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The Sliding Wear of Ceramics

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Abstract: The micromechanical and microchemical processes which take place during the friction of ceramics are not fully understood. The occurrence of surface plasticity and microfracture on a sub-grain size scale have been suggested but no clear experimental evidence has been provided. Tribochemical wear mechanisms are now considered to be critical to the wear performance of a ceramic. However, the mechanisms of tribochemical interaction remain unclear. This paper presents a detailed study of the wear of zirconia toughened ceramics against metal and ceramic counterfaces in the regime that the above mechanisms would be expected to operate. No evidence of surface plasticity or microfracture was obtained. The surface contact was found to be largely elastic with minimal transformation of the tetragonal to monoclinic phase. The dominant wear mechanism was tribochemical as a result of dissolution of the ceramic surface into a metallic oxide transfer film for the metal counterface, and the formation of an amorphous surface hydrate against a ceramic counterface. In both instances, it is considered that the tribochemical reaction dictates the minimum wear rate achievable and therefore particular attention should be paid to modification of the ceramic composition to optimise the surface chemistry to promote the optimum hydrate properties. © 1996 Elsevier Science Limited and Techna S.r.l.

1 INTRODUCTION

This paper will concentrate on the microstructural changes induced by the friction of zirconia toughened ceramics. Three main issues will be considered. Firstly, the interaction of the surface with the environment and the counterface. Secondly, the role of surface deformation will be discussed. Thirdly, the importance of surface fracture, both on a micro-scale and that associated with wear rate transitions, will be evaluated. The stress assisted transformation of the tetragonal to monoclinic zirconia will also be considered, although this was not found to be a dominant mechanism in the present study.

The repeated disruption of the surface by the counterface asperities leads to substantially enhanced reaction rates during the wear of virtually all materials. Engineering ceramics have been traditionally considered to be particularly resistant to chemical reactions. However, it is becoming increasingly apparent that the interaction of the ceramic with the environment and the counterface plays a critical role in determining the wear performance of the material. In many cases, it is clear that such interactions can determine the minimum wear rate achievable within a particular system.

The environment is also known to strongly affect the mechanical properties of the surface, known as chemo-mechanical effects, and results from absorption of chemical species at or near the surface. This phenomenon was first thought to result from a reduction in the surface free energy because of chemisorption (the Rebinder effect), but evidence is now available which shows that the mechanism is far more complex. For example, both hardness and drilling rate have been shown to be a strong function of the testing environment.[1–3] The zeta potential of the testing liquid has been found to give a good indication of the ceramic surface mechanical properties. However, it is difficult to separate the differences in lubrication and heating which result from changing the zeta potential, such that agreement between wear and zeta potential is far from precise.[1–3]

The hardness of the ceramic is, therefore, not a material property. Its value is a function of the environment in which the test is made, as discussed above, but also, below a critical load, the size of the indent. For example, Czernuszka and Page[1] have demonstrated a considerable rise in hardness at low loads for alumina, where the indentation diameter was found to scale with load dictated by the relationship:

$$L = Kd^n$$

where K is a constant and n represents the indentation size effect. This, therefore, allows the hardness of the material relevant to the asperity contact size to be determined. The load, for a given indentor size at which contact will change from elastic to elasto-plastic (i.e. at which the first dislocations are formed), can therefore be determined. By choosing an indentor size comparable to that of a contacting asperity, the load at which plastic contact will occur for a given true contact area can therefore be predicted. This load is found to change sensitively with environment and the crystallographic orientation of the individual grain.

It is now well established that the wear rate of a ceramic is a function of the crystallographic orientation. For example, Steijn[4] demonstrated hardness and wear anisotropy for different orientations of sapphire. Sliding on crystals with the prismatic plane parallel to the c-axis produced severe chipping and conchoidal fracture, whereas sliding on other directions in the prismatic planes and in any direction in the basal plane produced a smooth surface and a reduction in wear rate by two orders of magnitude. Similarly, Buckley[5] has shown that the minimum friction coefficient coincides with sliding along the slip direction for a ceramic crystal with the dominant slip plane parallel to the surface. These observations have led several authors to suggest that the wear of a ceramic depends on the relative ease of plastic deformation as opposed to brittle fracture.[6,7] However, there remains no clear evidence that plastic deformation occurs during the sliding wear of ceramics, and its role remains highly controversial. Moreover, if plastic flow does occur at the surface, the manner in which the chemo-mechanical effects alter this plastic flow remains unexplored. However, there is now considerable evidence that plastic deformation is the dominant mechanism during the abrasive wear of ceramics, as shown by Hockey[8,9] and Rainforth and Stevens.[10,11]

Not only do chemo-mechanical effects dictate the relative ease of plastic deformation as opposed to fracture on a micro-scale, but also they will have a strong effect on so-called tribochemical wear. Hydration of oxide ceramics and oxidation of nitride ceramics have been shown to promote significant wear rates. Evidence is usually indirect and has mainly been provided by an investigation into the wear debris structure. For example, Gates *et al.*[12] have identified bayerite (a hydrated form of alumina) in the wear debris from alumina on alumina sliding wear tests. Such hydrates have significantly lower hardnesses compared to α-Al_2O_3 and have been shown to offer the potential for reducing the friction coefficient. However, there remain several unanswered questions. Do these hydrates form on the sliding surface or are they formed from crystalline fragments which hydrate during subsequent attrition? Since α-Al_2O_3 is highly resistant to hydration does some intermediate phase form, such as δ-Al_2O_3 or γ-Al_2O_3, prior to hydration? Is tribochemical wear associated with purely elastic contact or elasto-plastic contact? This paper will address these issues.

2 EXPERIMENTAL PROCEDURE

Wear testing was undertaken on a tri-pin-on-disc machine, the details of which are given elsewhere.[13] The rig employs three 1 cm diameter pins with a truncated cone machined at one end, providing a 3 mm diameter contact face. The pins were held in a top plate which was prevented from rotating by two half-bridge strain gauges, whilst the disc was rotated. The design was such that only a few mm of the pin projected from the top plate surface in order to ensure maximum system stiffness. The head was placed on top of the annular disc, located by a central spindle. Loads were applied by dead weight which were secured directly to the top plate containing the pins.

A range of commercial ceramic materials were investigated. Yttria tetragonal zirconia polycrystals (Y–TZPs) with 2 and 3 mol% yttria were supplied by Dynamic Ceramic (Crewe, UK). Zirconia toughened alumina (ZTA) pins and discs were supplied by the same company. Mg–PSZ materials, with a nominal 8.5 mol% MgO, were supplied by Coors Ceramics.

Tests were conducted using ceramic on ceramic sliding couples and ceramic pins on a 1% Cr/1% C bearing steel disc. Tests were performed at 0.24 ms^{-1} and 0.016 ms^{-1} using loads in the range 5–55 N/pin under dry ambient conditions. All surfaces were prepared by lapping to a high standard of surface polish. The R_a of the zirconia disc was measured at 0.008 μm, and the pins were believed to have a similar value but were too small to measure directly. The wear rate was measured by weight loss. A control pin was kept next to the wear rig during tests and its weight measured at the same time as the pins in order to correct for errors in weight changes attributed to factors such as water absorption.

The worn surfaces were examined by optical microscopy (Nomarski contrast), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and X-ray diffraction. Specimens of the worn surface for TEM were obtained by argon ion milling from below the worn surface (back thinning), and in cross-section, the full details of which are given elsewhere.[14]

3 RESULTS AND DISCUSSION

3.1 Ceramic on metal wear

The wear rates as a function of load for a 2Y–TZP, a 3Y–TZP and an Mg–PSZ against a bearing steel disc are shown in Fig. 1. The toughness of the three materials was measured as 6 MPam$^{0.5}$ for the 3Y–TZP, 8 MPam$^{0.5}$ for the Mg–PSZ and 11 MPam$^{0.5}$ for the 2Y–TZP. Table 1 gives the % monoclinic on the worn surfaces for the ceramic pins worn at 0.24 ms^{-1} against the bearing steel counterface. Some transformation of the tetragonal to monoclinic phase has occurred, but the amount was substantially smaller than that obtained by grinding, for example. The maximum increase compared to the starting surface was 8.6% in the Mg–PSZ. Thus, the starting toughness (and therefore driving force for the tetragonal to monoclinic transformation) did not strongly affect the extent of transformation. This result is in agreement with the wear rate data presented in Fig. 1, which showed that the wear rate was independent of toughness. It is clear, therefore, that the wear mechanism was not determined by the material toughness, or the transformation of tetragonal to monoclinic.

An SEM micrograph of the worn surface of the 2Y–TZP, Fig. 2, shows two important features. Firstly, transfer of metal from the counterface has occurred and resulted in substantial surface damage. Secondly, the remainder of the worn surface is smooth, but each individual grain has worn to a different extent.

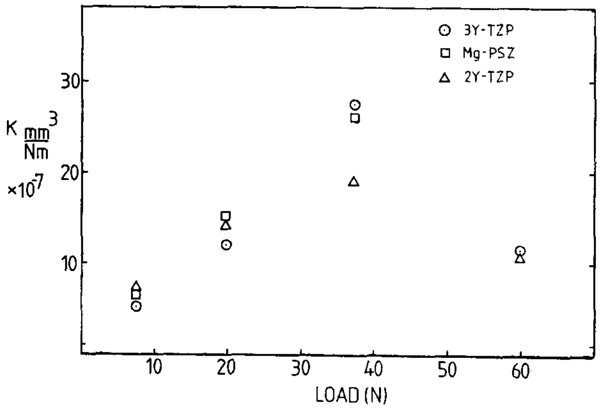

Fig. 1. Wear factor as a function of load for three zirconias worn against a steel disc.

Table 1. Volume % monoclinic for various zirconia surfaces before and after wear testing

Condition	Volume % monoclinic 2T–TZP	 3Y–TZP	 Mg–PSZ
Polished	1.3	0	10.0
Ground	22.1	15.7	36.5
6.6 N pin	7.5	4.3	18.6
19.6 N pin	8.6	3.1	11.2
37.6 N pin	7.8	6.8	17.7
59 N pin	6.3	0.9	—
Disc	—	—	7.9
As-sintered	—	—	6.9

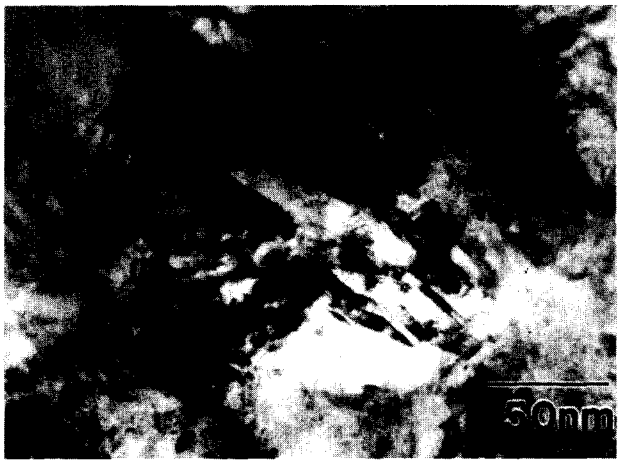

Fig. 2. Optical micrograph (Nomarski contrast) of a Y–TZP worn at 59 N/pin. Note the metal transfer (rough area) and grain relief over the rest of the surface.

To further investigate the wear mechanism, detailed TEM was undertaken of the worn surfaces, using both back-thinning and cross-sectional analysis. A back-thinned micrograph of the 3Y–TZP pin is shown in Fig. 3. Occasional grains had undergone the tetragonal to monoclinic transformation, but the majority of grains remained tetragonal, and exhibited residual strain effects. A cross-section of the surface, Fig. 4, shows the same features. Importantly, there is no evidence of microcracking, microfracture or plasticity.

A back-thinned micrograph from the Mg–PSZ is shown in Fig. 5. The majority of the precipitates are tetragonal, and it is only within the last 200 nm from the surface that any significant transformation to

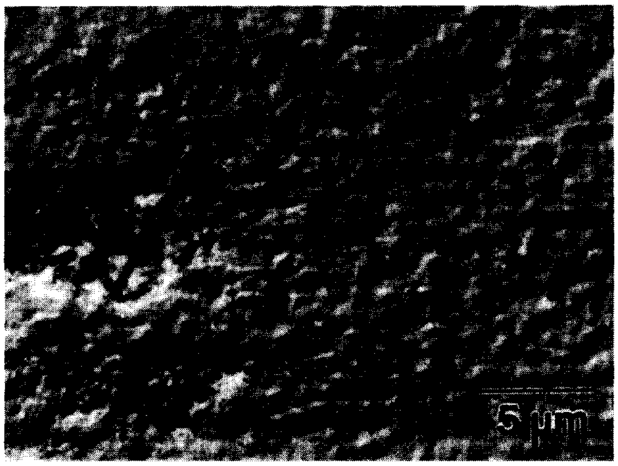

Fig. 3. TEM micrograph of a back-thinned 3Y–TZP showing the structure at the extreme worn surface. The central grain is monoclinic, surrounded by tetragonal grains. No evidence of dislocation flow was found, except an isolated dislocation at the centre.

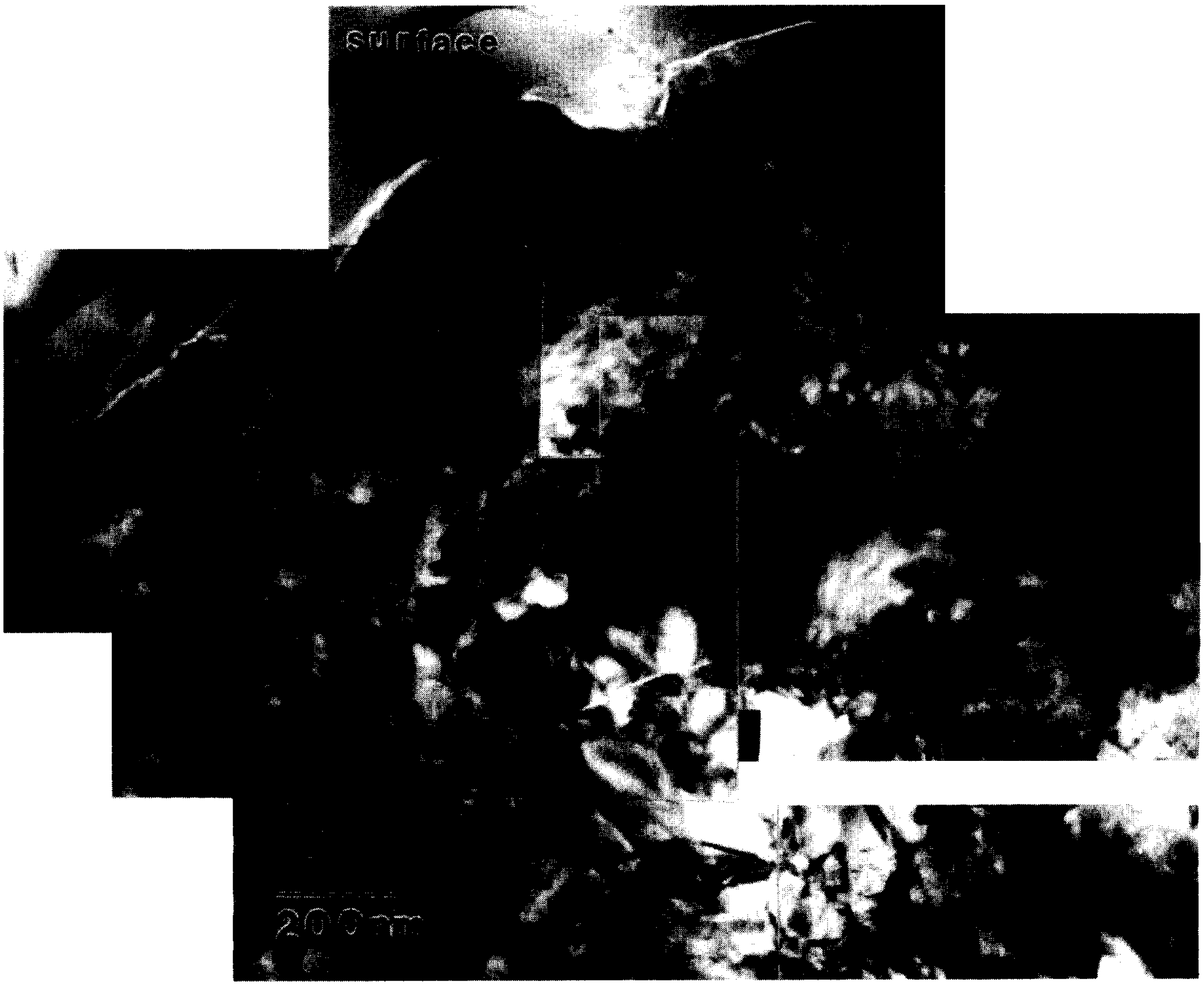

Fig. 4. Cross-section of the 3Y–TZP worn at 37.6 N/pin. The microstructure was obscured by a high level of residual strain. However, the majority of the structure was tetragonal with occasional monoclinic. No evidence of microfracture or plasticity could be found.

monoclinic occurred. A region was found in this material where the transfer layer from the counterface was still intact, Fig. 6. The layer was found to consist of a mixture of Fe_3O_4 and a fine iron oxide phase which had a non-equilibrium bcc structure. Interestingly, this transfer layer contained zirconia in solid solution, with no discrete ceramic particles being found, despite extensive investigation. Moreover, the interface between the ceramic and the oxide transfer layer was diffuse, and had apparently resulted in preferential removal of the cubic zirconia phase compared to the tetragonal.

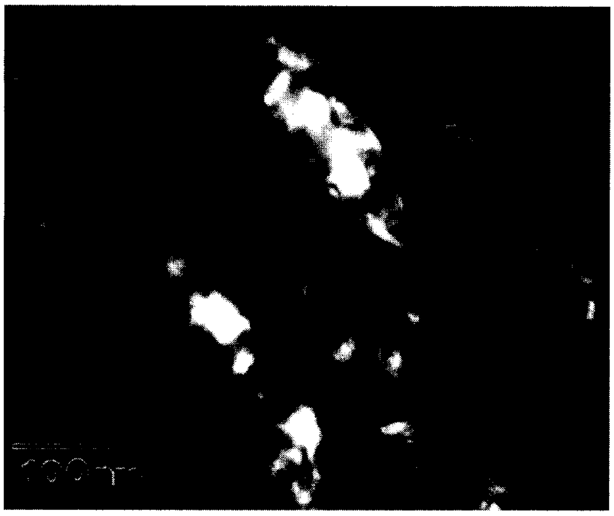

Fig. 5. Dark field TEM micrograph from just below the worn surface of an Mg–PSZ. The majority of the precipitates were tetragonal, with no evidence of plastic deformation. However, the image of the precipitates was clearly distorted by residual elastic strain.

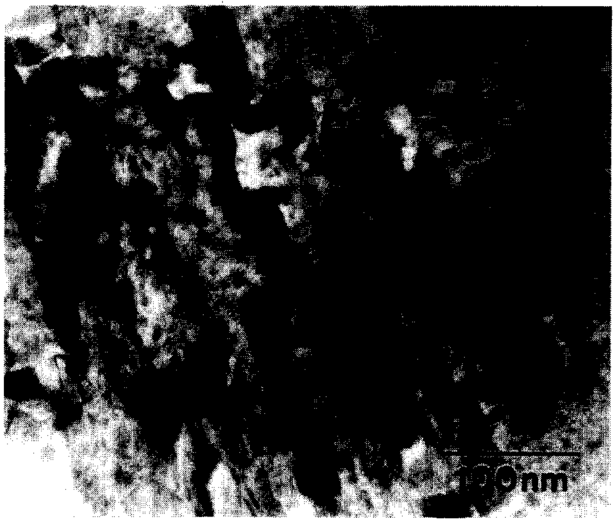

Fig. 6. TEM micrograph from a back-thinned Mg–PSZ showing the structure at the extreme surface. Isolated tetragonal precipitates are present surrounded by an iron based oxide. The cubic appears to have dissolved in the iron oxide. Note the diffuse interface between the zirconia and the transfer layer.

This investigation, therefore, has provided strong evidence for a tribochemical wear mechanism involving direct chemical reaction between the steel counterface and the zirconia. No evidence of mechanical based wear mechanisms was found. No microcracking was found or plastic deformation. No discrete zirconia wear debris was found in either the transfer layer or the debris liberated from the sliding interface. Rather, the wear rate appears to have been dominated by the rate at which zirconia was dissolved by the iron oxide transfer layer.

The grain relief resulting from differential wear rates between different orientations have been attributable to several different mechanisms. For example, Wallbridge *et al.*[7] suggest that some grains will undergo plastic deformation while others will be badly oriented which leads to microfracture and higher wear rates. The findings of Hockey[8,9] and Steijn,[4] discussed earlier, are cited as evidence. Other explanations suggest that the grain relief is merely a result of differences in elastic modulus as a function of crystallographic orientation leading to differences in deflection during the passage of an asperity. However, grain relief has been observed with equal intensity in the present study in materials with different elastic anisotropies, namely cubic zirconia, tetragonal zirconia and hexagonal alumina (see later), discounting elastic deflection as the only explanation. The present work has shown the mechanical based explanation to be untrue since no plasticity or microfracture was found. While the modules argument may play some role, it is considered that the dominant mechanism is the difference in chemical dissolution of the zirconia by the iron oxide as a function of the crystallographic orientation.

The wear rate in this study was low. Mechanical based wear mechanisms such as fracture would be expected to give higher wear rates. It would appear probable, therefore, that the minimum wear rate shown by a ceramic material is governed by the tribochemical wear rate. In many instances this wear rate can be surprisingly high.

3.2 Ceramic on ceramic wear

Wear testing at 0.24 ms^{-1} with zirconia pins on a ZTA disc resulted in catastrophic wear rates, largely as a result of the poor thermal conductivity of the zirconia, the details of which are considered elsewhere.[10] However, the tests of zirconia conducted at 0.016 ms^{-1} and of ZTA at 0.24 ms^{-1} exhibited low wear rates, Table 2.

An SEM micrograph of a 3Y–TZP worn against a ZTA disc at 0.016 ms^{-1} is shown in Fig. 7. The surface contained numerous fine scratches and a surface film which covered approximately 20% of the worn area. It was apparent that the scratches

Table 2. Wear rates and friction coefficients for ceramics on ceramic wear

Pin material	Load (N)	Sliding speed (ms^{-1})	Total distance (km)	Friction coefficient	Wear factor (mm^3/Nm)
3Y–TZP	19	0.24	11.1	0.12–0.44	8.9×10^{-4}
3Y–TZP	10	0.016	102	0.18–0.39	2.4×10^{-7}
ZTA	19	0.24	159	0.13	3.0×10^{-8}

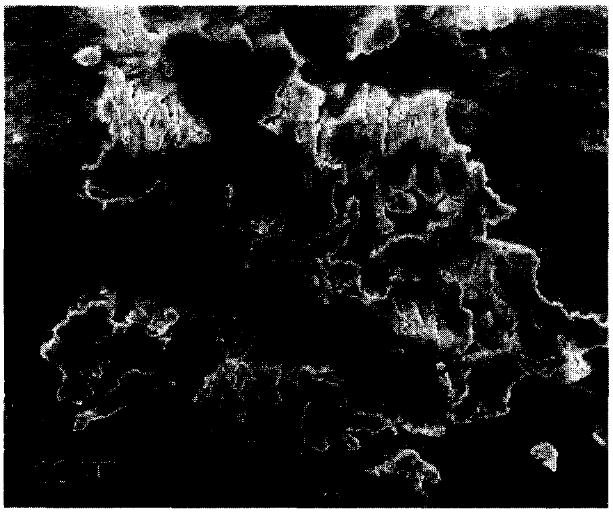

Fig. 7. SEM micrograph of a 3Y–TZP worn at 0.016 ms^{-1}. Note the smeared debris and the surface scratches.

Fig. 8. TEM micrograph of a two stage replica removed from the test shown in Fig. 7. The wear debris was amorphous, and consisted of a mixture of alumina and zirconia.

Fig. 9. Optical micrograph (Nomarski contrast) of a ZTA pin worn at 0.24 ms^{-1}. Note the grain relief.

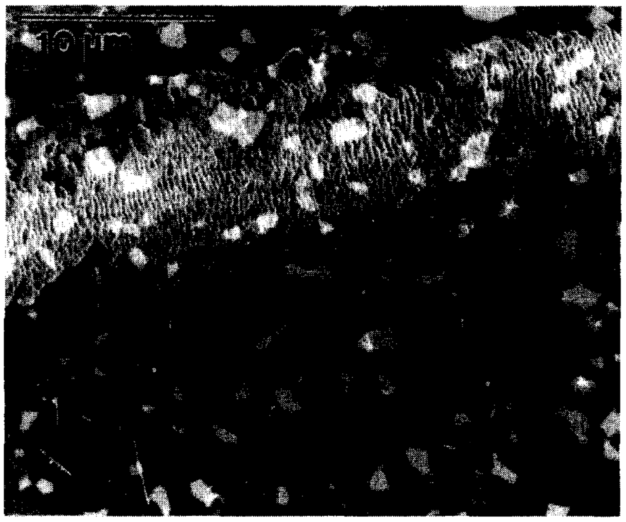

Fig. 10. Scanning electron micrograph of a ZTA disc (with a larger grain size than that in Fig. 9) worn at 0.24 ms^{-1}. Note the smeared debris and the fine rod-like material.

were produced by detachment of this film which then acted as a 3-body abrasive. In addition, other regions were found to be completely smooth and featureless. Unfortunately, because of the low wear rates there was insufficient worn area to undertake detailed TEM. However, the surface film was extracted (using standard acetate film replica techniques) and examined in the TEM. Figure 8 shows this film which was found to be amorphous. Microanalysis confirmed that both Zr and Al were present in the film.

Figure 9 shows an optical micrograph from a ZTA pin worn under identical conditions. Some pitting was present, but attributed to residual damage from the specimen preparation. The majority of the surface was smooth, but with evidence of grain relief. Once again, the wear rates were extremely low, giving a very limited area for the investigation.

The ZTA counterface also showed some interesting features from this test, Fig. 10. Two types of surface debris were found. Firstly, a smeared surface film can be seen in the centre of the micrograph, which was found to be adherent to the surface. Secondly, very fine rods of debris can be seen in the upper region of the micrograph. The fine detail in Fig. 11 shows that randomly shaped debris was also present which tended to be piled up at the trailing edge of those grains which had worn to a greater extent. Once again, replication techniques were used to remove the debris. All forms of debris were found to be amorphous, including the fine rolls, Fig. 12, with a chemical analysis which reflected that of the wearing materials.

Fig. 11. SEM micrograph showing piled-up wear debris in the recesses caused by differential grain wear rates. The debris in this case was primarily zirconia from the pin.

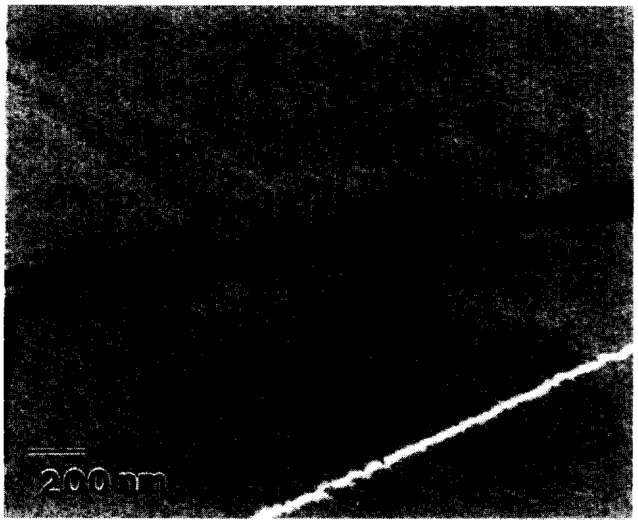

Fig. 12. TEM micrograph from an extraction replica showing amorphous rod-like debris.

The presence of amorphous wear debris has also been suggested by several other workers,[7] although rigorous experimental evidence has not always been provided. Nonetheless, it is clear that, within this wear regime, the wear rate is controlled by tribochemical mechanisms, and not by mechanical based wear mechanisms such as microfracture or plastic deformation. However, the mechanism of amorphous wear debris formation is not entirely clear. For example, does the phase transformation occur on the surface itself, or is crystalline wear debris liberated by microfracture followed by hydration as a result of debris attrition between the sliding interfaces? The difficulty of determining the exact mechanism is aggravated by the low wear rates and the small amount of amorphous wear debris liberated, which makes analysis by, for example, TEM and X-ray photoelectron spectroscopy very difficult. Nonetheless, the evidence available is in agreement that the amorphous debris is a hydrated phase and the water content of the atmosphere/lubricant is critical. This suggestion is supported by the observation that the wear rate of alumina and zirconia can increase with water lubrication, even if the friction coefficient is reduced.

The present work supports the view that the amorphous debris is formed at the sliding surface and not from crystalline wear debris. No evidence of the hydrated crystalline phases suggested by Gates *et al.*[12] was found. Extensive studies were undertaken and no evidence of crystalline debris was found. This is in conflict with the suggestion that crystalline hydrates of alumina are formed. However, reports in the literature have largely failed to obtain direct TEM evidence of the structure of the debris adhering to the surface.

The presence of wear debris in the recesses of grains, Fig. 11, which had undergone higher wear rates indicates that the grain relief could not be a result of differences in elastic deflection. Rather, tribochemical reaction rates as a function of crystallographic orientation have determined the local wear rate.

Recent evidence has suggested that the wear rate of the ceramic strongly depends on the rate of dissolution and the properties of the amorphous film produced by tribochemical wear. For example, Sasaki[14] examined the wear of self-mated zirconia and found that an increase in relative humidity increased wear rate and friction coefficient. However, Wallbridge *et al.*[7] have shown a decrease in friction coefficient but an increase in wear rate with increased water content at the sliding interface. The adherence of the film and the inherent friction coefficient of the film strongly determine whether it has a beneficial or detrimental effect on the wear rate and friction coefficient. With crystalline hydrated aluminas such as boehmite, the layered structure can strongly determine the value of the friction coefficient.[12]

It is clear that in the low load regime the wear rate of ceramics is principally controlled by the rate of chemical dissolution of the surface. In addition, the hardness and inherent friction coefficient of the adherent film are also important. This mechanism occurs predominantly under elastic contact and can lead to surprisingly high wear rates. Therefore, particular attention should be paid to the chemical composition of the ceramic in order to optimise the resistance to hydration and the properties of hydrated films formed. At higher loads, the importance of plastic contact still requires further investigation. The extent of plasticity will clearly have a bearing on the load at which a transition to gross surface fracture occurs.

4 CONCLUSIONS

The following conclusions can be drawn from the experimental work carried out in this paper:

1. No evidence of surface deformation or microfracture mechanisms was found. Wear rates can be significant under purely elastic conditions where no mechanical based wear mechanisms operate.
2. For the tribological regime investigated, transformation of the tetragonal to monoclinic phase was not an important factor.
3. The wear mechanism for both a metal and ceramic counterface was dominated by tribochemical wear mechanisms. In the case of a metal counterface the wear rate was determined by the rate of dissolution of zirconia into an iron oxide. For the ceramic on ceramic wear, the wear rate was determined by the rate of hydration of the surface, the removal of the hydrated film, and the damage caused by the film as a 3-body abrasive. This mechanism provided amorphous wear debris rather than crystalline.

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