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Microstructure–toughness–wear relationship of tetragonal zirconia ceramics

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Abstract

The goal of the present work is to investigate the influence of microstructural variables (grain size, overall yttria content and yttria distribution) and toughness on the tribological behavior of yttria-stabilised tetragonal zirconia (Y-TZP) ceramics. Unlubricated fretting tests were performed on Y-TZP ceramics against commercial hardmetal (WC-Co) ball under ambient conditions of temperature and humidity. The ceramics were processed from commercial yttria-coated and co-precipitated powder as well as the newly formulated powder mixtures with varying overall yttria content and yttria distribution. Microstructural investigation of the worn surfaces was performed and the wear mechanisms were studied. Based on the measured tribological data, the relationships among the friction coefficient, wear, toughness and microstructural variables were elucidated. Within the investigated fretting regime, phase transformation (tetragonal to monoclinic zirconia) induced microcracking and spalling was found to play a major role in the wear of high toughness TZP ceramics. The significant outcome of our research is that a trade-off between the fracture toughness and the wear resistance is achieved in the newly processed Y-TZPs.

Keywords: ZrO_2; Hot pressing; Grain size; Toughness and toughening; Wear resistance

1. Introduction

The advent of transformation toughened ceramics has stimulated tribologists to understand friction and wear mechanisms in order to realise their tribological applications.[1–4] Birkby et al. investigated the influence of transformation toughening on the lubricated sliding wear behavior of 2 and 3 mol% Y-TZP ceramics against steel counterfaces.[1] They proposed a qualitative relationship between the transformability and the wear of these ceramics. It was reported that the grain pull-out and subsequent removal of material is the major wear mechanism for highly transformable ceramics.[1] The grain size dependence of the unlubricated sliding wear of 5.7 mol% Y-TZP ceramics against SiC was studied in dry nitrogen.[2] This study revealed that the wear follows a Hall–Petch type of relationship i.e. the wear rate is inversely proportional to the square root of the grain size for TZP ceramics having grains finer than 0.7 µm. For Y-TZP materials having a coarser grain size (>0.9 µm), however the wear resistance was found to be inversely proportional to the grain diameter. The same group of researchers also investigated the influence of porosity of Y-TZP ceramics on the wear of a TZP-SiC tribosystem under nitrogen gas.[3] The wear rates of the flat TZP materials was observed to increase by a factor of five as the porosity increases from 1.5 to 7.0 vol%.

In a recent study,[4] Jansen et al. reported the influence of the grain size and ceria doping on the tribological behavior of 5Y-TZP ceramics against SiC in distilled water and dry nitrogen. Surface fatigue induced cracking and plastic deformation were identified to be the predominant wear mechanisms in dry nitrogen, whereas grain pullout was the dominating wear mechanism in water. In an earlier study, Fischer et al.[5] established an inverse fourth power relationship between the fracture toughness and the wear rate of self-mated yttria-doped zirconia ceramics in dry air (35–45% relative humidity). The investigated zirconia materials contained different yttria stabilisation levels (3–6 mol%), which is reported

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to change the phase assemblage from fully tetragonal to fully cubic in the investigated materials.

It should be mentioned here that all the research work (except Ref. [1]), discussed above, is carried out using either pin-on-disk or ball-on-plate testing in the unidirectional sliding mode. In the present article, the goal has been to investigate the friction and wear behavior of Y-TZP ceramics against WC-Co under reciprocating sliding (fretting) conditions.

It is well known that the fretting wear of ceramics depends on the material combination, their mechanical properties (combination of hardness and toughness) and microstructure (grain size, porosity, phase content and distribution), experimental parameters (normal load, sliding speed), contact geometry, the thermo-mechanical stress state in the contact area, the interaction with surrounding atmosphere (relative humidity, water or other lubricants). The role of the relative humidity on the fretting wear of self-mated Y-TZP ceramics have been investigated in our laboratory and is reported elsewhere.[6] To the best of the authors' knowledge, no detailed investigation has been performed to study the fretting wear properties of Y-TZP ceramics against hardmetal balls as a function of their microstructure and toughness. In the present work, systematic fretting experiments were carried out on a number of Y-TZP ceramics, fabricated from commercial yttria-coated and co-precipitated starting powders as well as newly formulated powder mixture grades with variable overall yttria content. The flat Y-TZP materials were fretted against commercial grade of hardmetal balls to elucidate the influence of the grain size, yttria content, yttria distribution and toughness on the wear behavior of Y-TZP ceramics.

2. Materials and experimental procedure

2.1. Materials

The mechanical properties and other details of the flat materials and the counterbodies are listed in Table 1. Commercially available hardmetal balls (WC-6 wt.% Co, grade H200C, Spheric Engineering, UK) were used. Different grades of Y-TZP ceramics have been used as flat samples. All the Y-TZP ceramics were hot pressed (HP) in boron nitride coated graphite dies, at 1450 °C for 1 h in vacuum (≈0.1 Pa) in a KCE hot press (W 100/150-2200-50 LAX, KCE Sondermaschinen, Rödental, Germany) under a mechanical load of 28 MPa with a heating rate of 50 °C/min and a cooling rate of 10 °C/min. The density of the specimens was measured in ethanol, according to the Archimedes method (BP210S balance, Sartorius AG, Germany). The Vickers hardness (HV_{10}) was measured on a Zwick hardness tester with a load of 10 kg. The fracture toughness (K_{Ic10}) calculations, based on the radial crack length measurements are according to the formula of Anstis et al.[7] The reported data are the mean of five indentations. X-ray diffraction (XRD, Philips, The Netherlands) analysis was used for phase identification. Grain sizes of the sintered ceramics were measured on smoothly polished surfaces, thermally etched at 1400 °C for 30 min in air.

Among the investigated Y-TZP, the Tio3 ceramic grade was processed from yttria-coated zirconia (Tioxide grade YZ5N) powder; whereas the T3 and D3 grades were obtained from commercially available 3 mol% yttria co-precipitated zirconia powders (Tosoh TZ-3Y and Daiichi HSY-3U respectively). T2 ceramics were based on the commercial 2 mol% yttria co-precipitated stabilised zirconia powder (Tosoh TZ-2Y grade). The experimental grades TM2 and TM2.5 were fabricated from powder mixtures of co-precipitated Tosoh (grade TZ-3Y) and monoclinic zirconia (Tosoh grade TZ-0) with the targeted overall yttria content of 2 and 2.5 mol% respectively. Similarly, DM2 and DM2.5 grades were processed from a powder mixture of Daiichi grade HSY-3U and Tosoh grade TZ-0. The yttria is expected to be homogeneously distributed in the T3 and D3 samples, whereas an inhomogeneous yttria distribution is expected in the Tio3 and all the powder mixture based Y-TZP. For the latter grades, the toughness of the materials is very reproducible and independent of the powder suppliers. The details of powder processing, sintering, mechanical properties and microstructural characterisation of these ceramics are described elsewhere.[8]

2.2. Fretting tests and wear characterisation

For the wear experiments, the flat samples (TZP grades) were ground and smoothly polished down to average surface roughness (R_a) of less than 0.05 µm. The counterbodies (hardmetal balls) are 10 mm diameter balls with average surface roughness (R_a) of 0.02 µm. Prior to the fretting experiment, the materials were ultrasonically cleaned in acetone. The fretting experiments have been performed on a computer controlled tribometer under dry unlubricated ambient conditions (room temperature 23–25 °C; relative humidity measured and maintained at 50–55%). The details of the experimental set up can be found elsewhere.[9] The ball-on-plate configuration is used and fretting vibration at the contact is actuated by a linear relative displacement of constant stroke (mode I, linear displacement sliding). The flat sample is mounted on a translation table, which oscillates at the required displacement with desired frequency by means of a stepping motor. The displacement of the sample is monitored by an inductive displacement transducer, and the friction force is measured with a piezoelectric transducer attached to the holder that supports the counterbody. The friction coefficient is

Table 1
Mechanical properties and other details of the ceramics used in the present work[a]

Materials	Designation	Powder source	Yttria content (mol%)	Mean t-ZrO_2 grain size (μm)	Hardness HV_{10} (GPa)	K_{Ic} (10 kg) (MPa $m^{1/2}$)
ZrO_2 (flat)	Tio3	Tioxide	2.7	0.199[b]	12.1±0.1	8.7±0.3
ZrO_2 (flat)	T3	Tosoh	3.0	0.311	11.6±0.1	2.5±0.1
ZrO_2 (flat)	D3	Zirconia Sales	3.0	0.339	12.3±0.1	3.5±0.1
ZrO_2 (flat)	TM2.5	In-house	2.5	0.350	12.6±0.1	5.7±1.0
ZrO_2 (flat)	DM2.5	In-house	2.5	–	12.2±0.1	5.7±0.1
ZrO_2 (flat)	T2	Tosoh	2.0	0.429	10.9±0.4	5.9±0.1
ZrO_2 (flat)	TM2	In-house	2.0	0.491	11.4±0.1	10.2±0.5
ZrO_2 (flat)	DM2	In-house	2.0	0.500	11.6±0.2	10.1±0.5
WC-Co (ball)	H200C	Spheric Engg.	–	–	16.4±0.3	10.0

[a] The ball data were obtained from the commercial supplier.
[b] Excluding coarse cubic zirconia grains from the measurement.

calculated from the on-line measured tangential force. During the test, fretting loops are recorded at a chosen time interval. A fretting loop gives the evolution of the tangential force as a function of the displacement amplitude during each cycle. The friction coefficient (COF) is further evaluated from the average of the two plateau values of the tangential force in the fretting loop, as described elsewhere.[10] In the present investigation, we have chosen a load of 8 N with a duration of 100,000 cycles (see Fig. 1). Preliminary work has shown that this condition leads to measurable wear within reasonable experimental duration. The combination of selected testing parameters resulted in gross slip fretting contact. For comparative reasons, all the tests are performed with identical experimental parameters. Detailed microstructural characterisation of the as-worn and cleaned surfaces, both on the flat and ball, has been performed with a Reichert-Jung POLYVAR MET optical microscope (Nomarski contrast), scanning electron microscope (PHILIPS XL-30 FEG), Raman microprobe and XPS (VG Escalab 220I-XL). After the fretting tests, the worn surfaces are ultrasonically cleaned prior to the profilometry measurements. A RM600X/Y-100 Rodenstock laser profilometer was used to evaluate the geometry and the wear volumes of the fretting wear tracks.

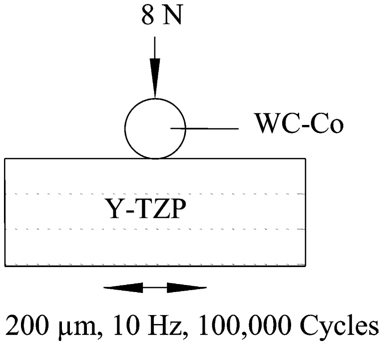


Fig. 1. Schematic of the fretting test with experimental parameters.

The Raman spectra from both the native surface as well as from different spots (at an interval of 20 μm) inside the wear track were obtained at room temperature under ambient conditions. The 514.5 nm Argon laser beam was focussed through a 100× objective lens of an optical microscope to a spot size of 1 μm on the flat samples. The backscattered light was analysed using a DILOR XY spectrometer, equipped with a double monochromator and liquid nitrogen cooled CCD detector. The accumulation time for each Raman spectrum was about 2 min.

3. Results and discussion

3.1. Microstructure of investigated Y-TZP ceramics

All the investigated flat ceramics can be considered as fully dense with comparable hardness (see Table 1). XRD analysis of the polished flat samples revealed the predominant presence of the t-ZrO_2 phase in all the samples. A very small amount (around 2.7 vol.%) of monoclinic zirconia phase was found in the powder mixture grades TM2 and DM2. Typical thermally etched microstructures of the yttria-coated powder based Tio3, the co-precipitated powder based T3 and the experimental powder mixture grade TM2 ceramics are shown in Fig. 2. No residual porosity could be detected in the microstructures. The grains in all the investigated ceramics are fairly equiaxed, except for the Tio3 based ceramic, where the grains are of irregular shape (see Fig. 2 a). The larger grains (>1 μm) in the microstructure of this material are cubic ZrO_2 grains, whereas the smaller grains are tetragonal. No such large cubic grains were found in the other ceramic grades.

Fifty EPMA point analysis were acquired to obtain the yttria distribution in some selected ceramics, as shown in Fig. 3. The major frequency of the yttria distribution occurs at 2 mol% in the TM2 ceramic and at 3 mol% in

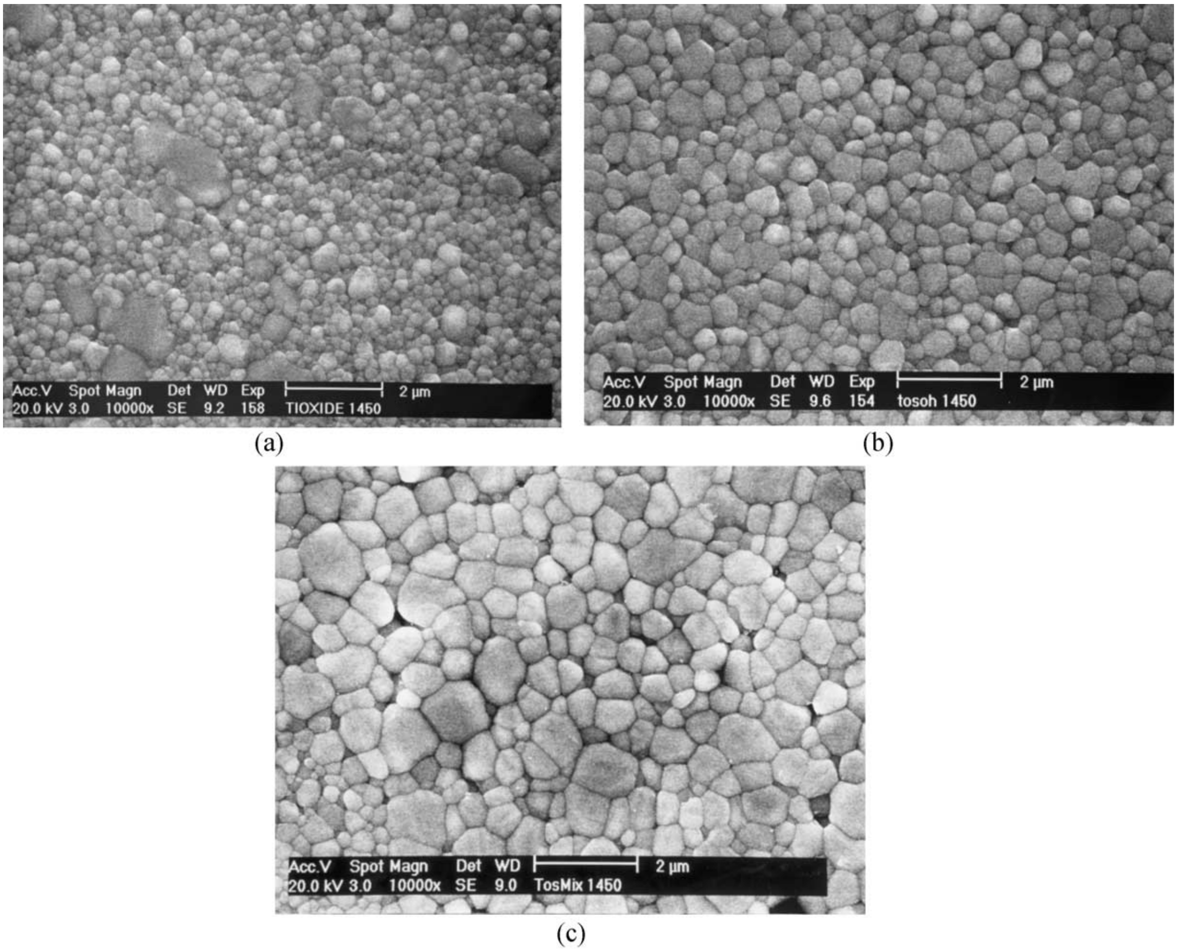


Fig. 2. Thermally etched microstructures of Y-TZP ceramics: yttria-coated powder grade Tio3, containing large cubic grains in a tetragonal zirconia matrix (a), co-precipitated powder grade T3 showing fine tetragonal zirconia grains (b) and powder mixture based grade TM2, revealing larger tetragonal grains (c).

the T3 ceramic, as expected. The yttria distribution in the yttria-coated Tio3 ceramic (Fig. 3a) is broad and symmetric around 3 mol% yttria, with some additional cubic grains having an yttria content above 5 mol%. It is to be noted here that the yttria distribution in the TM2 ceramic is not as narrow as compared to the T3 ceramic. Although, the yttria distribution in the TM2 ceramic (see Fig. 3c) reveals a major frequency at 2 mol% yttria, there is also a minor frequency maximum at 3 mol% and a significant amount of monoclinic zirconia particles without yttria. The presence of monoclinic grains in the TM2 sample and low yttria containing grains in the Tio3 grade is thought to be the source of the enhanced transformability of the metastable tetragonal zirconia grains and the resultant higher toughness.[8] The influence of the microstructure and toughness on the friction and wear of the Y-TZP ceramics against a hardmetal ball is discussed in detail in the following sections.

3.2. Influence of grain size and toughness on friction and wear behavior of Y-TZP

Fig. 4 a shows the frictional behaviour of Tio3 and different grades of Tosoh powder based Y-TZP materials when fretted against WC-Co balls (grade H200C) under a normal load of 8 N for 100,000 cycles. The grain sizes of the investigated Y-TZP grades are also indicated in Fig. 4a. All the friction couples behave in a similar way, in the sense that the average coefficient of friction (COF) starts off from a very low value and sharply rises to a steady state value within the running-in-period (the initial 10,000 cycles) and remains constant for the rest of the duration of the experiment. It should be noted here that the evolution of the COF of the Daiichi powder based Y-TZP ceramics, not shown in Fig. 4a, is quite similar to that of the Tosoh powder based ceramics. Comparing the steady state COF values with the tetragonal grain size of the Y-TZP flat materials (Fig. 4a), it is clear that the COF is strongly related

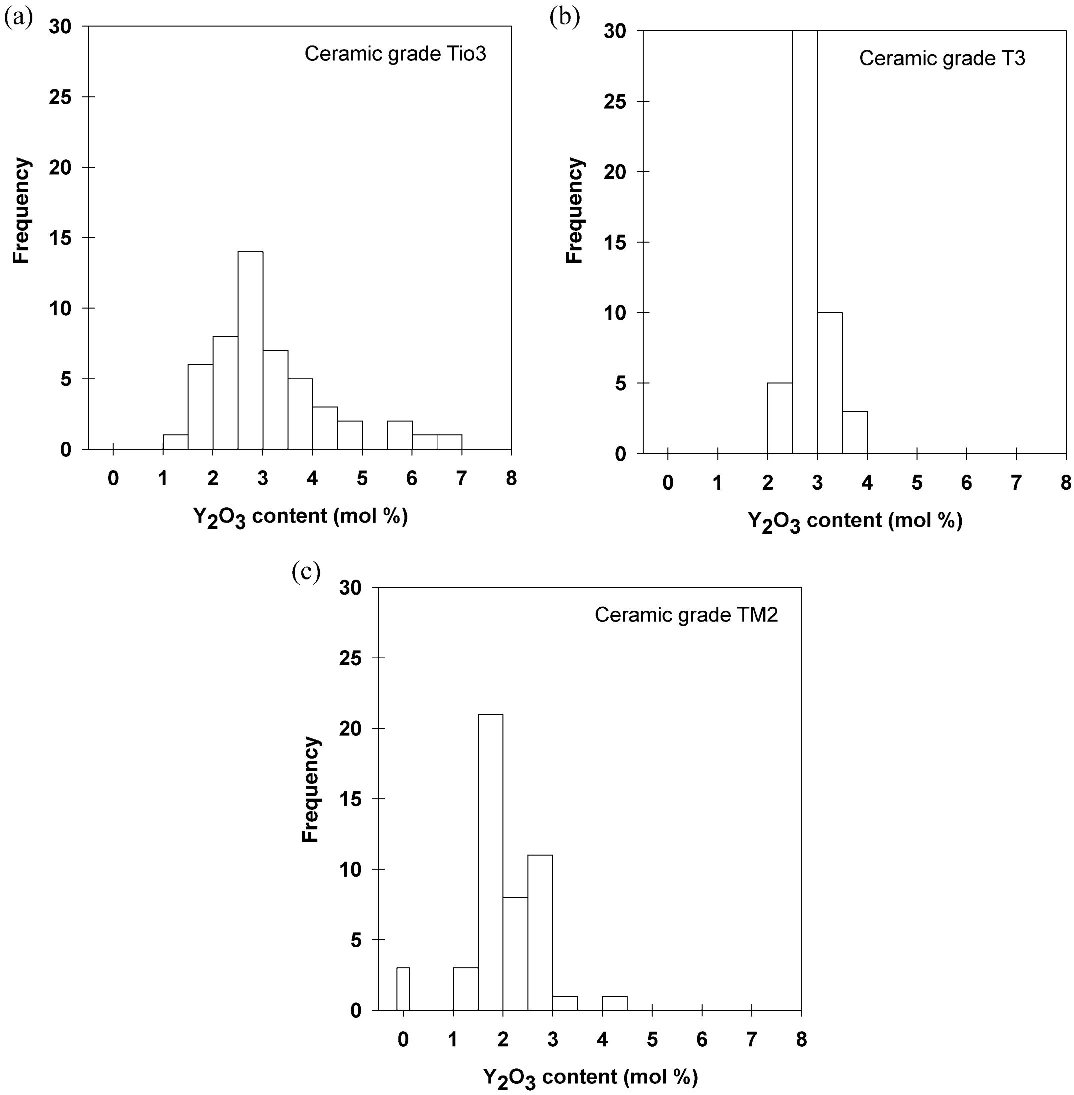


Fig. 3. Yttria distribution, as obtained by EPMA point analysis in some of the investigated Y-TZP ceramics: yttria-coated powder based Tio3 (a), 3 mol% co-precipitated powder based T3 (b) and the powder mixture based TM2 grade (c).

to the average grain size. It should be mentioned here, that the steady state friction behavior of self mated alumina ceramics also strongly depends on the grain size.[11] For the co-precipitated Tosoh powder based T2 and T3 ceramics, as well as the experimental powder mixture based Y-TZP ceramics TM2 and TM2.5, the COF is found to increase with increasing grain size. The highest COF (0.65) however is observed for the yttria-coated powder based Tio3 ceramic having the finest tetragonal zirconia grain size (0.19 µm).

The steady state COF of all the investigated friction couples is plotted versus the fracture toughness of the Y-TZP flats in Fig. 4b. The frictional behavior of two material groups (co-precipitated and powder mixture grades) is distinguished by using the dashed lines. It is clear that the COF increases with increasing fracture toughness for both the co-precipitated powder based ceramics (T2, T3 and D3) and the powder mixture based ceramics (DM2, TM2 and TM2.5). The COF for the yttria-coated powder based Tio3 ceramic substantially deviates from the linear relationship, clearly illustrating that this type of Y-TZP behaves differently in fretting contacts than the ceramics obtained via co-precipitation and the powder mixing route.

The wear volume measured on the Y-TZP flats in the Y-TZP/WC-Co friction couples is plotted versus the t-ZrO_2 grain size and fracture toughness in Figs. 5 and 6 respectively. In both the plots, the wear data obtained with two different grades of TZP materials (co-precipitated and powder mixture grades) are connected by the dashed lines for the ease of comparative study. The error bars in the wear data represent the standard deviation for at least three test results. The wear volume of the Y-TZP ceramics based on powders processed by the co-precipitation and powder mixing routes shows a strong correlation with the grain size (see Fig. 5). Comparing the

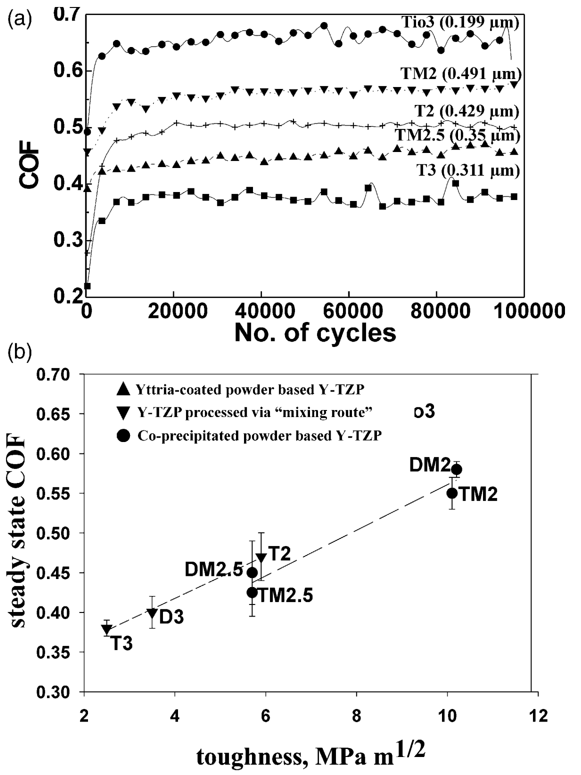


Fig. 4. (a) The evolution of friction when several grades of Y-TZP plates are fretted against hardmetal balls under the conditions given in Fig. 1 (a). The numbers inside the bracket indicate the grain sizes of the investigated ceramic grades. The steady state friction coefficient plotted as a function of the fracture toughness of the Y-TZP flats (b). To make comparative study on the frictional response for different TZP grades, two dashed lines in (b) connect and group the materials processed via two routes: co-precipitation (T3, D3 and T2) and powder mixing (TM2.5, DM2.5, TM2 and DM2).

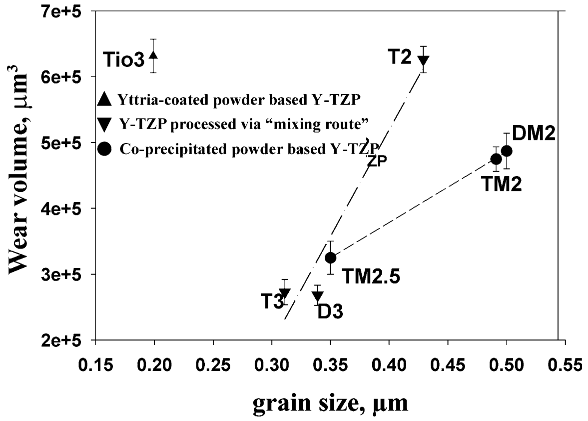


Fig. 5. Plot of the average grain size (Y-TZP flats) against the measured wear volume (flats) for the investigated Y-TZP/WC-Co friction couples. The fretting parameters are the same as mentioned in Fig. 1. In order to study the influence of grain size on wear, two dashed lines connect and group the materials processed via two different routes: co-precipitation (T3, D3 and T2) and powder mixing (TM2.5, TM2 and DM2).

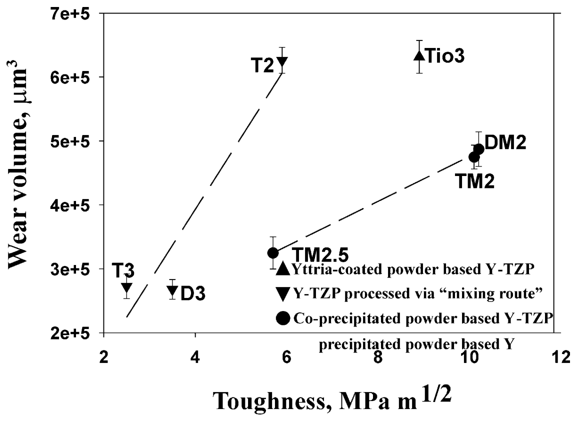


Fig. 6. Plot of the toughness (flat) against the wear volume of the Y-TZP flats, fretted against WC-Co balls. The fretting parameters are the same as mentioned in Fig. 1. In order to obtain qualitative dependency of wear on toughness for different TZP grades, two dashed lines connect and group the materials processed via two different routes: co-precipitation (T3, D3 and T2) and powder mixing (TM2.5, TM2 and DM2).

wear volume of the co-precipitated powder based (T3, D3 and T2) ceramics reveals that the volumetric wear loss increases with increasing tetragonal grain size. A similar relationship is observed for the powder mixture based ceramics. However, the influence of the grain size on the wear volume is much more pronounced for the co-precipitated powder based ceramics than for the powder mixture based grades, as indicated by the dotted lines in Fig. 5. It is also reported in the literature[12] that the sliding wear rate of self-mated alumina ceramics increases linearly with increasing grain size.

Close observation of the data in Fig. 5 further reveals that the fretting wear loss of the yttria-coated Tio3 ceramic is quite high, despite the much finer tetragonal grain size. The high volumetric wear loss of the Tio3 ceramic can be partly related to the presence of cubic zirconia grains, which are inferior in wear resistance as observed by Fisher et al.[5]

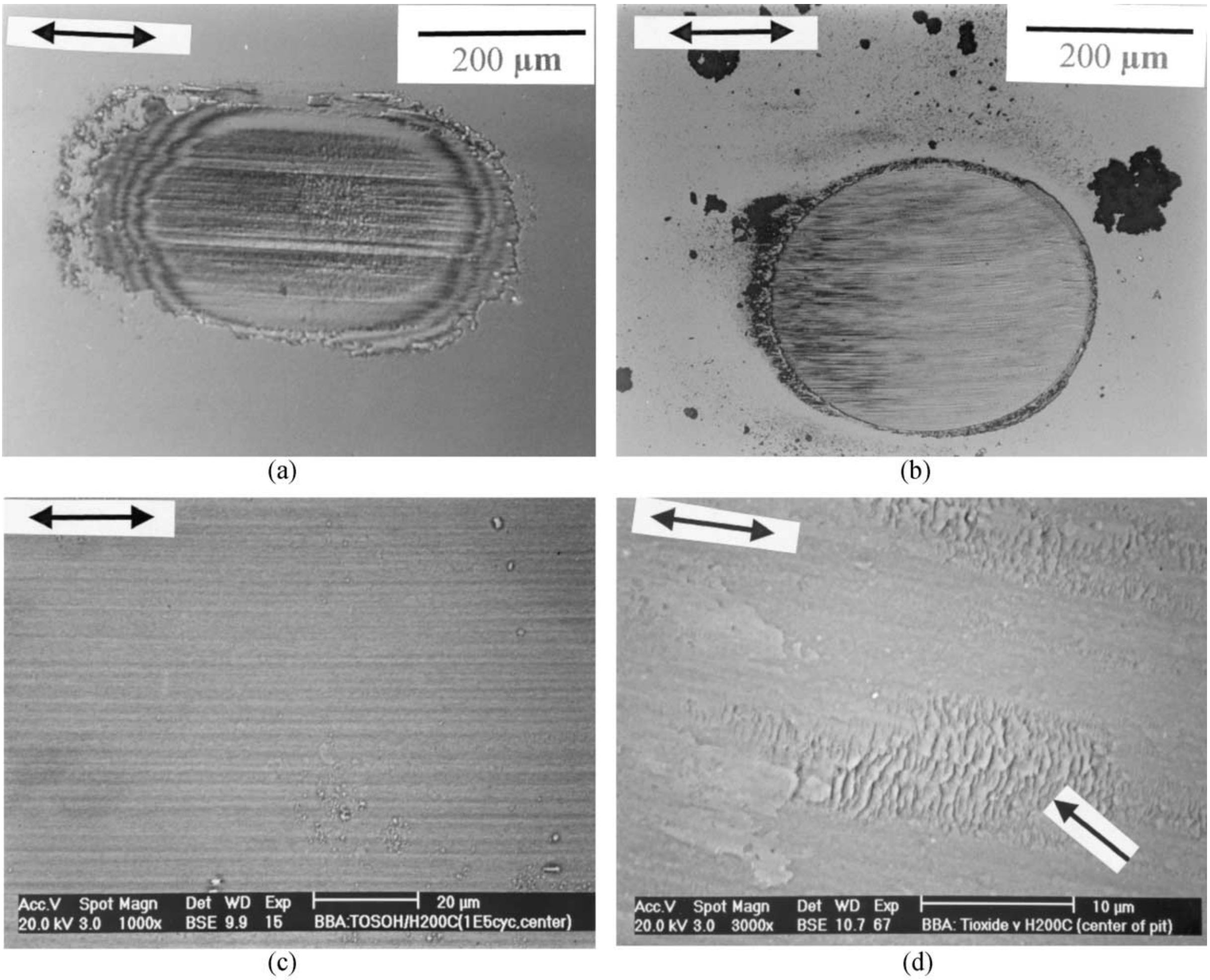
As it is well known that the toughness of Y-TZP ceramics is controlled by the grain size, it can be expected that the fretting wear resistance of such materials should be dependent on the toughness as well. For both the co-precipitated (T3, D3, T2) and the powder mixture grades (TM2.5, DM2.5, TM2, DM2), the wear volume increases with toughness (see Fig. 6). The highest wear loss is recorded with the Y-coated powder based Tio3 ceramic. Although the TM2 and DM2 ceramics have a higher toughness than Tio3 grade, the mixed grades exhibit a better fretting wear resistance under experimental conditions. This indicates that apart from toughness and grain size, the other microstructural variables i.e. overall yttria content and distribution, presence of cubic grains also play important roles in the fretting wear of Y-TZP ceramics. This will be discussed in detail in Section 3.4.

Summarising, the wear data reveals that the higher the fracture toughness, the higher is the fretting wear loss under the investigated fretting conditions. This implies that a compromise between the fracture toughness and the wear resistance needs to be achieved in order to realise successful applications of Y-TZPs as tribomaterials.

The morphology and details of the fretting pits on two different grades of Y-TZP flats are shown in Fig. 7. The wear pit is elliptical in case of the low toughness T3 ceramic and more circular for the high toughness Tio3 ceramic. Abrasive grooves parallel to the fretting direction are present in both worn surfaces. The wear debris is mainly accumulated around the edge of the wear pit. The compositional analysis of the transfer layer on the flats reveals the presence of W and Co. XPS analysis indicates the formation of WO_3 and CoO on the flat worn surface. This shows that material transfer from the counterbody and subsequent oxidation of the counterbody elements occurred during the process of fretting wear. The worn surfaces were ultrasonically cleaned prior to further microstructural investigation. The morphology of the cleaned worn surface on the high toughness Tio3 plate indicates the presence of microcracks in the central region of the worn surface. The microcracking patterns (see Fig. 7d) are found perpendicular to the sliding direction. Such patterns were not observed on low toughness materials (see Fig. 7c).

3.3. ZrO_2 phase transformation and fretting wear

The role of the tetragonal (t-ZrO_2) to monoclinic zirconia (m-ZrO_2) phase transformation during fretting wear of Y-TZP has been investigated by Raman spectroscopy. The Raman spectra, as shown in Fig. 8, are obtained from different locations, at an interval of 20 µm, inside the fretting pit (ambient humidity) on the worn Tio3, after it was fretted against WC-Co for 100,000 cycles in ambient humidity (50–55% RH). The characteristic Raman peaks related to the tetragonal



(a) (b)

(c) (d)

Fig. 7. The morphology (Nomarski contrast) of the wear pits and wear debris on the as fretted surfaces of two different Y-TZP plates: T3 (a) and Tio3 (b). SEM micrographs, taken from the ultrasonically cleaned worn surfaces, showing the center of the fretting pit on the low toughness T3 (c) and high toughness Tio3 plate (d). The fretting direction is indicated by a doubly pointed arrow. The arrow in (d) indicates the transformation induced microcracking.

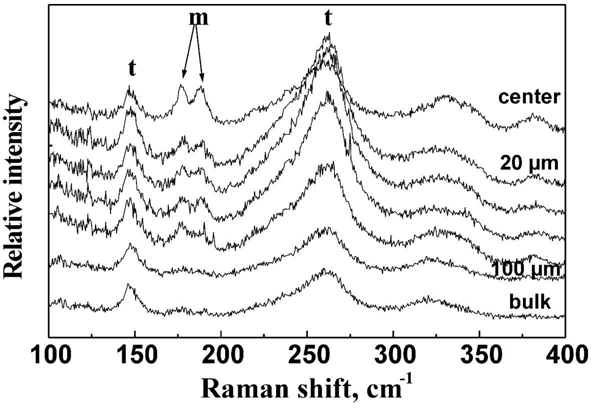


Fig. 8. Comparison of the Raman spectra taken from the polished surface (bulk) with those taken from different points (at interval of 20 µm) in the wear pit formed on the Tio3 flat after fretting against WC-Co for 100,000 cycles in ambient humidity.

phase (located at 145 and 267 cm^{-1}) and monoclinic phase (located at 185 and 197 cm^{-1})[12] are also indicated in Fig. 8. Although, the intensity of the m-ZrO_2 peak is rather low, the intensity of m-ZrO_2 Raman bands acquired from the worn surface is clearly much higher compared to that in the unworn surface, where the monoclinic Raman bands can hardly be discerned from the background. Also, XRD investigations could not detect any monoclinic zirconia on a polished Tio3 specimen. If we compare the Raman spectra taken from the virgin surface with those taken from the worn surface, we observe that there is a considerable amount of monoclinic phase produced during the fretting process. Also, the amount of m-ZrO_2 is clearly much higher in the centre than that at the edge of the wear pit, as revealed by the intensities of the m-ZrO_2 Raman band. The above observation is a clear proof that the t-ZrO_2 to m-ZrO_2 phase transformation occurs during the fretting wear process.

It is a well-known fact[13] that the martensitic *t-m* transformation in Y-TZP ceramics can be induced either thermally or by mechanical stresses (combination of both shear and tensile stress). Concerning the thermal effects, two interfacial temperatures should be considered: bulk and flash temperature.[14] In general, the contact surface temperature is a multi-parameter function of the size and shape of the real contact area, the friction coefficient, normal load, sliding velocity and thermal properties of the contacting bodies.[15] The bulk interfacial temperature under dry sliding conditions could increase to a steady state temperature, which is mainly controlled by the contact geometry. The flash temperature is the short duration microscopic temperature pulse mainly due to the asperity–asperity contact and frictional dissipation of heat.[14] Additionally, the flash temperature, as compared to bulk temperature, at the tribocontact is reported to significantly influence the tribological behavior. It is reported in the literature that the flash temperature for self-mated Y-TZP under unlubricated conditions could rise up to 500–800 °C depending on the combination of sliding speed and load.[16] This flash temperature has been calculated for the pin-on-disk configuration and for a range of sliding speeds (0.002–0.570 m/s). Since the flash temperature strongly depends on the thermal conductivity of the mating couple, it is reasonable to assume that the flash temperature should be below 500 °C at the TZP/WC-Co tribocontact (thermal conductivity of WC-Co 100 Wm^{-1}K^{-1}) under the present fretting conditions (maximum sliding speed 0.004 m/s). Furthermore, recent dilatometry measurements[17] have revealed that the TM2 and DM2 grade ceramics have the martensitic start temperature (M_s) around 300 °C. M_s temperature of the Tio3 and all other investigated TZP grades, however lies below room temperature. From the above discussion, it is clear that the t-ZrO_2 phase transformation in the high toughness Y-TZP, like Tio3 ceramic, under the fretting conditions is only triggered by the mechanical stress, whereas both the repeated thermal cycling and mechanical stress can induce the *t* to *m* transformation at the fretting contacts of TM2 and DM2 grade ceramics.

As it is well known that the *t–m* transformation is always accompanied by microcracking in the transformation zones,[18] the microcracks observed on the worn surfaces of the highly transformable ceramics (shown in Fig. 7d) can be attributed to the stress induced transformation of the tetragonal zirconia phase. These microcracks will eventually cause a local material removal during the course of fretting. This indicates that microcracking assisted spalling is the predominant wear mechanism within the investigated fretting regime.

3.4. Relationship among microstructure, toughness and wear

It is an established fact that the transformation toughening[19–21] plays a major role in the enhanced toughness of the Y-TZP ceramics. The effectiveness of such toughening mechanism primarily depends on the t-ZrO_2 transformability, strongly influenced by the grain size, yttria content etc.

The yttria-coated powder based ceramic is characterised by a bimodal microstructure consisting of large cubic zirconia grains embedded in a tetragonal matrix with finer grains. The overall yttria distribution is very broad (see Fig. 3a). The higher toughness of the Tio3 ceramics compared to T3 and D3 ceramics has been found to be caused by the inhomogeneous distribution of yttria.[8] The small number of low yttria containing tetragonal grains (Fig. 3a) are thought to be very susceptible to transformation under the applied mechanical stress (tensile and shear) conditions, such as during fretting, which makes the yttria-coated powder based Y-TZP materials very prone to fretting wear. The higher volumetric wear of the Tio3 ceramic can also be related to the presence of cubic zirconia grains, which are inferior in wear resistance as observed by Fischer et al.[5]

The co-precipitated powder based ceramics (T3, D3 and T2 grades) only contain t-ZrO_2 grains with a narrow yttria distribution (see for example Fig. 3b). The grain size, transformability and fracture toughness increases with decreasing yttria content. The observation that the wear volume increases with the grain size (see Fig. 5), can be attributed to the fact that a larger tetragonal grain size increases the transformability of the t-ZrO_2.[21] The transformation of the tetragonal to monoclinic phase causes microcracks at the fretting contacts, which enhances spalling of material from the contacting surfaces.

The powder mixture based ceramics (TM2, DM2 grades) consist mainly of t-ZrO_2 with a small amount of m-ZrO_2. The grain size, as well as the transformability and fracture toughness, is substantially higher than that of the co-precipitated powder based ceramics with the same yttria content. The yttria distribution in the powder mixture based ceramics is much broader (see Fig. 3c). The superior toughness of the TM2 and DM2 ceramics has been attributed to the enhanced transformability caused by the larger grain size coupled with the inhomogeneous yttria distribution due to the powder mixing process. Despite the higher toughness and grain size (see Table 1), the fretting wear loss of the TM2 and DM2 ceramics is found to be lower than that of the co-precipitated powder based T2 ceramic (see Figs. 5 and 6), which has same overall yttria content of 2 mol%. This clearly illustrates that the yttria distribution plays a significant role in controlling the fretting wear of Y-TZP ceramics.

From the results described above, it is clear that the newly formulated "powder mixing" route provides a way to make Y-TZP ceramics with toughness values that are much higher than could be obtained from the co-precipitated powder and even as high as that of yttria-coated zirconia powder based ceramics, but with a substantially reduced susceptibility to fretting wear against WC/Co hardmetal. For example, TM2 ceramic, processed via powder mixing route is tougher and more wear resistant than the co-precipitated T2 ceramic. Furthermore, both the TM2 and DM2 ceramics have the higher toughness and fretting wear resistance than the Tio3 grade.

The implication of the present work is quite significant as far as the tribological applications of the transformation toughened zirconia ceramics are concerned. The experimental results clearly indicate that apart from the toughness and grain size, the fretting wear of the Y-TZP ceramics is also influenced by other microstructural variables, especially for the yttria-coated and the powder mixture based Y-TZP materials. Other microstructural variables influencing the fretting wear resistance are the phase assemblage (in particular the presence of cubic phase), overall yttria content and the yttria distribution in the sintered microstructure. The toughness of the sintered Y-TZPs has been found to be extremely important in controlling the fretting wear of Y-TZP/WC-Co friction couples. The present relationship among the wear (a system dependent property), toughness and microstructure may not be valid for other tribosystems containing Y-TZP and different counterfaces. But certainly, the present investigation strongly indicates that the optimisation of the microstructure and toughness is crucial to tailor the fretting wear resistance of Y-TZP ceramics. These factors should therefore be critically considered to design Y-TZP based materials for specific tribological applications.

4. Conclusions

(a) The steady state coefficient of friction of the Y-TZP/WC-Co couples strongly depends on the grain size and toughness of the zirconia materials. Within the investigated fretting regime, the COF was found to increase with increasing tetragonal grain size and concomitant toughness of the co-precipitated powder and powder mixture based ceramics. The highest COF is measured with the yttria coated TZP.

(b) The present work clearly indicates that the fracture toughness is an important parameter in determining the tribological behavior of the engineering ceramics. Within the investigated toughness range, the volumetric wear loss increases with increasing toughness for the co-precipitated and powder mixture based Y-TZP ceramics. The wear volume measured with the yttria-coated powder based ceramics is substantially higher and is due to the presence of a significant number of cubic grains.

(c) Raman spectra obtained from the worn surfaces clearly reveal that the fretting wear is accompanied by the phase transformation of tetragonal to monoclinic symmetry for highly transformable TZP ceramics. The t–m ZrO_2 transformation is observed to cause extensive microcracking at the worn surfaces.

(d) Based on the topographical observations of the worn surfaces, the fretting wear mechanism is proposed. The morphology of the wear pits indicates that a mild abrasion is the major wear mechanism for the low toughness Y-TZP ceramics, whereas microcracking assisted spalling is the major wear phenomenon for the high toughness Y-TZP materials.

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