination of the surface voids during sliding against an alumina ball. The wear track shows no significant surface damage except some narrow wear grooves, which seem to be formed by ploughing. All these wear-track features are in good agreement with the observed mild wear situation. A surface profile across the wear track is shown in Fig. 3. As can be seen from the figure the roughness inside the wear track is much less than that of the area outside the wear track (as-polished surface). Additionally the surface of the wear track is slightly elevated. The elevation of the wear track surface is likely to be caused by deposition of wear debris from both the alumina ball and the tested CuO doped 3Y-TZP sample.

More details on the morphology of the same wear track are shown in Fig. 4. Some smooth dark areas with various sizes and irregular shape can clearly be observed inside the wear track (Fig. 4a). These dark areas also give lower yield of back-scattered electrons on the SEM image (Fig. 4b), indicating the presence of elements with lower atomic number if compared with other parts of the wear track and is best illustrated by the surface void adjacent to a large dark area as marked by the white circle in Fig. 4a. It is assumed that this void already exists prior to the wear experiment and is caused by polishing of the sample. During wear test debris is generated from both the tested sample disc and the alumina ball. Under influence of the high contact pressure during sliding,

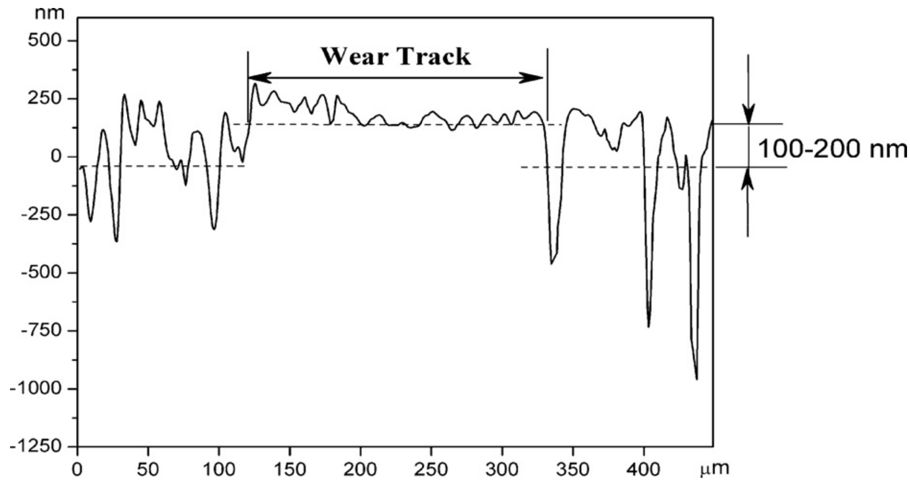

Fig. 3. Surface profile across the wear track after 0.2 km sliding (8 mol% CuO doped 3Y-TZP).

wear debris is continuously pressed into the voids. This explains the elimination of surface voids in the wear track (Fig. 2).

Fig. 4c and d shows enlarged morphologies of areas as marked by the white boxes I and II in Fig. 4a. Significant micro-fracture patterns perpendicular to the sliding direction are visible on area I (as e.g. pointed by the white arrows in Fig. 4c), although the amount and size of these cracks is rather small. Area-II shows a very similar feature as that of the smooth dark areas as observed in Fig. 4a. This suggests that area-II consists of the same material as the smooth dark areas, i.e. the wear debris. It is very likely that an outermost layer of wear debris material is deposited in area-II. But the layer is too thin to be recognized by the back-scattered electron image, which normally collects signals of the region up to 100 nm underneath the material surface.

It is important to note that the formation of the thin patchy layer of debris material in the wear track as shown in Fig. 4d is independent of the presence of surface voids. In the wear track on a better polished sample without surface voids, which shows also a low coefficient of friction ($f = 0.25$ when a normal load of 5 N and a sliding velocity of 0.1 m s^{-1} were applied), these patchy layers were also observed.

These patchy layers play an important role in the reduction of coefficient of friction of the tribosystem system. A sound knowledge on the characteristics of these layers, for instance, chemical composition and mechanical properties, is important to understand the mechanism of the reduction in friction. A rough estimation of the thickness based on the surface profile (see Fig. 3) shows that it is in the range between 100 and 200 nm. The chemical composition of the patchy layer is difficult to determine directly because its thickness is too small to be analyzed properly by methods like EDX. However the wear debris compacted in the surface voids is thick enough to be analyzed by EDX attached to the SEM. This is actually the reason why samples with surface voids are presented in this work.

Fig. 5 shows the elemental distribution of the same region as shown in Fig. 4, as measured by the EDX mapping technique. Quan-

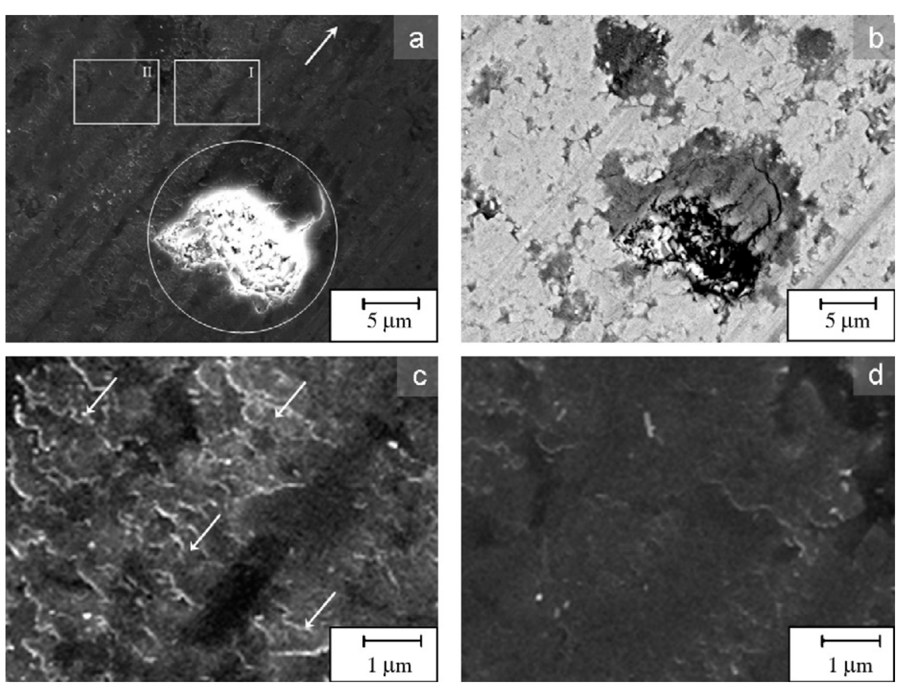

Fig. 4. Higher magnification SEM images of the same wear track as shown in Fig. 2. (a) Secondary electron image, white arrow denotes the sliding direction; (b) back-scattered electron image; (c) enlarged image of area I in a), white arrows denotes micro-fracture pattern; (d) enlarged image of area II in a).

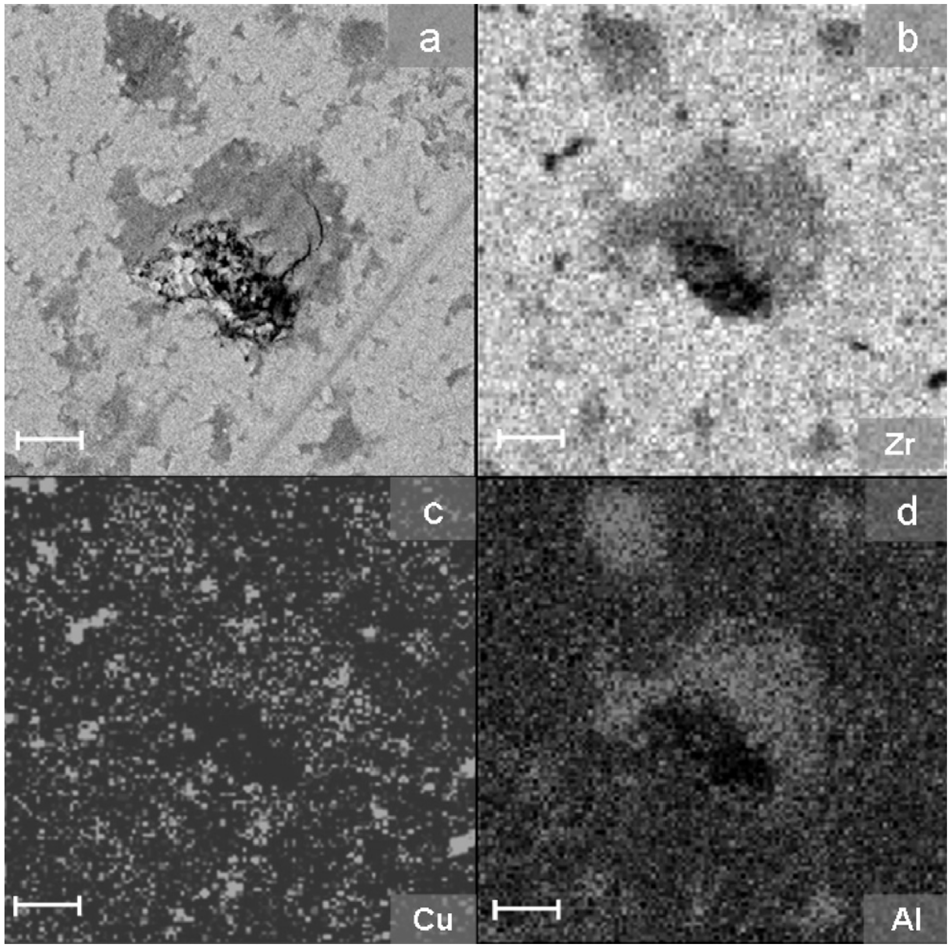

Fig. 5. Elemental distribution as determined by EDX mapping of the wear track as shown in Figs. 2 and 4 The bar represents 5 μm. (a) Back-scattered image; (b) Zr distribution; (c) Cu distribution; (d) Al distribution.

titative analysis inside and outside the dark areas was performed by means of EDX point analysis (see Table 1). It is clearly revealed that the both Al and Cu are enriched in the patchy layers. The presence of a copper-rich layer in the wear track is confirmed by XRD analysis inside (patchy layer) and outside (bulk material) the wear track (see Fig. 6). As can be seen in Fig. 6 the strongest peak of Cu_2O is clearly visible in the pattern made inside the wear track but is not that pronounced in the pattern of outside the wear track. These results strongly suggest that the presence of Cu (in a form of copper oxide) in the material system is important for the formation of the smooth interfacial patchy layer.

3.3. Mechanism of reduction in coefficient of friction

As described in the previous section, during sliding a patchy layer is formed by means of deposition of Cu- and Al-rich wear debris. A mechanism of the reduction in coefficient of friction by means of this layer will be discussed now.

Nano-indentation measurements were conducted inside and outside the wear track. The hardness values as determined by this technique are plotted as a function of the penetration depth (Fig. 7). As can be seen in this figure the hardness values of the surface inside the track and outside the wear track are almost the same for low indentation depths (10 nm). This might indicate that a patchy layer can already be formed during polishing. It is also possible that a thin layer of adsorbed substances gives the low hardness value. With increasing indentation depth the hardness measured outside the wear track increases quickly to 14 GPa, which is in a good agreement

Table 1
Metallic elemental composition in the wear track.

ID	Position	% Metallic elements		
		Zr	Cu	Al
a	Inside dark area	75 ± 1	13 ± 1	12 ± 0.5
b	Outside dark area	97 ± 1	1.7 ± 0.5	1.2 ± 0.5

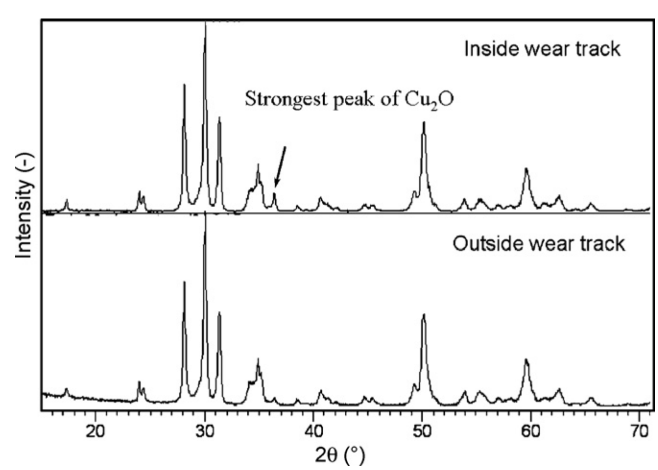

Fig. 6. XRD pattern measured in and out the wear track on the 8 mol% CuO doped 3Y-TZP ceramic after tribological test.

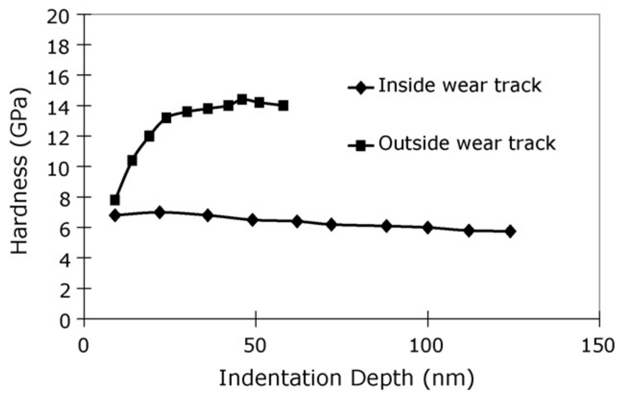

Fig. 7. Hardness as a function of indentation depth of CuO doped 3Y-TZP ceramic after tribological test.

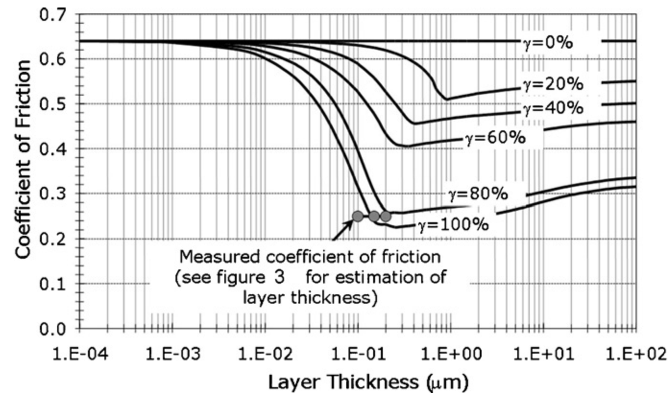

Fig. 8. Coefficient of friction of CuO doped 3Y-TZP sliding against alumina calculated according to Pasaribu's friction model as a function of thickness and coverage of the soft layer in wear track [9].

with the value of bulk 3Y-TZP ceramic [2]. However the hardness as measured in the wear track remains as low as 6 GPa at an indentation depth of 120 nm. This clearly indicates that the patchy layer inside the wear track, as generated during sliding, is significantly softer than the bulk material. Thus inside the wear track the material possess a layered structure, which can be characterized as a soft layer supported on a hard substrate.

According to the theory of Bowden and Tabor [10] the macroscopic coefficient of friction of a layered surface can be calculated by using the following equation when no ploughing effect is considered:

$$f = \frac{\tau}{H} = \frac{0.192H_{\mathrm{l}}}{H_{\mathrm{s}}} \tag{1}$$

where τ is the interfacial shear strength; H is the hardness; subscripts l and s denotes the layer and substrate. If the hardness values of the top layer and substrate in the wear track on the CuO doped 3Y-TZP ceramic are inserted in Eq. (1), a coefficient of friction of 0.082 can be calculated. This value is much lower than the experimentally measured coefficient of friction (0.2–0.3).

To explain the coefficient of friction value as measured on our CuO doped 3Y-TZP ceramic sliding against alumina, other factors should also be taken into account. Halling [11] developed an analytical friction model of a flat layered surface sliding against a rough surface based on the adhesion friction theory of Bowden and Tabor, indicating that the friction of a layered surface varied as a function of the layer thickness. It is shown that for a very thin layer the coefficient of friction is about the same as that of the substrate without a layer. As the thickness of the layer increases, the coefficient of friction is reduced to a minimum value after which the coefficient of friction increases again, and for a very thick layer the value of the coefficient of friction is the same as that of the layer material when used as a bulk material. This is in good agreement with the experimental observation of Bowden and Tabor on a steel rider sliding against various thicknesses of indium layers on steel [10]. In our case the thickness of the patchy layers generated during sliding is difficult to be accurately determined. It is suggested by the surface profile that the thickness of the top layer is in the range between 100 and 200 nm (see Fig. 3).

Recently Pasaribu [9] developed a deterministic friction model of a rough surface sliding against flat layered surfaces, which extends the capability of Halling's model and shows a better prediction of the coefficient of friction as a function of layer thickness. This model is used to calculate the coefficient of friction for CuO doped 3Y-TZP sliding against alumina as studied in this work. Due to the fact that soft layer in the wear track is not uniform but patchy, an additional parameter is introduced in the calculation: the percentage of wear track that is covered with the soft layer (γ). Fig. 8 shows the calculated coefficient of friction as a function of the thickness and degree of coverage of the soft layer in the wear track. As shown above the measured coefficient of friction is 0.2–0.3 and the thickness of the soft layer is around 100–200 nm. According to Fig. 8 the value of γ can be estimated to be close to 80%. This value seems to be slightly over-estimated. Referring the SEM image of the wear track as shown in Fig. 4, one can see that a γ value around 60% is more reasonable. However during preparation for SEM some of the debris can be released. Nevertheless, the deterministic friction model as developed by Pasaribu clearly reveals the mechanism of reduction in friction of the tribosystem studied. During sliding a thin soft patchy layer is generated by deposition of wear debris in the interface, acting as a solid lubricant and reduces the coefficient of friction. This mechanism is in a good agreement with the self-lubricating model as proposed by Alexeyev and Jahanmir [12].

3.4. Transition from low to high friction

It is shown that the coefficient of friction increases suddenly from 0.2 to 0.3 to a very high value (0.6) after operation of the test for in this case 1.2 km (see Fig. 1). Simultaneously the wear rate drastically increases. SEM images were taken from the wear track associated with the high friction (after sliding for around 1.5 km, see Fig. 9) in order to study the mechanism of the transition in tribological behavior.

In Fig. 9 the detachment of the top layer is clearly visible. The wear track indicates that delamination becomes to be the dominant wear mechanism during this sliding stage (adhesion wear mechanism seems to be dominant before the transition). Obviously a quick lost of material arise from this delamination, consequently resulting in a drastic roughening of the wear track. High coefficients of friction can be expected once such a heavy surface damage occurs. It is interesting to have a brief speculation of the process of the transition in wear mechanism. In Fig. 9 it can be seen that the detached top layer in the wear track exhibits a rather smooth surface, which is very similar with the patchy layer as show in Fig. 4d. It is very likely that this detached top layer is actually formed by accumulation of patchy layers generated by deposition of wear debris formed during prolonged sliding. As a consequence the patchy layer gets thicker and larger. As indicated in Fig. 9, this layer can cover most of the area in the wear track. However, surface micro-cracks, which inevitably exist, are propagating during sliding. Crack propagation is expected to proceed preferably along the interface between the soft top layer and the hard substrate and ultimately the top layer is detached chip by chip.

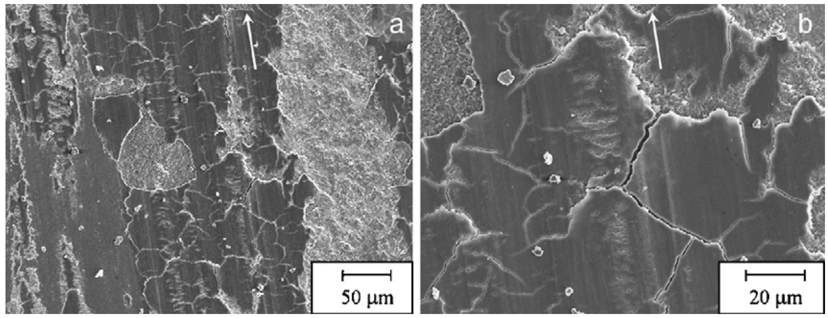

Fig. 9. SEM images of the wear track after tribological test for a sliding distance 1.5 km. White arrows in the images denote the sliding direction. (a) Lower magnification; (b) higher magnification.

4. Conclusions

The tribosystem of an 8 mol% CuO doped 3Y-TZP ceramic (pressureless sintered at 1500 °C) sliding against an alumina ball shows a promising tribological behavior (specific wear rate $k < 10^{-6}$ mm^3 N^{-1} m^{-1}; coefficient of friction $f = 0.2$–0.3) under dry sliding conditions. Self-lubricating is recognized as the mechanism of the reduction in coefficient of friction. During sliding a soft patchy layer at the interface is formed by deposition of wear debris, which acts as a lubricant. The presence of Cu in the wear debris is important for the formation of the soft interfacial patchy layer.

A transition from mild to severe wear takes place after the tribosystem has operated for a long sliding distance (1.2 km). This transition in tribological behavior is caused by detachment of top layers in the wear track.

Acknowledgements

The Dutch Technology Foundation (STW) is gratefully acknowledged for the financial support.

References

[1] H. Czhichos, D. Klaffke, E. Santner, M. Woydt, Advances in tribology: the material point of view, Wear 190 (1995) 151.

[2] Y.J. He, Tribological and mechanical properties of fine-grained zirconia and zirconia–alumina ceramics, Ph.D. Thesis, University of Twente, The Netherlands, 1995.

[3] Y.J. He, A.J.A. Winnubst, D.J. Schipper, A.J. Burggraaf, H. Verweij, Effects of a second phase on the tribological properties of Al_2O_3 and ZrO_2 ceramics, Wear 210 (1997) 178.

[4] B. Kerkwijk, E. Mulder, H. Verweij, Zirconia–alumina ceramic composites with extremely high wear resistance, Adv. Eng. Mater. 1 (1999) 69.

[5] Y. Kong, Z. Yang, G. Zhang, Q. Yuan, Sliding friction and wear of alumina-reinforced zirconia-toughened mullite composites, Wear 252 (2002) 607.

[6] M. Woydt, J. Kadoori, K.-H. Habig, H. Hausner, Unlubricated sliding behavior of various zirconia-based ceramics, J. Eur. Ceram. Soc. 7 (1997) 135.

[7] B. Kerkwijk, M. Garcia, W.E. Van Zyl, A.J.A. Winnubst, E.J. Mulder, D.J. Schipper, H. Verweij, Friction behaviour of solid oxide lubricants as second phase in Al_2O_3 and stabilised ZrO_2 composites, Wear 256 (2004) 182.

[8] H.R. Pasaribu, J.W. Sloetjes, D.J. Schipper, Friction reduction by adding copper oxide into alumina and zirconia ceramics, Wear 255 (2003) 699.

[9] H.R. Pasaribu, Friction and wear of zirconia and alumina ceramics doped with CuO, Ph.D. Thesis, University of Twente, The Netherlands, 2005.

[10] F.P. Bowden, D. Tabor, Friction and Lubrication of Solids, Part I, Clarendon Press, Oxford, England, 1950.

[11] J. Halling, The rule of surface films in the frictional behavior of lubricated and dry contacts—a unifying influence in tribological theory, ASLE Trans. 24 (1983) 528.

[12] N. Alexeyev, S. Jahanmir, Mechanics of friction in self-lubricating composite materials. Part I: mechanics of second phase deformation and motion, Wear 166 (1993) 41.