Friction and wear behaviour of ceramic-hardened steel couples under reciprocating sliding motion

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Abstract

The friction and wear behaviour of $\text{ZrO}_2\text{--Y}_2\text{O}_3$, $\text{ZrO}_2\text{--Y}_2\text{O}_3\text{--CeO}_2$ and $\text{ZrO}_2\text{--Al}_2\text{O}_3$ composite ceramics against hardened steel AISI-52100 were investigated using a pin on plate configuration under reciprocating motion. The reproducibility of the results was examined in this configuration. Wear characteristics were separated into system and material contributions. Under the conditions used, all the ceramic components exhibited rather low wear rates (less than $10^{-6} \text{ mm}^3 \text{ N}^{-1} \text{ m}^{-1}$). The frictional behaviour of ceramic–metal couples depended on a metallic layer transferred from the steel plate to the ceramic pin. A relation was determined between surface hardness and friction of ceramic–metal pairs. It was shown that the affinity for the transfer of the metal towards ceramic surfaces depended on the physical properties of the materials. In the tribosystems investigated, the effect of the hardness of the ceramics on friction and wear behaviour is found to be more important than that of toughness of the ceramics.

Keywords: Ceramics; Sliding; Friction; Wear; Adhesion

1. Introduction

Fine structured ceramics are being developed for a wide variety of engineering applications including metal cutting tool inserts, drawing dies, roller bearings, water pumps, automotive engine parts. In all these cases, excellent tribological characteristics are required [1]. Many studies are performed on the friction and wear behaviour and chemical interactions of metal–ceramic couples in sliding contacts with non-oxide ceramics such as silicon nitride, silicon carbide, etc. These non-oxides, however, demonstrate poor chemical stability in air at high temperature and even suffer from oxidation under tribological sliding conditions [2]. Considerable attention has been paid to the development of toughened zirconia and toughened alumina ceramics in the past few years owing to their good mechanical properties and chemical resistance.

Transformation-toughened ZrO_2 has widened the scope of application of oxide ceramics owing to its excellent fracture toughness. The primary mechanism of toughening in ZrO_2 ceramics with grain sizes surpassing a critical value is the transformation of a retained metastable tetragonal phase to a stable monoclinic phase in the vicinity of propagating cracks.

The volume dilation accompanying the transformation produces compressive zones which retard crack propagation [3]. The tetragonal phase of zirconia can be retained by addition of a certain amount of rare earths oxides as yttria, ceria or both. Zirconia-toughened alumina (ZTA) with improved toughness has been developed by the introduction of the metastable tetragonal zirconia phase in an alumina matrix [4,5]. Narutaki et al. [6] have reported that ZTA exhibits superior resistance to crater wear in face milling, which can be attributed possibly by reversible tetragonal to monoclinic transformation of ZrO_2 during milling wear. Sornakumar et al. [7] also expected that this cyclic transformation can result in a better surface texture and reduce surface roughness in alumina–zirconia composite cutting tools. However, the occurrence of microcracks on the surface owing to stress-induced transformation [8] may reduce the wear resistance of ZTA.

It has been reported that some ceramic–metal pairs have lower coefficients of friction than ceramic–ceramic sliding contacts [9]. Experiments have demonstrated that the wear mechanisms of some metals when rubbed against ceramics under dry conditions are governed by a transfer of metal to the ceramic surface [9,10]. It is found that wear and friction of metals against ceramics strongly depends on the chemical

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reactivity of the metal [11]. For effective application of these materials more detailed research of the interaction of the ceramic–metal couples and the dominant wear mechanism are very important.

In this paper, friction and wear behaviour between zirconia matrix ceramics and hardened steel AISI-52100 are investigated under reciprocating sliding conditions. The experiments were carried out using ceramic pins which were loaded and slid against hardened steel plates under different conditions, such as unlubricated sliding motion in air and sliding motion in distilled water. The transferred metal layers on the wear scar surface of the ceramics were characterized by a microindenter and a scanning electron microscope (SEM) with energy-dispersive X-ray (EDX) system. The wear track morphology was determined by SEM as well.

2. Experimental procedure

2.1. Materials for testing

In the present study three kinds of ceramic materials and one type of steel were used. Ultra fine tetragonal zirconia powders ZY5 (zirconia doped with 5 mol% $\text{YO}_{1.5}$), ZY4Ce4 (zirconia doped with 4 mol% $\text{YO}_{1.5}$ and 4 mol% CeO_2) and a ZTA composite (85 wt.% Al_2O_3 –15 wt.% ZrO_2) powder were synthesized by a gel precipitation technique as described in detail by Groot Zevvert et al. [12]. All the ceramic compacts were prepared by cold isostatic pressing at 400 MPa. After that ZY5 and ZY4Ce4 samples were sintered at 1150 °C for 10 h. A grain size of 0.18 μm was obtained in both ZrO_2 materials. While ZTA was sintered at 1450 °C for 2 h and had an Al_2O_3 grain size of 0.8 μm and a ZrO_2 grain size of 0.3 μm . Grain sizes D were determined by the linear intercept technique from SEM micrographs of a polished and thermally

etched surface, using $D = 1.56L$, where L is the average linear intercept [13]. The ceramic specimens, formed into cylinders with 5 mm diameter and 10 mm length, slid reciprocally against hardened bearing steel (AISI-52100). The roughness R_a along the axis direction of the TZP cylinders is 0.5 μm and R_a of ZTA is 0.2 μm . The stationary steel plate with dimensions of 56 mm $\times$ 18 mm $\times$ 5 mm, had a mean surface roughness R_a of 0.5 μm . Before testing, all samples were cleaned ultrasonically with ethyl alcohol. Subsequently the samples were annealed for 10 min at 950 °C for ZY5 and ZY4Ce4 and 1350 °C for ZTA in order to remove residual stresses caused by machining. Physical and mechanical properties of ZY5, ZY4Ce4 and ZTA ceramics and AISI-52100 hardened steel are listed in Table 1. All properties of AISI-52100 hardened steel were quoted from a metals handbook [15]. The densities of the sintered ceramics were measured by the Archimedes technique in mercury. The bending strength and the fracture toughness were measured by 4 point bending and single edge notched beam, respectively, as described in [5]. The Vickers hardness of ceramics were measured using a microindenter (Shimadzu Dynamic Ultra Hardness Tester DUH-200) with a maximum load of 2 N and a loading speed of $1.44 \times 10^{-3} \text{ kg s}^{-1}$. A hold time was used of 10 s. The Young's modulus is calculated using the unloading vs. indentation depth curve after loading test [16]. The dynamic hardness of the ceramics and the steel, as obtained from load and indentation depth [17], is measured using the same microindenter with the loads from 0.2 to 50 gf.

2.2. Test equipment

Friction and wear tests were performed on a pin on plate type sliding wear tribometer (code: S-tribometer). This S-tribometer, as shown schematically in Fig. 1(a), consists of a reciprocating pin sliding on a stationary plate with its axis

Table 1
Mechanical and physical properties of the ceramic and the metallic materials

Material	ZY5	ZY4Ce4	ZTA	AISI-52100 hardened steel
Chemical composition	95 mol.% ZrO_2 , 5 mol.% Y_2O_3	92 mol.% ZrO_2 , 4 mol.% Y_2O_3 , 4 mol.% CeO_2	85 wt.% Al_2O_3 , 15 wt.% ZrO_2	1.1% C, 0.40% Mn, 0.1% Ni, 0.30% Si, 1.5% Cr, 0.01% V, 0.005% Mo, residual Fe (wt.%)
Density ($\times 10^3 \text{ kg m}^{-3}$)	5.8	5.9	4.1	7.9
Vickers hardness (GPa)	13.0	12.2	17.0	7.6
Dynamic hardness (GPa)	8.1	7.6	10.2	6.3
Fracture toughness ($\text{MPa m}^{1/2}$)	8.6	6.5	5.2	20
at T_{room}				
Young's modulus (GPa)	191	173	262	213
Poisson's ratio	0.30	0.30	0.30	0.29
Strength ^a (MPa)	454	430	380	345
Coefficient of thermal expansion ($\mu\text{m m}^{-1} \text{ K}^{-1}$)	9.3 ^b (20–400 °C)	9.3 ^b (20–400 °C)	7.5 ^b (20–400 °C)	12.6 (20–100 °C)
Thermal conductivity ($\text{W m}^{-1} \text{ K}^{-1}$)	2.5 ^b (at 150 °C)	2.5 ^b (at 150 °C)	5.5 ^b (at 150 °C)	45.0 (at 100 °C)

^a Four-point bending strength for the ceramics; yield strength for the steel.

^b Data from ref. [14].

Fig. 1. (a) S-tribometer. (b). Contact situation of the pin on the plate.

parallel to the steel plate. The plate is fixed by a holder, which is mounted on a heat exchanger, which in turn are supported by two steel blade springs which only allow parallel movement in the sliding direction. The pin is fixed in a loading arm, which is connected to the support. The support, guided by two cylindrical bars that are supported by a system of 4 roll-blocks, is driven by a crank mechanism. The pin, therefore, exerts a sinusoidal motion with an amplitude $A = 23$ mm. The pin is loaded by pressurizing the bellows, in which the pressure is kept constant by connecting it to an air-accumulator. The bellows pressure is measured by a manometer. The friction force, induced between cylindrical pin and plate, is measured by a piezoelectric force transducer and recorded, using a digital oscilloscope. In Fig. 1(b) the contact situation is schematically shown. The initial contact between the pin specimen and the plate specimen is a linear contact.

2.3. Test procedure and characteristics

The experiments were carried out under dry sliding conditions at room temperature of 22–24 °C with a relative humidity of about 50% and under lubricated conditions in distilled water. All experiments are performed at a frequency of 0.22 Hz with a mean velocity of 20 mm s⁻¹ and a normal load varying from 65 to 200 N, corresponding to an average value of the initial hertzian contact pressure of unworn surfaces from 170 to 320 MPa, respectively, which is calculated by a formula given in ref. [18]. The wear experiments from which friction and wear are obtained as a function of sliding distance are performed at a mean sliding velocity of 20 mm s⁻¹ and a load of 65 N. The volume loss is calculated from the weight loss and the density of the coupled elements. The specific wear rate k_{inst} , at a given stage of the process, is calculated from the equation as given below:

$$k_{\text{inst}} = \frac{1}{F_n} \frac{dV}{dS} \quad (1)$$

in which V is the volume loss and S the sliding distance at a normal force F_n . Thus, k is proportional to the slope of the volume loss vs. sliding distance curves.

The values of the coefficient of friction are calculated from the normal load and the friction force obtained from a digital oscilloscope.

After the tests, the wear scars of the ceramic cylinders and the wear debris were examined using a scanning electron microscope (SEM) (Jeol JSM-35CF) equipped with an energy-dispersive X-ray (EDX) analyzer or an SEM (Hitachi S800) with an ultra-thin-window EDX (for light element analysis down to boron) analyzer to determine the surface degradation process and the dominant wear mechanisms. The phase composition was analyzed by X-ray diffraction (XRD) using a Phillips PW1370 diffractometer with Cu K α radiation. The characteristics of the wear debris and adhesive layer were examined by XRD analysis and ultra-thin-window EDX.

After sliding tests the dynamic microhardness of the worn surfaces or the metallic layer which was transferred from the steel to the ceramic surface was determined by the microindenter as described in Section 2.1 above. In this case, classical microhardness could not be measured because the metallic layer was only a few microns thickness. As a consequence, the dynamic hardness was used in this study. The surface roughness of the samples was measured with a Dek-Tak profilometer.

3. Experimental results

3.1. Reproducibility of tribological results

Figs. 2 and 3 show the friction and wear results of ZY5 and ZY4Ce4 ceramics after duplex testing under the same

Fig. 2. Coefficient of friction vs. sliding distance for different tribological couple combinations. I (dotted line) and II (solid line) reveal the results of two tests performed at the same conditions.

Fig. 3. Wear rate of the ceramics vs. sliding distance for different ceramic-metal couples.

testing conditions. It is clear from these figures that the results obtained show a very good reproducibility. This reproducibility is of an importance in specifications of the quality of the materials used and is an indication of the reliability of the tests. For a tribosystem the reproducibility depends on two aspects:

- (1) The material itself must have a homogeneous and reproducible microstructure, and surface properties of the coupled elements like roughness and microhardness must remain the same.
- (2) During friction and wear testing, constant environmental conditions such as temperature, chemical nature and relative humidity are necessary. The cylinder pin must be in line with the plate in its axis direction. A decrease of contact line or area, due to misalignment, will increase the contact pressure (the loading force is constant), which may result in different values for wear and coefficient of friction.

From the results it can be concluded that the ceramic materials used and the results obtained from the tribosystems used in this investigation are useful data.

3.2. Influence of different ceramic components on friction

Representative friction registration curves for all three experimental ZY5-, ZY4Ce4- and ZTA-AISI-52100 specimen pairs are plotted in Fig. 2 as a function of the sliding distance. The frictional behaviour of material pairs with different ceramic components is significantly different. A large change in the value of the coefficient of friction μ with increasing sliding distance was found for the ZTA-AISI-52100 couple during the running-in period. In this couple as can be seen from Fig. 2 the initial value of the coefficient of friction was 0.65, then increased with sliding distance to a value of about 0.9 remaining steady for approximately 4 km. After 4.5 km the friction coefficient decreases to another steady value of about 0.75.

In contrast, for ZY5- and ZY4Ce4-AISI-52100 steel couples, a coefficient of friction μ of 0.3–0.4 is measured, which remained almost constant during the test. The values of the coefficient of friction show a smaller variation during the running-in period if compared with the ZTA-AISI-52100 couple. The different values in coefficient of friction between ZTA and TZP (ZY4Ce4 and ZY5) are suggested to be related to the adhered film on ceramics, which will be discussed later. The test with ZTA was also associated with the highest noise level. In the case of ZY5- and ZY4Ce4-metal couples, noise was hardly generated during sliding.

3.3. Wear rate of the tribological components

Ceramic wear rate vs. sliding distance is shown in Fig. 3. The TZP samples show a decrease in wear rate when the sliding distance increases (dotted line in Fig. 3) which is due to the running-in for ZY5 and ZY4Ce4 ceramics at the beginning of wear process. The wear subsequently reached a steady state after a sliding distance of approximately 1 km.

As shown in Fig. 3, the wear rate of ZTA ceramic is a factor of 3 to 4 lower than for ZY5 and ZY4Ce4. The wear rate values for ceramics and steel after about 6.8 km of sliding distance are summarized in Fig. 4. For the ZTA-AISI-52100 couple the steel plate had a significantly higher wear, i.e. $83 \times 10^{-6} \text{ mm}^3 \text{ N}^{-1} \text{ m}^{-1}$. While for the tests with ZY5 and ZY4Ce4, the wear rates of the metallic plates were $1.6 \pm 0.3 \times 10^{-6} \text{ mm}^3 \text{ N}^{-1} \text{ m}^{-1}$ and $0.4 \pm 0.1 \times 10^{-6} \text{ mm}^3 \text{ N}^{-1} \text{ m}^{-1}$, respectively.

Comparison of the results of both TZP-AISI-52100 couples indicates that there is a slight difference in the specific wear rates between ZY5 and ZY4Ce4 ceramics, whereas the wear rate of the AISI-52100 metal in combination with ZY5 as mentioned before is approximately a factor of 4 higher than in the ZY4Ce4-metal couple.

After the tests, it was found that the ceramic wear scars were black, dark red or brown, indicating that metal particles

Fig. 4. The ranking order for the specific wear rate values of the tribosystem and the individual material components after a sliding distance 6.8 km.

(a)

(b)

Fig. 5. SEM of wear tracks of ZTA surface after the dry tribological test at a sliding speed of 20 mm/s and a normal load of 65 N. (a) Overview of the wear track: the thick metallic layer on the surface. (b) High magnification detail of the layer. O, Original surface; W, wear track. The arrow indicates the sliding direction.

or metal oxides were transferred to the ceramic cylinder surface in all cases.

Wear tracks of the ceramics after sliding are shown in Fig. 5 and Fig. 6. Much more metal is transferred from the AISI-52100 plate to the surface of ZTA as shown in Fig. 5(a) if compared with TZP (Fig. 6). The wear track revealed a continuous and thick metallic film adhered on the ZTA surface. Examination of a polished cross-section of the wear scar of the ZTA pin by SEM indicated that the thickness of the layer is about 3 μm . Many flat and thick areas were found together with rough areas. These rough areas are due to the delamination of the thick layer and the loss of particles from the metallic layer (see Fig. 5(b)). Ultra-thin-window EDX used for analyzing the metallic layer indicates the existence of iron oxides qualitatively. In the thick layer adhered on the ZTA surface the signal of the aluminum element is hardly found by this method. These results also confirm the presence of the metallic layer on the ceramic surface.

The wear surface of ZY5 is smooth and some grooves in the sliding direction are visible as shown in Fig. 6(a). The amount of metallic material deposited on ZY5 surface is very

small as analyzed by EDX. Only a few thicker traces (black parts) in a small scale adhered to the surface are observed (Fig. 6(a)). In most cases, however, the presence of metallic particles attached to the surface can be identified only by the brown colour on the worn surface using optical microscopy. In addition, some microfracture of the ceramic surfaces took place within the limits of area. Very smooth wear tracks are observed in ZY4Ce4 ceramics (Fig. 6(b)). A very thin metallic film is adhered to the ceramic surface. Only limited relative thick metallic films can be found on the surface as was also observed for ZY5.

The wear debris was collected after testing. For ZTA–AISI-52100 the wear debris is black or dark red, whereas for TZP–AISI-52100 the wear debris was brown. The change in colour from black to brown would be in correspondence with an increase in contact temperature during wear test processes as suggested by Stachowiak et al. [10]. Also a correlation exists between the colour of the debris and the relative amounts of ceramic wear and metal wear as indicated by Libsch et al. [19]. If ceramic wear is the same or higher

(a)

(b)

Fig. 6. SEM of wear tracks of TZP surface after the dry tribological test at a sliding speed of 20 mm/s and a normal load of 65 N. (a) Wear track of ZY5 surface: microfracture on small scale, very small amount of metallic particles as islands attached to the surface, grooves in the sliding direction and microfracture in small areas. (b) Wear track of ZY4Ce4 surface. O, original surface; W, wear track. The arrow indicates the sliding direction.

Table 2
Characteristics of the ZTA–AISI-52100 couple after 3.4 km sliding wear

Load (N)	Coefficient of friction	Specific ceramic wear rate ($\text{mm}^3 \text{N}^{-1} \text{m}^{-1}$)
65	0.9	$0.33 \pm 0.02 \times 10^{-7}$
130	0.8	$0.19 \pm 0.02 \times 10^{-7}$
200	0.8	$0.51 \pm 0.10 \times 10^{-7}$

(a)

(b)

Fig. 7. SEM of the wear surfaces of ZTA. (a) Sliding wear test at normal load of 65 N. (b) Sliding wear test at normal load of 200 N. The arrow indicates the sliding direction.

relative to metal wear, then the wear debris colour is light. If ceramic wear is less than metal wear, then the wear debris colour is dark [19]. This explanation was based on the fact that the wear debris was a mixture of dark iron oxide from the metal and light coloured ceramic powder. Thus the wear debris produced in ZTA–AISI-52100 couple contains less amount of the ceramic powder than in TZP–AISI-52100, which is in agreement with the results of wear rates where ZTA ceramics show much less wear loss than TZP ceramics. The XRD pattern of the wear debris indicates that the wear debris contains iron oxide products (Fe_2O_3 and Fe_3O_4), metallic and ceramic turnings. The presence of the iron oxides confirms that a tribochemical reaction exists. The presence of iron oxide also indicates that the accumulation of heat

during dry sliding is sufficient to oxidize the fine crushed debris. This accumulation of heat is due to the low thermal conductivity of the ceramic materials. Numerous studies have reported a tribochemical interaction during sliding tests of ceramics against metal under dry conditions [10,19–23]. Ravikiran et al. [23] also found the existence of FeAl_2O_3 and FeAlO_3 besides iron oxides during dry sliding of alumina pins against a steel disc (En24). However, these spinel products were not detected for the ZTA–AISI-52100 couple in the present study.

3.4. Effect of loading force on tribological properties

The effect of loading force in the range of 65 to 200 N on the tribological behaviour was examined for the ZTA–AISI-52100 steel pair combination. The friction and wear values for the ceramic part are listed in Table 2.

The friction coefficient values appeared to be nearly independent of load in agreement with the observations of [10]. The variation in the wear rate of ZTA ceramic indicates that the effect of load on the wear loss is not very straightforward. However, increasing the load is associated with a rapid increase of metal wear, resulting in the accumulation of metal debris at the borders of the wear track. The morphology of the metallic film on the ceramic is examined by SEM as shown in Fig. 7. Comparison of the wear tracks between sliding at 65 N (see Fig. 7(a)) and 200 N (see Fig. 7(b)) normal loads reveals that the only difference at high load is that the metallic film becomes more flat and that its continuity is decreased, e.g. more original ceramic contact surface is exposed (Fig. 7(b)). But no more changes in the metallic film are observed for all loads. It can be concluded that there is no difference of the friction and wear values as function of load in the ZTA–metal system.

3.5. Wear behaviour of ZY4Ce4 ceramic against metal in water

Fig. 8 and Fig. 9 show the coefficient of friction and wear loss for the ZY4Ce4–AISI-52100 couple during sliding in air

ZY4Ce4 against metal S-tribometer

Fig. 8. Friction coefficient as a function of sliding distance for ZY4Ce4 under dry sliding and lubricated (water) conditions.

Fig. 9. Wear rates for ZY4Ce4 as a function of sliding distance under dry sliding and lubricated (water) conditions.

and in water, respectively. At the beginning, water acts as a lubricant and reduces the friction force, resulting in a lower friction coefficient. After a certain sliding distance, the coefficient of friction increases, which probably corresponded to the formation of iron oxide products owing to the strong metal oxidation observed during the sliding test. It can be seen from Fig. 9 that the wear loss in water is larger than that in air. This result corresponds to the fact that water promotes wear owing to tribochemical reaction between water and zirconia which will be discussed later. The wear loss of the metal plate cannot be measured because of oxidation.

4. Discussion

4.1. Amount of metal adhered on the ceramic surface

For discussion concerning friction and wear it is important to take the influence of the transferred films into account. A difference in metal adherence on the various ceramics is observed, i.e. the metallic layer attachment to ZTA ceramic (see Fig. 5) is much more stronger than to ZY5 and ZY4Ce4 (see Fig. 6). The transferred metallic layer prevents direct contact between metal and ceramic, and therefore controls the friction and wear behaviour of the sliding couples. This is in agreement with the results for tribological tests with metal–ceramic couples in Refs. [10,20–22]. For ZTA–AISI-52100 couple, an increase in the coefficient of friction is an indication of the onset of the deposition of a metallic film on the ceramic surfaces [10].

In contrast, much less transferred metallic particles are detected with TZP ceramics. It is well known that generally, metallic films attach well to ceramic contact faces because of a strong interfacial adhesion between the sliding surfaces. The difference in the ability of metal attachment to the ceramic surface between ZTA and TZP is probably related to the difference of interfacial energy between the ceramics and the metal.

Howe [24] introduced the use of the work of adhesion W_{ad} which is the work required to separate a unit area of interface into the two original surfaces. W_{ad} can be separated into $W_{ad} = \gamma_m + \gamma_c - \gamma_{mc}$, where γ_m and γ_c are the surface energies of the metal and ceramic, respectively, and γ_{mc} is the metal–ceramic interfacial energy. This indicates that the work of adhesion W_{ad} increases with decreasing the metal–ceramic interface energy γ_{mc} . Probably the interfacial energy for ZTA–metal couple is much less, in which a larger work of adhesion is generated if comparing to that for TZP–metal couples. A direct evidence is that a larger amount of the metal adhered on the ZTA than on the TZP. Esposito et al. [20] found that stainless steel (nominal composition: Cr 17.2; Ni 8.3; Fe 71.2; Si 1.2 wt.%) has a greater tendency to transfer metal to the Al_2O_3 contact face than superalloy (Cr 20.0; Ni 73.5; Ti 2.5; Al 2.0 wt.%). A strong adhesion of Fe on Al_2O_3 is observed in literature [20] which indicates that the amount of metallic film transferred to the ceramic surface depends on the physical properties of metal [10]. In the present study, the metallic particles adhere less to the TZP surfaces if compared with ZTA which is presumably due to the presence of Al_2O_3 . This is in agreement with the results obtained by Libsch et al. [19]. They reported that for SAE 4620 carburized steel against ceramics a thick film was formed on the ceramic wear surface of Al_2O_3 – ZrO_2 materials whereas only a very few metallic particles were transferred to the ceramic surface of ZrO_2 – Y_2O_3 materials. It can be suggested that the metal particles (specially for steel) have a strong adhesion on Al_2O_3 materials or Al_2O_3 based materials such as ZTA.

4.2. Frictional behaviour vs. the adhered metallic film in the ZTA–metal couple

For the ZTA–AISI-52100 pair the coefficient of friction (μ) reveals a significant variation with increasing sliding distance. This trend in the coefficient of friction results from the formation of a metallic film on the ceramic surface. It was found that after a few minutes a metallic film was transferred from the AISI-52100 steel plate to the ceramic surface. The metallic layer on the ZTA ceramic, however, was not yet well developed and was discontinuous. With the sliding process continuing, much more metallic particles were transferred from the steel plate to the ceramic surface, resulting in an increase of thickness and area coverage, and finally forming a thick and relatively continuous layer. Owing to variation in thickness of the transferred layer in the running-in period the coefficient of friction may vary, according to the theory described by Bowden and Tabor [25]. That is

$$\mu = \frac{\tau_i}{H} \quad (2)$$

where τ_i is the shear strength of the layer and H is the hardness of (a) the metallic layer in the case of a thick layer or (b) the hardness of the softest contacting partners, in this case the metal, for the situation when a relative thin layer is present. This equation indicates that the coefficient of friction depends

on the metallic layer. When the transfer layer thickness reached a certain level, the metallic film became relatively constant, i.e. the average hardness of the metallic layer kept a constant value, so a constant coefficient of friction is obtained. A thick and continuous film has been observed from the wear track of ZTA (see Fig. 5(a)). A similar observation of a variation of the coefficient of friction owing to the formation and the increase of the thickness of a transferred metallic layer on the ceramics was also pointed out by Stachowiak et al. [10].

The stable values of the coefficient of friction are in the range of 0.75–0.9 for ZTA–AISI-52100 pair, which is in good agreement with the values (0.75–0.85) obtained by Czichos et al. [21,22] for Al_2O_3 –AISI-52100 pairs. Their experiments were performed with a ceramic pin by using the pin-on-disk test system. The microhardness (16.1 GPa) of their Al_2O_3 was nearly the same as for ZTA (in Table 1) used in the present experiments. Environmental conditions were almost the same, but normal load and surface roughness of the specimen used were different. In this study it is found that the coefficient of friction is independent of normal load in this study (Table 2) and metallic particles adhered to ceramics independence of surface roughness is found by [10]. Comparison of both ZTA–AISI-52100 and Al_2O_3 –AISI-52100 pairs indicated that the presence of a similar thick metallic film transferred from the steel to the ceramic and the same softer metal partner resulted in a similar value of coefficient of friction.

4.3. Difference in coefficient of friction between ZTA- and TZP-metal couples

In Fig. 2, it is shown that the coefficient of friction for ZTA–AISI-52100 pairs is nearly a factor of about 2.6 higher than the TZP–AISI-52100 pair owing to the presence of a thick metallic film. With the adhesion friction theory as given by Bowden and Tabor [25], the difference is explained as follows.

The dynamic hardness H_{Di} of the metallic film on the ZTA ceramic surface is 2.3 GPa. H_{D} of the original surface of the materials is given in Table 1. The dynamic hardness of the worn surface of both TZPs is almost the same as the original surface. It is assumed that the shear strength (τ_i) is the same in all cases. Then the coefficient of friction found for TZP–AISI-52100 couples is

$$\mu_{\text{TZP}} = \frac{\tau_i}{H_{\text{AISI-52100}}} \quad (3)$$

and for ZTA–AISI-52100 couple is

$$\mu_{\text{ZTA}} = \frac{\tau_i}{H_{\text{Di}}} \quad (4)$$

where $H_{\text{AISI-52100}}$ is the hardness of AISI-52100 steel, the softest contact partner. H_{Di} is the hardness of the thick metallic layer.

The ratio is

$$\frac{\mu_{\text{ZTA}}}{\mu_{\text{TZP}}} = \frac{H_{\text{AISI-52100}}}{H_{\text{Di}}} \approx \frac{6.3}{2.3} \approx 2.7$$

This value is in agreement with the measured coefficient of friction, i.e. $\mu_{\text{ZTA}} \approx 0.9$, $\mu_{\text{TZP}} \approx 0.35$ which gives a ratio of 2.6 for the respective friction coefficients.

4.4. Wear mechanisms in ZTA

For ZTA ceramics, a thick and continuous metal layer is found on the overall wear track (see Fig. 5(a)) which obviously plays a protective role. This interfacial adhesion layer prevents contact of ZTA to the steel. The predominant wear takes place between the metallic layer and the steel. Grain pull-out of the ceramic may only occur, when the strength of the adhesive bonds of metal to ceramic is larger than the grain boundary strength. This is not of common occurrence in the present case.

The hardness, as defined as the resistance against plastic deformation, plays an important role on the wear values when a hard ceramic slides against a relative softer metal as expressed in Archard's theory [26]. The hardness value of ZTA ceramic ($H_v = 17.0$ GPa or $H_D = 10.2$ GPa) is much higher than that of AISI-52100 hardened steel ($H_v = 7.6$ GPa or $H_D = 6.3$ GPa). So ZTA ceramic has a high resistance to scratching due to the steel and to plastic deformation in the contact area during sliding wear. In contrast to ZTA ceramic, there is a considerable evidence of plastic deformation in the steel surface, which leads to wear loss of the steel by plastic scratching and plastic adhesive wear. The strong effect of this hardness ratio on wear rate was also found by Zum Gahr [27]. Who revealed that the wear rate of a metallic ring increased with increasing hardness ratio, while the wear losses of the ceramic pin decreased in that case.

According to Libsch et al. [19], ceramics with high toughness can withstand higher loads without macrodamage. They found that in the fracture toughness range of 2.5–6.6 $\text{MPa m}^{1/2}$ of ZTA ceramics, a macrodamage (chipping and cracking) occurs at loads of about 136 N. In the present study, surface damage (chipping and cracking) did not occur in the ZTA ceramic with fracture toughness value of 5.2 $\text{MPa m}^{1/2}$ at loads of 65–200 N as observed by SEM (see Fig. 5). Only few grain pull-out by adhesive wear was found. The thick continuous and relative homogenous metallic layer can reduce local loads or stresses on the ceramic surface. The difference between the present results and those of Libsch may be due to the difference in tribological test system. They used the Falex ring on ceramic block test technique where the Falex S-25 rings are made of SAE 4620 carburized steel. For the ZTA–AISI-52100 couple, the dominant mechanism under dry sliding is adhesive wear of the metallic layer on the ceramic surface.

4.5. wear mechanisms in TZP

In contrast to the ZTA–AISI-52100 couple, where wear was hardly observed at the ceramic specimens but mainly on the steel components, the wear rates of steel and ceramic are comparable for both TZP ceramics. Comparison of the wear between ZTA and both TZP ceramics indicates that the wear rates of the TZP ceramics are about a factor of 3 or 4 higher than that of ZTA. A very thin metal film adhered on TZP ceramic surfaces was observed (judging by the colour using an optical microscope) at overall area and also a few thick and small islands are present on the TZP surfaces (see Fig. 6, black parts). These islands contain iron oxides, metallic and ceramic turnings.

The hardness ratio of the TZP pin–metallic plate is much lower than that for the ZTA–metal couple. Along Zum Gahr's line of discussion [27], one might expect that the wear rate of TZP ceramics will increase and the wear rate of the steel will decrease if compared with the ZTA–metal couple, which is in agreement with our results.

During the sliding process, a plastic deformation of the surface layer of the wear track takes place. This plastic deformation may produce subsurface cracking and may cause surface damage [19]. Very large local stresses on the ceramic surface produced by asperity contact cause surface or subsurface cracking on a very fine scale which also result in surface damage. Fig. 10(a) shows a micrograph of surface damage or microfracture along weak grain boundaries, which gives considerable evidence of intergranular fracture. In these areas, the wear debris can easily be entrapped, smeared out and pressurised to form a small thick and dense islands during sliding as seen in Fig. 10(b). These isolated thick islands can provide a protection for further microfracture, but in most cases they cause local stress concentration. If the bonding between particles of the island or between the islands and the ceramic surface is strong enough, it is assumed that these islands can cause subsurface cracking or grain pull-out under high local stresses, resulting in further surface damage. The high toughness of TZP ceramics provides a large resistance for the propagation of cracks and counteracts microfracture on a large scale. This is the reason that microfracture is limited to a small scale and no large main cracks are found in this case.

On the wear track of TZP ceramics, grooves are clearly visible in the sliding direction. This groove wear is caused by harder wear particles, which can be ceramic particles or iron oxide products. Some wear particles of TZP ceramics adhered or embedded on the steel surface (identified by EDX analysis) in combination with the iron oxide particles of the steel surface promote groove wear.

Observation and examination of the whole wear track of TZP under dry sliding show that the main wear mechanism is a combination of adhesive wear, plastic deformation and groove as well as some microfracture on small scale.

For the ceramics tested wear rates were measured less than $10^{-6} \text{ mm}^3 \text{ N}^{-1} \text{ m}^{-1}$ which is acceptable in practical appli-

(a)

(b)

Fig. 10. Morphology of the TZP surface damage after dry sliding: (a) microfracture; (b) isolated thick islands of the wear debris on the track.

cations. If a very high wear resistance of ceramic components is required, for example cutting tools, ZTA is a good candidate. For high wear resistance of both components in ceramic–metal couples, however, ZTA is not favourable owing to the high wear rate of the contacted metallic partner. In this case the use of TZP ceramics is favourable.

4.6. Effect of water on the tribology of TZP ceramics

The SEM micrograph in Fig. 11 shows no microcracks on the worn surface after wear experiments in water. SEM observation of the worn surface and EDX analysis indicate the absence of a metallic layer transformed to the TZP surface in water condition. The worn surface is smooth, even more smooth than the worn surface under dry condition. The water treated samples, however, contain small shallow pits. These pits indicate that the TZP plate is less resistant to wear damage in water, which has also been found by other researchers [28]. Recent studies have pointed out that water has a marked influence on the friction and wear behaviour of zirconia ceramics, although the results are often conflicting. In comparison with the wear behaviour in air, both increased

Fig. 11. SEM micrograph of the TZP wear track in water condition, smooth wear track with small shallow pits.

[27,29,30] and decreased [31] wear of zirconia ceramics in water have been reported.

A wear acceleration mechanism reveals that water promotes wear by stress corrosion reaction [30–32] on the sliding surface due to the reaction of ceramic with water. It is expected that soft hydroxides are formed on the TZP surface, which result in a tribochemical wear. Tribochemical reactivity does not depend on the surrounding temperature, but the reactivity of stress corrosion cracking is accelerated with increasing the temperature [33]. Although the soft reaction products may relax the shear stress on the contact surface by plastic deformation, they can greatly reduce the mechanical strength of materials, resulting in easy removal of wear particles from the ceramic surface. Sasaki [33] mentioned that water is adsorbed on the fresh surface and reacts with zirconia, involving a chemisorption of OH^- ions at the surface and breaking the Zr-O-Zr bonds. This promotes the phase transformation from tetragonal to monoclinic zirconia and generates a network of microcracks, which deteriorates the strength of the surface and thus increases wear. The influence of the phase transformation on the wear does not take place in the present study since no monoclinic phase is detected. The prevention of this phase transformation is based on the small grain size of zirconia [34]. In other literature [35] it is expected that water penetrates and interacts with microcracks at interfaces, replacing strong solid–solid interaction by weak solid–liquid–solid interaction. Finally the interface attraction or interface energy is reduced by capillary condensation, which is described in detail by Lawn [35], resulting in more wear loss of the ceramic during sliding in water.

On the other hand, the wear particles forming a colloidal suspension with water can be entrapped at the interface and promote fine scratching or fine polishing of TZP surface, which lead to accelerative wear. Another factor of acceleration of the wear in water is that the iron oxidation on the steel surface is promoted by water. Comparing with dry condition, another factor is the absence of a metallic layer on the ceramic surface.

5. Conclusions

- (1) The test results of the friction and the wear in the present tribosystems are reproducible.
- (2) In ZTA–AISI-52100 couples, a thick metallic film is transferred on the ceramic surface. In contrast, only a very thin metallic film adheres to the ceramic surface in both TZP–AISI-52100 couples. The adhesion of the metal layer on ZTA ceramics is stronger than that on TZP ceramics. The presence of soft and thick metallic layer is responsible for the high coefficient of friction of the ZTA tribological system.
- (3) The coefficient of friction of the ZTA–AISI-52100 couples is a factor of 2 more than that of the TZP–AISI-52100 couples. The values of the coefficient of friction depend on the shear stress and the hardness of the contacted surfaces or the hardness of the transformed metallic layer if adhesive wear occurs as the main process.
- (4) Wear rates less than $10^{-6} \text{ mm}^3 \text{ N}^{-1} \text{ m}^{-1}$ for all tested ceramics are obtained at the following conditions: at normal load of 65 N, sliding speed of 20 mm s^{-1} and unlubricated testing distance of 6.9 km. The best wear resistance of the three ceramic materials is ZTA ceramic, i.e. $0.2\text{--}0.5 \times 10^{-7} \text{ mm}^3 \text{ N}^{-1} \text{ m}^{-1}$; however, the highest wear rate is generated at the metal plate, i.e. $8.3 \times 10^{-5} \text{ mm}^3 \text{ N}^{-1} \text{ m}^{-1}$. For the tribosystem as a whole, the TZP–metal couples are favourable if compared with the ZTA–metal couple. The variation of loads from 65 to 200 N does not affect the tribological properties of the ZTA–AISI-52100 system.
- (5) For ZTA–AISI-52100 couple, adhesive wear based on metal transfer to the ceramic surfaces is the dominant mechanism. For TZP–AISI-52100 couple, there is a combination of adhesive wear, plastic deformation and groove as well as some microfracture on small scale.
- (6) During wear tests in water, the metal plate showed strong oxidation. A slightly larger wear rate of the ceramic pin is found if compared with the results obtained in air. This phenomenon can be contributed by the following factors: (i) a softer hydroxide produced on the TZP surface due to tribochemical reaction between water and TZP ceramics, (ii) water, penetrating and chemically interacting with crack interfaces, which reduces interface energies, (iii) absence of the thick metallic layer on the ceramic surface. However, all these factors may not provide a strong influence on the wear of TZP ceramics as observed. In this study, no phase transformation from tetragonal to monoclinic form occurs on the contacted area.

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