ASPECTS OF THE WEAR BEHAVIOUR OF ZIRCONIA SLIDING AGAINST SILICON CARBIDE

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SUMMARY

The development of a high speed pin-on-disc wear testing rig has been undertaken and it has enabled the wear behaviour of zirconia sliding against silicon carbide to be examined. Sliding wear experiments were conducted for zirconia pins and silicon carbide discs under both water-lubricated and unlubricated conditions. Under water-lubricated conditions, tests at a relative sliding speed of 6 m s⁻¹ showed that wear was geometry dependent and the exact alignment of the pin was crucial. At this speed it was possible, with pins polished in-situ on the rig, to achieve hydrodynamic lubrication (HDL) which resulted in low wear. Increasing the nominal contact pressure to 70 MPa resulted in the breakdown of the lubrication and led to high wear coefficients (e.g. 1.1 x 10⁻⁶ mm N⁻¹ m⁻³). Under unlubricated conditions, the zirconia pin wore faster than with water lubrication present, the wear rate increasing with speed and nominal contact pressure in the range 1-6 m s⁻¹ and 2-14 MPa. Wear coefficients ranged from 1.4 x 10⁻⁶ to 5.1 x 10⁻⁶ mm N⁻¹ m⁻¹. The wear tests were followed by examination of the worn surfaces, using a variety of techniques including reflected light and scanning electron microscopy, in order to elucidate likely wear mechanisms. These techniques revealed that there was some degree of commonality between water-lubricated and unlubricated tests, suggesting a universal mechanism which operates over a broad spectrum of testing conditions. The electron microscopy study, combined with observations in the literature, led to the development of a physical model for the wear mechanism, including surface modification and material removal. During the initial stages of wear, and under mild testing conditions, grooves were formed on the surface by plastic deformation due to counterface asperities and trapped debris. The surface was further smeared and deformed as the test proceeded. A deformed surface layer built up which caused intergranular cracks parallel to the surface, at a depth of approximately 3 µm. Wear occurred when these cracks linked up with the surface, a process which may be helped by the formation of a network of cracks parallel and normal to the sliding direction. The mechanism of formation of these crack networks remains controversial but is thought to involve thermal shock. Once material is removed from the surface, it is either thrown out of the contact or trapped in it causing further damage.
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<td>a</td>
<td>unit cell dimension</td>
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<tr>
<td>A</td>
<td>area of segment</td>
</tr>
<tr>
<td>a_i</td>
<td>indentation half diagonal length</td>
</tr>
<tr>
<td>b</td>
<td>component half width (thermal shock)</td>
</tr>
<tr>
<td>c</td>
<td>unit cell dimension</td>
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<tr>
<td>c_r</td>
<td>mean length of radial cracks</td>
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<tr>
<td>d</td>
<td>indenter diagonal</td>
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<tr>
<td>d_{hkl}</td>
<td>separation of lattice planes</td>
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<tr>
<td>E</td>
<td>Young's modulus</td>
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<tr>
<td>E_t</td>
<td>Young's modulus away from the microcracked area</td>
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<tr>
<td>hkl</td>
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<td>h_s</td>
<td>height of segment</td>
</tr>
<tr>
<td>H</td>
<td>mean indentation pressure</td>
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<td>Vickers hardness</td>
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<td>K</td>
<td>wear coefficient</td>
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<td>ΔK_{rs}</td>
<td>toughening increment caused by residual stress related transformation toughening</td>
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<td>ΔK_{m}</td>
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<td>K_{fc}</td>
<td>fracture toughness</td>
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<td>load applied during wear test</td>
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<td>P</td>
<td>indentation load</td>
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<tr>
<td>r</td>
<td>radial co-ordinate</td>
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<td>R_w</td>
<td>surface finish</td>
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<tr>
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<td>disc radius</td>
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<td>R_p</td>
<td>pin radius</td>
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<tr>
<td>R</td>
<td>thermal shock resistance parameter</td>
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<td>R'''</td>
<td>“</td>
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<tr>
<td>R_{st}</td>
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$s$ total sliding distance
$t$ disc thickness
$T$ temperature
$\Delta T$ temperature difference
$u$ transformation zone height
$V_{cr}$ critical velocity
$V_f$ volume fraction of transforming phase
$V$ volume
$w$ compressive load applied to disc
$z$ slider width
$\alpha$ coefficient of linear thermal expansion
$\beta$ Biot modulus
$\chi$ specific heat
$\delta$ indenter included angle
$\varepsilon$ dilational stress free strain
$\phi$ permanent strain due to dilatant microcracking
$\gamma$ surface energy
$\eta$ surface heat transfer coefficient
$\kappa$ thermal diffusivity
$\lambda$ X-ray wavelength
$\nu$ Poisson's ratio
$\mu$ coefficient of friction
$\rho$ density
$\theta$ angle between X-rays and lattice planes
$\sigma$ splitting stress in compressed disc
$\sigma_r$ radial stress in rotating disc
$\sigma_t$ tangential stress in rotating stress
$\sigma_t$ tensile fracture strength
$\sigma_{ts}$ thermally generated surface tensile stress
$\sigma_{real}$ real thermal stress in the material
$\sigma_{max}$ maximum thermal stress
$\omega$ angular velocity
$\psi$ stress reduction factor
CHAPTER 1: INTRODUCTION

1.1 PROJECT BACKGROUND

In order to increase efficiency and component lifetimes, designers and engineers are continually striving to develop materials with improved wear resistance. The correlation of superior wear resistance and high hardness often observed in metallic materials suggests a logical progression to the use of ceramic materials, allowing exploitation of their superior hardness, stiffness and chemical inertness. However, the relationship between hardness and wear resistance is not straightforward. Despite this, ceramic materials do have good prospects for development in tribological applications, particularly under severe chemical environments and at high temperatures. As a consequence of this, the wear of ceramics has received a lot of attention over several years and ceramics are finding increasing applications in situations involving wear. Examples include adiabatic diesel engines, gas turbine engines, cutting tools, drawing dies, pump components, roller and slider bearings and replacement hip joints.

One such application is in a sub-sea hydraulic pump. A lower cost control system for sub-sea oil and gas wells is sought and may be achieved with a remote power supply and sea water hydraulics system. Conventionally, hydraulic oil is used as the control fluid to open and close the valves controlling the well flow, either in a closed loop system, or with a high pressure oil supply via an umbilical supply line. The proposed system will allow elimination of this expensive and potentially unreliable umbilical. The power will be provided by a turbo generator positioned in the flow operating on produced fluids. This drives a motor which powers a hydraulic pump which is used to operate sea floor equipment. The pump pressurises the sea water
and pumps it to the valve actuator via pilot valves. It is an axial piston, fixed angle swash plate positive displacement hydraulic pump incorporating ceramic pistons, cylinder block and port plate. The area of interest in this study is the sliding interface between the port plate and the cylinder block. The wear of these components is critical to pump performance as it will directly affect the output flow.

A pump has been manufactured and trials run for different port plate and cylinder block materials. A combination that has been successful in the initial stages involves a zirconia cylinder block and a silicon carbide port plate. Zirconia offers a higher toughness than many other ceramics due to transformation toughening and this was an important factor in selecting it for a pump component. The type used was yttria-stabilised tetragonal zirconia polycrystals (YTZP). Preliminary information from this system suggests that the zirconia is the more interesting half of the couple because most of the wear occurs on this material. Therefore the focus of the thesis is on the wear of zirconia sliding against silicon carbide. It is important to consider the effect of variations in loads, speeds and operating conditions to extend knowledge of the wear of the components.

The manufacture of prototype components is expensive and testing can be time consuming. These disadvantages were circumvented by smaller scale wear testing in the current work. The conditions in the pump are potentially quite severe as high speeds and loads are involved and experiments were designed to simulate some of these conditions. Although the pump is designed to run with water lubrication, unlubricated tests were also conducted as this represents an extreme limit of lubrication which may occur under certain conditions. The mechanisms of sliding wear are complex and involve many processes, thus predicting wear rates is difficult, and a prediction can only accurately apply to one particular experimental set up. It is, however, useful to extend knowledge of wear rates and mechanisms in a qualitative
manner. Thus, the aim of this project is to understand the wear mechanisms during sliding of zirconia against silicon carbide at high speeds and loads under both water-lubricated and unlubricated conditions. The approach that was taken involved measuring wear for tests under various conditions of speed, load and lubrication, followed by analysis of worn surfaces. Wear coefficients were compared for different conditions and observations from scanning and transmission electron microscopy led to a model for the wear mechanism.

1.2 THESIS OUTLINE

As most of the wear in this couple is concentrated on the zirconia, this material is studied in more detail than the silicon carbide. Following the introduction, an overview of the literature associated with YTZP and its sliding wear behaviour is presented. Mechanisms of transformation toughening are discussed, followed by the degradation of YTZPs in water-containing environments. Wear mechanisms presented in the literature under both water-lubricated and unlubricated conditions are discussed.

In order to assess the wear behaviour of a sliding couple, it is necessary to have a knowledge of the unworn materials. Chapter 3 presents a characterisation of the YTZP and silicon carbide studied, using various forms of microscopy and indentation studies. A description of the testing rig used in this work is given in chapter 4, followed by details of the individual wear tests undertaken. The results derived from the wear tests are presented in chapter 5, followed by details of microscopical analysis. A preliminary discussion is included in this chapter, including calculation of wear coefficients and microscopical analysis. In chapter 6, the results are discussed in more detail and a model for the wear mechanism is presented, supported by evidence from a variety of techniques and literature findings. The conclusions that are
drawn from the work in this thesis are presented in chapter 7, followed by suggestions for further work.
2.1 INTRODUCTION

This thesis is concerned with the wear behaviour of zirconia sliding against silicon carbide. As mentioned in § 1.1, preliminary indications are that in this couple most of the wear is concentrated on the zirconia and so this is the material that is studied in detail here. Before examining the wear behaviour, it is necessary to consider the material. Zirconia is of special interest because under certain conditions it undergoes a phase transformation from tetragonal to monoclinic with an associated increase in volume of 5%. This leads to compressive stresses in the surrounding material and so the transformation can cause an increase in toughness, a phenomenon known as transformation toughening. This was first described by Garvie et al., (1975) and has since led to considerable interest in the material and several reviews are available (Stevens, 1986, Nettleship and Stevens, 1987 and Lee and Rainforth, 1994).

Zirconia is a distinctive ceramic and therefore this literature review is split into two parts. The first will deal with background information about zirconia and will cover the crystal structure and the polymorphs of pure zirconia. The binary phase equilibrium of zirconia stabilised with yttria is discussed. The tetragonal to monoclinic transformation is described followed by a description of the development of tetragonal zirconia polycrystals (TZP) and a brief description of partially stabilised zirconia (PSZ). This is followed by sections outlining the mechanisms of transformation toughening and the degradation of TZP in water-containing environments. The second section of the literature review covers the wear of zirconia, concentrating on sliding wear. The main mechanisms of plastic deformation and fracture are discussed, followed by the effect of water on wear. The notation used in this thesis will be the same as that commonly found in the zirconia literature, namely placing the cation of any
stabilising oxide in front of the type of zirconia, PSZ or TZP. If a number is given in front of this, it refers to the mol. % of the stabilising oxide, e.g. 3YTZP = 3 mol. % Y₂O₃ TZP.

2.2 ZIRCONIA

2.2.1 STRUCTURE

Pure zirconia exists as four different polymorphs: monoclinic (m), tetragonal (t), cubic (c) and orthorhombic (o). The monoclinic form is stable up to a temperature of about 1170 °C where it transforms to tetragonal. The tetragonal polymorph is then stable up to 2370 °C when the structure becomes cubic and remains so up to the melting point of 2680 °C. The orthorhombic polymorph is only found under high pressures in pure zirconia and can also be observed in magnesia PSZ and ternary Mg-Y-PSZ, in bulk samples only at high pressure and low temperature, and in very thin e.g. TEM specimens under ambient conditions. Other phases may form in alloy systems under certain conditions, for example a rhombohedral phase may form as an intermediate step in the t→m transformation (Kim et al., 1995 and Burke and Rainforth, 1997(a)).

Crystallographic data for zirconia are shown in table 2.1. and a schematic diagram of the polymorphs is shown in figure 2.1 (note that the tetragonal structure in table 2.1 is referred to in terms of a body centred tetragonal Bravais lattice (from the JCPDS card), but for simplicity, it is now more usual to refer to it in terms of a larger face centred tetragonal lattice. Thus, the lattice parameter quoted for the a axis (a₁) from now on will be for the fcc cell, which is equal to a₁√2 where a₁ refers to the body centred cell).
A directional volume increase of 5% accompanies the $t \to m$ transformation on cooling, and the associated stresses in a polycrystalline sample are sufficient to cause fracture, even in small grains. Hence the production of large components of pure zirconia is not possible because of failure on cooling. It is possible, with the addition of various oxides, to stabilise the cubic or tetragonal forms to room temperature. Stabilised zirconias show increased toughness by the mechanism of transformation toughening which will be discussed later. Examples of stabilising oxides are MgO, CaO, $Y_2O_3$, and CeO$_2$. The criteria for selecting cubic or tetragonal stabilising ions are that they must have an ionic radius within about 40% of Zr$^{4+}$ (Lee and Rainforth, 1994) and be able to form a solid solution with zirconia. The first criterion can be fulfilled by several elements in the periodic table, but in practice the range is restricted to magnesium, calcium and the rare earth elements due to lack of solid solubility. Understanding the phase equilibria of zirconia with other oxides is crucial to its application and development. Although rare earths can be used in the more expensive technical ceramics, they are too expensive for larger applications. If there is not enough stabilising oxide present in the material, a partially stabilised structure will result, which consists of the cubic solid solution ($C_{ss}$) and tetragonal phase, which can transform to monoclinic on cooling. The tetragonal structure can also be retained in a metastable state by constraint from the surrounding material.
Chapter 2: Literature Review

2.2.2 ZrO$_2$-Y$_2$O$_3$ PHASE EQUILIBRIUM

The zirconia used in the current study is stabilised with Y$_2$O$_3$ and this is an important system because of the wide range of solubility of yttria in the tetragonal zirconia phase. The phase diagram due to Scott (1975) is the most widely used for this system and is shown in figure 2.2. There are still contradictions in the literature as to the position of the tetragonal to tetragonal plus monoclinic phase boundary in the range 1300 °C to 1600 °C (Nettleship and Stevens, 1987). The eutectoid reaction in this system is not of great interest because the temperature at which it occurs (not fully determined) is so low that it is not encountered in normal conditions and diffusional decomposition can be ignored (Lee and Rainforth, 1994). The most important feature is the size of the tetragonal phase field which has a limit of 2.5 mol. % Y$_2$O$_3$ solid solution. This enables a fully tetragonal ceramic to be produced (tetragonal zirconia polycrystals, TZP). A further condition is that the grains are small enough to retain the metastable tetragonal phase, which can be accomplished by sintering the powders in the range 1400-1500 °C. If the spontaneous t→m transformation would be undesirable, ceramics in this system can be over-stabilised, despite potentially not achieving the best properties. Over-stabilisation allows a larger critical particle size to stay metastable if constraint is removed. With greater yttria contents, the tetragonal plus cubic phase field is entered. This allows partially stabilised zirconia (PSZ) to be formed. Microstructures of materials containing more than about 3 mol. % Y$_2$O$_3$ are usually called partially stabilised because they are two phase (i.e. not fully stabilised); however, some of the microstructural features associated with YPSZ ceramics can be produced in YTZPs and TZPs may contain appreciable quantities of cubic phase. Therefore there is some overlap between the definitions of YPSZ and YTZP. To form a PSZ, sintering is carried out at a higher temperature, around 1700 °C, to allow sufficient tetragonal phase to be taken into solid solution so that fine metastable tetragonal precipitates are formed. The room temperature structure depends
on the subsequent heat treatment. Rapid cooling results in a displacive transformation, and the formation of a non-transformable tetragonal phase, $t'$, whereas slow cooling followed by ageing gives transformable tetragonal precipitates in a cubic matrix.

2.2.3 **Tetragonal-Monoclinic Transformation**

This transformation is thought to be a diffusionless shear transformation, with a transformation hysteresis between heating and cooling (see figure 2.3). A volume increase of 3-5% accompanies the transformation causing a strain which must be accommodated by the monoclinic grain or surrounding matrix. This results in the formation of a series of variants, particularly when the transforming particle is embedded in a matrix which constrains macroscopic shape deformation (Evans *et al.*, 1981), see figure 2.4. For a given particle size, a high twin density has associated lower strain energy and higher interface energy than a low twin density (Evans *et al.*, 1981). Microcracking can accompany the transformation, due to the associated volume increase. The surface phenomena of twinning and microcracking introduce a size effect into the total free energy change for transformation, as well as reducing the strain energy (Lange, 1982(a)), so that there is a critical size below which transformation does not occur. Particles greater than this size will spontaneously transform on cooling. The percentage of each phase in the ZrO$_2$-Y$_2$O$_3$ system has been measured for various grain sizes and yttria contents (Lange, 1982(b)). A critical grain size to retain $>90\%$ tetragonal was determined for various Y$_2$O$_3$ contents and was 0.5 μm for 2.5 mol. % Y$_2$O$_3$, see figure 2.5.

2.2.4 **Tetragonal Zirconia Polycrystals (TZP)**

TZP is the name given to materials with a microstructure consisting mainly of the fine (0.2-2 μm) equiaxed tetragonal grains. However, it should be noted
that tetragonal crystals of zirconia can be present as lens-shaped precipitates in the cubic phase (to form partially stabilised zirconia), or as clusters of tetragonal grains in matrices of other materials, for example alumina.

The toughness of zirconia ceramics increases with the amount of retained tetragonal phase and this has led to the development of a wholly tetragonal ceramic, which is TZP. TZPs are usually made in the ZrO$_2$-Y$_2$O$_3$ system because of the range of solid solubility of yttria in tetragonal zirconia, the low eutectoid temperature and the relatively large critical particle size below which the tetragonal phase will be retained to room temperature. As well as the tetragonal phase, some TZP materials contain the cubic phase, the grain size being larger than the tetragonal grains, typically 4-8 μm. Generally, 2.5YTZP contains about 10% cubic phase, if sintered at temperatures of 1500 °C and above. The higher the yttria content, the higher the percentage of cubic there will be. Cubic phase is also common if inhomogeneous powders are used. An accurate prediction of the amount of cubic phase is difficult due to the dispute regarding the position of the t→t+c phase boundary. The exact yttria content is important to transformability of the tetragonal phase and therefore to toughness.

A glassy grain boundary phase between 2 and 10 nm thick is sometimes present in YTZP which is thought to be an SiO$_2$-Al$_2$O$_3$-Y$_2$O$_3$ amorphous phase from milling media or powder contamination. With small amounts of this phase present, microcracks are sometimes formed due to thermal expansion anisotropy. Where this phase is thick, above the glass transition temperature of 750 °C, the soft glass or liquid can accommodate thermal expansion anisotropy and so the level of residual stress is reduced. This also affects the transformability, and so a thicker grain boundary phase leads to a lower toughness product. This phase also aids sintering and helps to produce a fully dense structure.
There is increasing work on the CeTZP system as CeO₂ is a cheaper stabiliser than Y₂O₃. Also, YTZP is susceptible to spontaneous t→m transformation after annealing in water at temperatures as low as 65 °C (Sato and Shimada, 1985), see § 2.2.7. A fully tetragonal microstructure can be obtained in the range 12-20 mol. % CeO₂, which is a wider range than Y₂O₃. Generally the grain sizes of CeTZP are larger (2-30 µm) than YTZP and toughness is higher, although the maximum strength is lower than YTZP. A detailed review of TZP by Nettleship and Stevens (1987) is available.

2.2.5 Partially Stabilised Zirconia (PSZ)

As mentioned in § 2.2.2, there is some overlap in the definitions of YPSZ and YTZP. Partially stabilised zirconia (PSZ) is the name given to those zirconia ceramics in which the cubic form is not completely stable at room temperature as a result of alloy additions. They are phase mixtures of cubic and tetragonal and/or monoclinic. The stabilising oxide stabilises the cubic form which is solution treated to form a supersaturated solid solution. The concentration of stabilising oxide must not exceed that required to completely stabilise the cubic form to room temperature. Typical stabilising oxides are MgO, CaO and Y₂O₃. The material is solution treated in the cubic solid solution phase field, then quenched which causes some c→t transformation and the formation of small (5-10 nm) precipitates. This is followed by isothermal ageing resulting in small lens-shaped precipitates in a cubic matrix.

The advantages of a TZP compared to a PSZ are the lower sintering temperature required, and the lower eutectoid temperature (500 °C in YTZP (Lee and Rainforth, 1994)). However, annealing in water has been shown to induce transformation in both ceramics.

In the current work, TZP will be used to describe materials which consist principally of tetragonal grains, but may contain small amounts of cubic or
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monoclinic phase. PSZ will be used to describe materials consisting of cubic grains containing tetragonal and/or monoclinic precipitates. There is some confusion in the literature over these definitions and occasionally PSZ is used to describe a material that is, according to the above definitions, TZP.

2.2.6 Transformation Toughening Mechanisms
2.2.6.1 Background

The low toughness of ceramics compared to other materials has limited their development in engineering applications, and the discovery of transformation toughening in zirconia in 1975 (Garvie et al., 1975) has led to the development of a wide range of zirconias with increased strength and toughness. The retention of the metastable tetragonal phase is the key to transformation toughening and so the particle size effect is important. The transformation to the monoclinic phase occurs under the influence of stress. There are two principal toughening mechanisms, one related to the residual stresses following transformation and volume increase and the other microcrack related. Other proposed toughening mechanisms include crack blunting at m and t particles and crack deflection by particles, causing reduced driving force on the deflected part of the crack, for example in PSZ at elevated temperatures (Evans, 1983).

2.2.6.2 Residual Stress Related Toughening

This mechanism is also referred to in the literature as simply transformation toughening, but this is a general term and the transformation can enhance toughness by different mechanisms. In this thesis, residual stress related transformation toughening will be differentiated from microcrack related transformation toughening. The mechanism of residual stress related toughening is a stress induced t→m transformation. As a crack extends under applied stress, large tensile stresses are generated around the crack,
especially ahead of the crack tip. These stresses release the constraint on the
tetragonal grains which transform to monoclinic symmetry if the tensile stress
is high enough. The associated volume expansion leads to compressive
stresses in the matrix and so there are closure forces acting on the crack
faces. More work is then required to advance the crack through the matrix in
the vicinity of the transformed phase, thus increasing the toughness (figure
2.6). The extent of the closure forces increases as the crack propagates and
causes more particles to transform. Integration of these closure forces over
the transformation zone results in equation 2.1 for the toughening increment
due to residual stress related transformation toughening, $\Delta K_{rs}$ (McMeeking and
Evans, 1982)

$$\Delta K_{rs} = \frac{0.22E\varepsilon V_f \sqrt{u}}{(1-\nu)}$$

where $E$ is Young's modulus, $\varepsilon$ is dilational stress-free strain, $V_f$ is the volume
fraction of the transforming phase, $u$ is the transformation zone height and $\nu$ is
Poisson's ratio. This equation has been found to underestimate the
toughening effect by a factor of $\sim 2$, and this is attributed to neglecting shear
effects in the analysis.

2.2.6.3 Microcrack Related Toughening

Microcracks can occur in the matrix either as a result of the $t \rightarrow m$
transformation on cooling, or as a result of stress induced transformation of a
retained metastable tetragonal particle. Whichever mechanism causes the
transformation, the microcrack formation is similar. The transforming
tetragonal particle can be in a matrix of cubic zirconia or another ceramic, e.g.
alumina. The volume expansion of the particles associated with the
transformation leaves the particle in compression and causes tangential
stresses around them, which induce microcracks in the matrix (Stevens,
(1986), figure 2.7). These microcracks can extend in the stress field of a
propagating crack or deflect the crack, so absorbing or dissipating the energy of the crack. This increases the toughness of the material, the toughness increment depending on the microcrack density (Faber, 1983). The optimum toughness obtained in this way occurs when the particles are large enough to transform, but small enough to cause only limited microcrack development (Stevens, 1986). The toughening increment due to microcracking is given by equation 2.2 (Faber, 1983)

\[ \Delta K_m = 0.25E_f f_s \sqrt{\phi} \]  

where \( E_f \) is the Young's modulus of material away from the crack tip, \( f_s \) is the microcrack density, \( \phi \) is permanent strain due to dilatant microcracking and \( u \) is the height of the transformed zone. The increase in toughness caused by microcrack related toughening is smaller than that caused by residual stress related toughening.

### 2.2.6.4 Combined Effects of Toughening Mechanisms

The effects of the two mechanisms together may or may not be additive, and there is some disagreement on this point. On one hand, Evans (1983) states that transformation and microcrack toughening are non-additive and the onset of microcracking after a stress induced transformation would lead to a lower toughening level than with transformation alone. For transformation in the absence of microcracking a strain discontinuity occurs on transformation. This is reflected in a corresponding change in the stress ahead of the crack tip. The crack tip stress is lowered by the transformation resulting in crack shielding. However, when microcracking accompanies the transformation, the microcracked material has a reduced modulus which results in a permanent strain of smaller magnitude and therefore a lower residual stress in the wake. Claussen (1983), however, noted that a combined effect of martensitic \( t \rightarrow m \)
transformation and microcrack nucleation and propagation seems possible as both mechanisms involve energy absorption.

### 2.2.7 Degradation in Water-Containing Environments

Several studies have been conducted to investigate the degradation of YTZPs in water and humid air (Watanabe et al., 1983, Nakajima et al., 1983, Sato and Shimada, 1985, Lange et al., 1986, Yoshimura et al., 1987, Hecht et al., 1988, Sato et al., 1988, Winnubst and Burgraaf, 1988, Hughes et al., 1993, Kim, Jung and Park, 1994, Li et al., 1996, Burke and Rainforth, 1997(b) and Li and Watanabe, 1998) and the principal conclusion has been that water increases the degradation of YTZP by causing the premature t→m transformation at the surface resulting in a strength reduction by micro- and macro-cracking. The degree of degradation that occurs depends on the amount of stabiliser, the grain size, ageing time and temperature. The exact mechanism for the promotion of the t→m transformation in water is uncertain. Strength degradation is caused by micro cracks which accompany the transformation and these were observed by Sato and Shimada (1985) and Sato et al. (1988).

There is a temperature range over which YTZP ceramics are most susceptible to degradation in water (140 - 250 °C). For example, Sato et al. (1988) found the critical temperature to be 200 °C and Hughes et al. (1993) found it to be 250 °C. The time taken for degradation to occur ranges from hours to days. It is convenient to measure the degree of degradation by surface X-ray diffraction (XRD) in which the percentage of monoclinic phase at the surface is measured after ageing under various conditions and for various times. For example, Sato et al. (1988) found that there is a maximum percentage of 70 % monoclinic phase that forms at the surface, and that this amount of transformation had occurred after annealing a 3YTZP for 50 hours at 200 °C and 1.54 kPa water vapour pressure. However, the transformation initially proceeded rapidly with 50 % monoclinic phase detected after ~18 hours.
Water pressures in the range 0.46 kPa - 7.35 kPa were studied and increasing the water vapour pressure increased the amount of monoclinic phase formed below 200 °C (Sato et al., 1988).

The maximum amount of monoclinic phase that forms increases with decreasing yttria content, as observed by Nakajima et al. (1983). A similar trend was found by Sato and Shimada (1985) and Winnubst and Burgraaf (1988).

There seems to be a critical grain size, \( D_c \), below which the transformation in water does not occur. For example, Watanabe et al. (1983) found that \( D_c \) increased from 0.2 to 0.6 \( \mu \)m as the yttria content of the YTZP increased from 2 to 5 mol. %. Winnubst and Burgraaf (1988) found that after ageing in water the amount of monoclinic phase formed decreased with decreasing grain size. The grain size effect was investigated by Li and Watanabe (1998) and they concluded that in water, transformation is initiated by the dissolution of yttrium, occurring preferentially at grain boundaries. As the grain boundary area decreases with increasing grain size, transformation becomes increasingly more difficult. Also, yttrium can be enriched at grain boundaries during long sintering periods in which grain size increases. Transformation becomes more difficult because more yttrium must be drawn out for the formation of nucleation sites. On the other hand, increasing the grain size facilitates transformation by lowering the nucleation barrier because the intrinsic phase stability of a tetragonal grain decreases as grain size increases. The effect of grain size on transformation in water, is therefore complicated by these factors.

Lange et al. (1986) discovered clusters of small (20-50 nm) crystallites adjacent to monoclinic and cubic grains after ageing a TEM sample. These were identified as \( \alpha-Y(OH)_3 \). They proposed that water reacts with \( Y_2O_3 \) to form the \( \alpha-Y(OH)_3 \) phase resulting in an yttrium rich surface layer. Following
this reaction there is a decrease in the amount of yttrium in the grain, and
when low enough, the t→m transformation occurs in the yttrium deficient area.
This monoclinic nucleus grows by further depletion of yttrium. Once it has
achieved a critical size it will grow with no further yttrium depletion and
transform the tetragonal grain in which it was growing. If this grain is larger
that a critical size, a microcrack will form. Winnubst and Burgraaf (1988)
agreed with this mechanism and they suggested that to compensate for yttria
loss, the critical grain size must be lower for samples aged in water, compared
to those aged in air. Li et al. (1996) also supported this mechanism and they
found that Y-OH bonds were formed by reaction with water, although Zr-OH
bonds were not. Li and Watanabe (1998) postulated that the preferred
hydration of yttrium occurs at the grain boundary, providing nucleation sites for
transformation inside the grain.

Sato and Shimada (1985) and Yoshimura et al. (1987) proposed a mechanism
that involves breaking of a Zr-O bond by reacting with H₂O to form a Zr-OH
bond although they disagreed as to how the t→m transformation was caused
following this Zr-O bond breakage. Sato and Shimada (1985) suggested that
the Zr-OH bond at the surface acts like a crack causing t→m transformation to
occur nearby as Zr-O bonds proceed to be broken. Restraint on the tetragonal
phase may be released on the surface under aqueous environments.
Yoshimura et al. (1987), however, argued that the Zr-OH formation causes a
stressed site by accumulation of OH⁻ migrated into the surface of the lattice
near the Zr-O broken bond, nucleating defects of monoclinic phase in the
tetragonal grains. However, evidence to explain the breakage of the Zr-O
bond is needed and also the interaction of OH⁻ with vacancies in the lattice.

Hughes et al. (1993) suggested that the presence of extra oxygen anions in
the lattice caused strain to build up at the surface, inducing the t→m
transformation. They suggested that hydroxide formation (Zr or Y) only occurs
after severe treatment and is therefore symptomatic of the degradation, rather than an initiator of the $t \rightarrow m$ transformation.

Kim, Jung and Park (1994) also noted that diffusion of $\text{OH}^-$ in the lattice is the controlling factor in the $t \rightarrow m$ transformation. They suggested that $\text{OH}^-$ diffuses through oxygen vacancies into the lattice even without breaking Zr-O bonds. The formation of Zr-OH bonds at vacancy sites by the interaction of $\text{OH}^-$ ions with oxygen vacancies leads to the formation of a tensile strain field. As the number of Zr-OH bonds builds up with annealing time, the tensile strain field builds up and ends with the onset of the $t \rightarrow m$ transformation as the tensile strain releases the constraint to stabilise the tetragonal phase.

Burke and Rainforth (1997(b)) conducted degradation studies on YTZP in super heated water at 180 °C and observed the existence of a rhombohedral as well as a monoclinic phase. They noted that this phase forms as an intermediate step in the $t \rightarrow m$ transformation and is promoted by shear stresses (rather than hydrostatic stresses which favour the $t \rightarrow m$ transformation). They considered that promotion of the $t \rightarrow r$ transformation enhanced degradation resistance and that the grain boundary structure is important. A material with chemically heterogeneous grain boundaries and yttria segregation would be more degradation resistant than materials with a glassy phase at the grain boundaries.

No one clear mechanism for the degradation of YTZPs in water is suggested in the literature, although the effect of various material and experimental parameters is reasonably well understood. It is agreed, however, that YTZP is susceptible to degradation in water-containing environments by the premature occurrence of the $t \rightarrow m$ transformation, resulting in subsequent strength degradation.
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2.3 WEAR OF ZIRCONIA

2.3.1 INTRODUCTION

The study of contacting surfaces in relative motion is called tribology. It involves friction, lubrication and wear behaviour which are usually interdependent. The tribological properties of a system depend on the physical and chemical nature of the surfaces and the surrounding environment as well as the bulk mechanical properties of the materials.

Wear is the deformation of one or both surfaces due to responses to the contact stresses at the surface causing permanent mass (or material) loss. This loss can take the form of loss from the system or displacement from the original position. Wear may involve the production of wear debris either adherent to one surface (transfer) or loose in the system (creating three-body wear). The mechanisms by which material is lost, or shape change occurs, can involve plastic deformation, adhesion, ploughing, fracture, fatigue and environmental attack. In most practical situations the wear process will involve a combination of some of these mechanisms. Wear mechanisms are classified into different groups for convenience, but in reality the boundary between them is diffuse. Wear mechanisms rarely occur in isolation of each other; one may dominate but be assisted by others, leading to wear rates greater than the sum of either alone (synergism).

Ceramics possess many of the desirable properties of a wear resistant material, such as high hardness and stiffness, resistance to chemical attack and low thermal expansion coefficients. Moreover, they retain these properties at high temperatures. Another important property is a high thermal conductivity, which many ceramics do not have. Ceramics are brittle and in some ceramic materials crack growth is sensitive to environment. With very smooth conforming surfaces, surface stresses can be low and so wear resistance is good, but increased surface roughness or counterformal contact can increase the local
contact stress and the likelihood of fracture. It is envisaged that an improvement in toughness and thermal conductivity would lead to the use of ceramics in tribological applications becoming more widespread. The relatively high toughness of zirconia due to transformation toughening has led to increased interest in zirconia as a wear resistant material.

Three-body abrasive wear of zirconia is not extensively covered in the literature, perhaps because it is not often encountered as a starting condition in practice. The generation of wear particles at the contact may, however, turn the two body case into a three body case if the loose particles themselves cause wear. The two-body wear of zirconia, which is more relevant to this study, has been covered extensively in the literature for both PSZ and TZP. Various experimental situations and several environments have been investigated to simulate different applications of wear parts under both dry and lubricated conditions. Although different factors potentially affecting wear have been investigated and wear rates reported, the conclusions drawn on the effects of each parameter can be confusing because of differences in materials studied and conditions under which tests were conducted.

2.3.2 MECHANISMS OF SLIDING WEAR
2.3.2.1 Introduction

For zirconia, the principal sliding wear mechanisms have been attributed to plastic deformation, intergranular fracture, transgranular fracture, fatigue fracture, delamination (due to lateral cracks), adhesive wear and thermal shock fracture. The extent to which each of these mechanisms operates varies with experimental conditions and specific microstructure. This will be discussed in the following sections.
2.3.2.2 Plastic Deformation

Plastic deformation, or grooving, is the most widely reported phenomenon to occur during sliding of zirconia. This is not necessarily as would be expected given that ceramics under tensile loading rarely deform plastically and usually fail by brittle fracture. However, the stress system during sliding wear is complex and includes shear, compressive and tensile components which may lead to plastic deformation. As with metals, the generation and movement of dislocations is a fundamental deformation mechanism and can occur more easily at high temperature. Dislocation production and motion is more difficult than in metals, but limited numbers of dislocations can be produced and plastic deformation of ceramics can occur at room temperature under the right conditions.

There is now evidence that plastic deformation can be a dominant mechanism during sliding wear of ceramics (Hockey, 1971, Hockey 1972, Rainforth and Stevens 1993, Barceinas-Sánchez and Rainforth, 1997 and Rainforth and Stevens 1998). It is known that the wear rate of a ceramic depends on the crystallographic orientation. For example, Steijn (1961) showed that the wear mechanism of sapphire (single crystal alumina) altered with orientation from a brittle mechanism of chipping and conchoidal fracture when the rubbing direction was parallel to the c-axis, to a high wear resistance and smooth surface formation when sliding in other directions on the prismatic planes and any direction on the basal plane. It was concluded that plastic flow occurs during rubbing of sapphire in certain directions. Hockey (1971) found the plastic deformation of Al₂O₃ to be a consequence of the nature and magnitude of the local stresses under indenters and abrasive particles. Hockey (1972) found that subsurface regions of a ground and abraded Al₂O₃ contained high densities of dislocations and numerous twins were introduced by grinding, and concluded that plastic deformation is an important mechanism in the abrasive wear of alumina, and that its occurrence is responsible for the anisotropic wear and
grinding rates of single crystals. The relative ease of plastic deformation and fracture will affect the wear mechanisms.

Plastic deformation during sliding manifests itself as small or large grooves and smearing. It does not usually occur in isolation. The amount of plastic deformation that can occur in ceramics is limited by the available slip systems and twinning modes; hence the abrasive wear can be aided by fracture mechanisms (Birkby et al., 1989). For example, fracture occurs after a critical strain has been reached in MgPSZ (Arnov, 1987(a)). The defect content of the surface asperities will affect their response to stress, and it is not safe to infer that the defect content, or the elastic-plastic response, of surface asperities will be the same as the bulk (Arnov, 1987(a)). The surface may be affected by the environment, with modified flow or fracture properties (Breznak et al., 1985). The ambient temperature at which the wear test is conducted affects the extent to which plastic deformation occurs. The temperature generated at the contact may induce plasticity with a fall in hardness and flow stress at high surface temperature.

and Glaeser, 1987, Ajayi and Ludema, 1989, Dufrane, 1989, Lee et al., 1993, Rainforth and Stevens, 1993) are mentioned. Plastic deformation as part of the wear process may or may not lead to material removal. If not, it is usually associated with mild wear. Lee et al. (1993) studied the wear behaviour of YTZP on itself in a ball on three flats configuration with and without lubrication at slow speeds. They observed a wear transition as load was increased which corresponded with a change in mechanism from plastic deformation causing mild wear to brittle fracture causing severe wear. Arnov (1987(a)) observed plastic flow in the direction of motion of MgPSZ sliding against itself and suggested that strong adhesive bonds formed between the two surfaces led to intensive plastic deformation of surface layers. Wear particle generation was attributed not to adhesion, but most likely to low cycle fatigue because of the absence of directional grooves and scratches. A 3YTZP was used as a steel wire drawing die under lubricated conditions and showed a plastically deformed surface with no evidence of the intergranular fracture that was observed for a similar, more transformable, 2YTZP die (Birkby et al., 1989). Rainforth and Stevens (1993) found evidence of plastic deformation in an MgPSZ pin in the form of occasional three-body abrasive grooves formed by wear debris after sliding against a bearing steel disc. An area containing grooving was observed in the TEM and the authors found that the precipitate structure of the PSZ had been destroyed and replaced with fine cubic grains (10-30 nm) within the coarse (80 μm) parent cubic grain. This is suggestive of considerable dislocation flow, but it was thought that the generated high temperature alone could not be the cause as the wear event is short, thus not allowing the tetragonal precipitates time to dissolve.

A high dislocation density is indicative of plastic deformation and Barceinas-Sánchez and Rainforth (1997) examined cross sections of 3YTZPs worn against MgPSZ in the TEM and found evidence of plastic deformation in monoclinic grains with high dislocation densities. Tetragonal grains to ~2 μm below the surface were elongated in the direction of sliding and had a high dislocation density.
density indicating dislocation flow as the cause of the shape change. Rainforth and Stevens (1998) conducted a detailed TEM study of microstructural changes at the worn surface of a 3YTZP, after sliding against a zirconia toughened alumina (ZTA) disc. They found that the microstructure had changed over a depth of 10 µm from the surface. Monoclinic zirconia was found at 5-10 µm below the surface. Above this, the tetragonal grains were progressively more elongated as the surface was approached. Dislocations were observed, some of which had formed pile-ups or loose tangles. Aspect ratios of 30:1 were found for tetragonal grains 3 µm below the surface. It was found that the {111} planes in these grains were preferentially aligned parallel to the worn surface, indicating some mild crystallographic texture. Above the elongated grains there was a region of fine (50 nm) equiaxed tetragonal grains. The outer surface consisted of an amorphous phase containing both Al and Zr, fractured alumina particles and fine precipitates. The authors considered the mechanisms which could have caused the tetragonal grain elongation to be dislocation flow, diffusion and physical displacement via intragranular microcracks, although grains in the lower part of this region did not contain the intragranular microcracking and grain boundary displacement found in the upper part of this region, so they could have deformed only by lattice diffusion and/or dislocation flow.

2.3.2.3 Fracture

Overview

Fracture of one type or another is widely reported to occur during sliding of zirconia under various conditions and brittle fracture is perhaps the most important ceramic wear mechanism (Ajayi and Ludema, 1987). Fracture toughness has been recognised as an important property influencing wear behaviour and models incorporating it have been presented (e.g. Hokkirigawa, 1991, Kim, Kim and Hsu, 1994). Fractures observed on worn zirconia surfaces include those attributed to thermal shock, phase transformation, fatigue and tensile stresses induced by the contact.
Brittle Fracture

Fischer et al. (1987) observed that the wear resistance of a tough tetragonal zirconia was higher than a brittle cubic zirconia over a range of environments. The cubic zirconia showed intergranular fracture on a much larger scale than the tetragonal zirconia. In a later paper Fischer et al. (1989) investigated wear of various zirconias with different fracture toughness values and found that the wear resistance (inverse of wear rate, \(1/\text{mm}^3\text{N}^{-1}\text{m}^{-1}\)) increased with the fourth power of fracture toughness. They suggested that wear produces a feedback mechanism which leads to increased wear in brittle materials as fracture produces a rougher contact surface which increases the stress and further increases fracture. Therefore they concluded that fracture is a major determinant in the wear behaviour of all brittle materials.

Brittle fracture induced material removal can occur as a result of considerable surface deformation by a critical strain induced fracture or fatigue mechanism. Arnov (1987(b)) investigated sliding of MgPSZ on itself and suggested that fracture occurred after a critical plastic strain was induced and noted that the rate of the sequential process is controlled by the rate of the slowest process. At room temperature, fracture was a controlling factor (i.e. crack propagation, not initiation) - plastic strains were small and wear high. Birkby et al. (1989) suggested that on a small scale (<1 \(\mu\text{m}\)) the intersection of slip bands or twins with barriers such as grain boundaries, particles or other slip bands can commonly lead to stresses which give rise to crack nucleation and growth. He et al. (1996) noticed that the wear mechanism varied with grain size in YTZPs and for grain sizes less than 0.7 \(\mu\text{m}\) the wear mechanism was controlled by microfracture which was caused by plastic deformation and/or flaws. They suggested that the condition to cause microfracture arises when the sum of all stresses acting (accumulated stress during the sliding process, tensile stress due to the applied stress field and the internal stress resulting
from thermal expansion anisotropy of the grains) is larger than the strength of
the material.

**Thermal Shock Fracture**

Local frictional heat generation during ceramic sliding can be high. For example, Griffioen *et al.* (1985) measured flash temperatures up to 2700 °C for unlubricated sliding of sapphire and silicon nitride. Additionally, heat dissipation may be restricted by low thermal conductivity. This can cause localised thermal gradients and thermal shock in the material resulting in crack nucleation and propagation. Zirconia is particularly susceptible to thermal shock compared to other ceramics due to its low thermal conductivity and high coefficient of thermal expansion. Several authors have proposed thermal shock as a mechanism for fracture during wear of zirconia (Breznak *et al.*, 1985, Dufrane, 1986, Dufrane and Glaeser, 1987, Dufrane, 1989, Bundschuh and ZumGahr, 1991, Lee *et al.*, 1993, ZumGahr *et al.*, 1993, Anderson and Lintula, 1994, Tucci and Esposito, 1994, Ravikiran and Pramila Bai, 1995, Birkby *et al.*, 1995 and Esposito *et al.*, 1998).

A rectangular network of fine cracks, parallel and normal to the sliding direction, on the worn surface of zirconia has been referred to as typical of thermal shock damage during wear by several authors (Breznak *et al.*, 1985, Dufrane, 1986, Dufrane and Glaeser, 1987, Dufrane, 1989) with no clear supporting reasons. An example of this type of crack network is given in figure 2.8. Dufrane (1986) noted the formation of visible hot spots during self-mated sliding of 3YTZP with mineral oil lubrication and attributed this to thermoelastic instability (TEI). The phenomenon of thermoelastic instability arises when part of the surface is heated more rapidly than surrounding areas and is particularly significant when this gives rise to concentrations of loading on nominally uniform and flat surfaces. For a flat slider, in most cases, loading is assumed to be uniform and so therefore, is the temperature distribution. Thermoelastic
instability begins with the concentration of load on small regions of the apparent contact area causing an increase in heating on a small region of the surface and the appearance of a non-uniform temperature distribution. This results in a differential thermal expansion of that material leading to a higher pressure (locally) and heating. The locally protruding areas are subject to wear (which tends to reduce any localised heating by preferentially wearing the higher pressure areas) and the contact region is transferred to nearby areas, due to the effects of wear and lateral heat transfer. The locally heated regions traverse across the surface. The thermoelastic phenomenon is a balance between the thermal expansion of the sliding materials caused by uneven surface heating and the wear of the expanded regions.

YTZP is more susceptible to thermal shock fracture at high sliding speeds than at low speeds. Dufrane (1986) has adopted the concept of a critical velocity (Dow and Burton, 1973 and Dow and Stockwell, 1977) for self-mated sliding of YTZP, which, once exceeded, will lead to the onset of thermoelastic instability. He associated this with surface cracking due to thermal shock. The critical velocity is described by the material properties, the coefficient of friction and the contact width. The equation for the onset of thermoelastic instability is

\[
v_{cr} = \frac{4k_{th}^2}{(\mu \alpha E)^{2/3} \pi \kappa z}
\]  

(2.3)

where \(v_{cr}\) is the critical velocity, \(k_{th}\) is the thermal conductivity, \(\mu\) is the coefficient of friction, \(\alpha\) is the thermal expansion coefficient, \(E\) is Young's modulus, \(\kappa\) is the thermal diffusivity \((k_{th}/\rho \chi)\), \(\rho\) is the density, \(\chi\) is the specific heat and \(z\) is the width of the slider. Applying this equation in a flat-on-flat geometry (which simulates the piston/ring interface of advanced engines) reveals critical speeds of 0.09, 0.94 and 15 m s\(^{-1}\) for values of coefficient of friction of 0.12, 0.04 and 0.01 respectively. The critical velocities calculated for the test conditions used were found to be lower than the maximum speeds
used in the experiments for the YTZP, which showed extensive surface cracking. Dufrane (1986) commented that for the critical velocity to be within a practical range for engine applications, the coefficient of friction would have to be reduced to 0.01, a value that could only be achieved under conditions of hydrodynamic lubrication and even then, the surface would be susceptible to damage during starting, stopping of brief periods of overload or lubricant starvation.

The critical velocity concept was also adopted by Lee et al. (1993) who used measured wear scar diameter and coefficient of friction values to determine the critical velocity under various lubrication conditions. They plotted contours of $v_{cr}$ for various load and speed conditions and found good agreement with their wear transition boundaries. When the critical velocity was exceeded, severe wear caused by thermal-shock-induced brittle fracture was observed. The largest deviation from the model was seen for water-lubricated conditions where their experiments indicated transitions to higher wear regimes at loads and speeds higher than those predicted by the critical velocity model. The authors attributed this to either stress corrosion or hydrolysis reactions although it seems likely that water-lubrication is reducing the interface temperature and so reducing the potential for thermal shock. The authors suggested that their results meant that the model was capable of describing the effects of thermal shock under boundary lubrication conditions.

Birkby et al. (1995) conducted self-mated sliding wear tests on 2YTZP and 3YTZP. 2YTZP demonstrated a superior performance as compared to 3YTZP during the initial stages of the test, and they postulated that as the 2YTZP material is tougher, this could be due to increased resistance to thermal shock induced crack propagation, as indicated by the higher value of the thermal shock resistance parameter, $R'''$
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$$R'''' = \frac{E\gamma}{\sigma_f^2(1-\nu)}$$

(2.4)

where $E$ is Young’s modulus, $\gamma$ is fracture surface energy, $\sigma_f$ is tensile fracture strength and $\nu$ is Poisson’s ratio. Transformation of the tetragonal phase in 2YTZP may occur in the vicinity of a propagating thermal shock crack. Birkby et al. (1995) pointed out that this argument is only valid when the region which is arresting a thermal shock crack remains below 300 °C otherwise transformation is unlikely to occur. During the initial stages of a test the number of asperity contacts is relatively low and it is more likely that the bulk temperature is less than 300 °C and that material in this region retains a transformation capability. As the wear test proceeds, the bulk temperature increases as the contact area increases; there is then a reduction in potential for transformation toughening. This seems a reasonable explanation for the superior wear resistance of 2YTZP compared to 3YTZP in the initial stages and the small difference in wear rate at the end of the test. Esposito et al. (1998) attributed the high wear of 3YTZP to very low thermal diffusivity, causing thermally induced stresses and fracture leading to detachment of material in layers. Tucci and Esposito (1994) also attributed extensive cracking and material loss of 3YTZP during sliding to the low thermal shock resistance of the material.

**Fracture Associated with Phase Transformation**

The tetragonal to monoclinic phase transformation ($t \rightarrow m$) has associated with it a volume change which can cause microcracks to develop in the material and this may be the cause of crack nucleation eventually leading to wear particle formation through crack propagation. Phase transformation has been reported as contributing to the wear mechanism by several authors (Iskigaki et al., 1987, Rainforth et al., 1989, Bundschuh and ZumGahr, 1991, Rainforth and Stevens, 1993, Reuhkala et al., 1991). The stress induced $t \rightarrow m$ phase
transformation in PSZ generates a dilatation of transformed particles causing microcracks in the matrix and then the material with a high density of microcracks is easily removed. Microcracks form at grain boundaries as a result of the stress-assisted transformation in TZP and this leads to subsequent material removal of surface grains. Following microcracking, larger surface cracks can be formed as a result of crack coalescence. This was observed in MgPSZ (Rainforth and Stevens, 1993). All cracks were aligned along the (100) direction (parallel to the long axis of one of the three precipitate orientations).

**Fatigue Fracture**

The contact stresses in a wear process are very often cyclic and can induce fatigue in the surfaces. Surface fatigue may be particularly important in a reciprocating rather than unidirectional sliding situation (Bundschuh and ZumGahr, 1991, ZumGahr et al., 1993). Fatigue fracture is a mechanism mentioned by several authors in the literature (Rice and Wu, 1985, Arnov and Mesyef, 1986, Ajayi and Ludema, 1987, Arnov, 1987(a), Ajayi and Ludema, 1989, Bundschuh and ZumGahr, 1991, ZumGahr et al., 1993 and He et al., 1997). Arnov and Mesyef (1986) and Arnov (1987(a)) suggested that low cycle fatigue fracture of MgPSZ after sliding against itself was caused by severe plastic deformation. Ajayi and Ludema (1987, 1989) suggested that fatigue initiation following plastic deformation was more pronounced in water than in air.

**Delamination Fracture**

Wang et al. (1993) postulated that concentrated loading and unloading of the surface caused stresses which initiated shallow sub-surface microcracks at voids and other imperfections. These microcracks grow to the surface creating thin delaminated sheets of PSZ. Delamination was also observed by
Stachowiak and Stachowiak (1989) in both TZP and PSZ after unlubricated sliding. The delamination followed the formation of a deformed surface layer. He et al. (1996) observed the removal of a surface layer by delamination in YTZPs with grain sizes above 0.9 μm. They attributed the delamination to tensile stresses in a layer below a layer of compressive stress at the surface, due to the t→m transformation, producing microcrack nucleation. Fatigue lateral microcracks could also be produced. Material is removed by delamination when these subsurface cracks intersect the surface.

**Corrosion Cracking**

A further mechanism to cause cracking is stress induced corrosion cracking, referred to by several authors (Fischer et al., 1987, Sasaki, 1989, Bundschuh and ZumGahr, 1991, Fischer and Mullins, 1992 and Lee et al., 1993). Sasaki (1989) suggested that adsorption of polar molecules induces stress corrosion cracking which plays a major role in the wear process, especially at low relative humidity (~20%). As the atmosphere becomes more humid it was thought that the lubricative effect of the adsorbed layer begins to dominate. The effect of water on wear is discussed more fully in section 2.3.4.

**Nature of Fracture**

The various causes of fracture already mentioned can manifest themselves as either grain boundary (intergranular) fracture, or transgranular (intragranular) fracture. Breval et al. (1986) analysed wear debris of a tetragonal yttria stabilised zirconia and found evidence of both inter- and intra- granular fracture. Ajayi and Ludema (1987) also observed intragranular fracture as did ZumGahr et al. (1993). They noticed that transcrystalline shear fracture of individual grains was more pronounced for small grain sizes. Increasing the grain size resulted in increasing the tendency for intercrystalline fracture although this was followed by spalling or fragmentation of individual grains on
the surfaces of coarse grained zirconia. They noted that low fracture
toughness promotes intercrystalline microfracture under wear loading.
Bundschuh and ZumGahr (1991) noted that in TZP cracks may propagate
intergranularly along boundaries of transforming grains while in PSZ the
mechanism was predominantly transgranular.

2.3.2.4 Tribochemical Reaction

Reactions of a ceramic with the environment or the counterface can occur
more rapidly under sliding conditions. This can be due to high asperity flash
temperatures, exposure of fresh surface by the wear process or mechanical
stimulation. These tribochemical reactions can significantly affect the wear
rate by modifying the sliding interface, sometimes leading to the formation of
transfer films.

Tribochemical reaction was the wear mechanism for a 3YTZP worn against a
ZTA counterface at 0.24 m s⁻¹/19 N and 0.016 m s⁻¹/10 N (Rainforth, 1996).
The author found no evidence of surface plasticity or microfracture under
these conditions. The wear debris was amorphous and consisted of a
hydrated material, containing both Zr and Al. He suggested that the wear rate
was controlled by the rate of hydration of the surface, the removal of the
hydrated film, and the damage it caused as a third body abrasive.

2.3.3 Wear at High Sliding Speeds

Most of the work in the literature has been conducted at low sliding speeds
(< 1 m s⁻¹). This can provide useful information on wear mechanisms without
the complicating effects of high temperature generation at the interface.
However, many practical applications demand high sliding velocities which
cannot be reduced without considerable component redesign. Therefore it is
useful to investigate wear at high sliding speeds. This was recognised by
Wodyt and Habig (1988) who investigated the wear behaviour of self-mated MgPSZ under unlubricated conditions at sliding speeds in the range 0.3 - 3 m s\(^{-1}\) and temperatures from 22 to 1000 °C. They found that the sliding velocity has an important influence on wear, because the wear increases from a low wear regime to a high wear regime. The wear was dependent on, and increased with, temperature at velocities up to 1 m s\(^{-1}\) but interestingly, was independent of temperature at velocities of 3 m s\(^{-1}\). The wear transition was related to phase transitions of the starting material, as samples from the high wear regime were found to be completely cubic. They noted that the influence of temperature on wear behaviour can also be realised by changing the sliding speed. Although they did not expand this point, it suggests that the effect of a high sliding velocity is similar to conducting the test at high temperature, or that a high temperature is generated during sliding at high speed. Woydt and Habig (1989) reported similar findings and noted that cracks formed on the surface of a sample worn at 3.3 m s\(^{-1}\) and 22 °C and attributed this to m→t or m→c phase transformations. Woydt et al. (1991) investigated self-mated unlubricated sliding of Y and MgPSZ and YTZP and YFSZ. For 3YTZP, a distinct velocity dependent wear transition was observed at 0.08 m s\(^{-1}\). Above the wear transition, wear depends on the materials’ response to stress, which can be caused by point and cyclic contact pressure, thermal dilation and phase transformation. They considered phase transformations to be most significant, as the high temperatures generated meant that all monoclinic and tetragonal transforms to the cubic phase.

Chen et al. (1990) conducted sliding wear tests on MgPSZ and 2 and 4YTZP against a steel counterface in the speed range 5-50 m s\(^{-1}\). They found that there was a maximum wear rate at between 10 and 20 m s\(^{-1}\) for all zirconias and a second, smaller, maximum at 40 m s\(^{-1}\) for the TZPs. They noted that the effect of sliding speed is not independent of other parameters, affecting the interface temperature and vibrational behaviour of the tribometer as well. They cited the main wear mechanism of TZP to be delamination due to the
phase transformation (t→c) as the debris was found to be completely cubic. The difference in the critical speed needed to cause a transition to high wear compared to the work of Woydt et al. (1991) may be due to the higher thermal conductivity of the steel counterface.

2.3.4 Effect of Water on Wear

2.3.4.1 Introduction

The effect of water on the wear of zirconia has been reported by many authors and the findings appear contradictory. While some workers have found that the presence of water increases the wear rate (Hannink et al., 1984, Scott, 1985, Ajayi and Ludema, 1987, Habeeb et al., 1987, Fischer et al., 1987, Sasaki, 1989, Fischer, 1990, Bundschuh and ZumGahr, 1991, Fischer and Mullins, 1992, Lancaster et al., 1992, Lee et al., 1993, Liang et al., 1993 and Amin and Nag, 1995), others have found that it decreases the wear rate (Fischer et al., 1987, Iskigaki et al., 1987, Löffelbein et al., 1993, Stachowiak and Stachowiak, 1993 and Krell and Klaffke, 1996). A possible explanation for this difference of opinion is the different conditions under which the tests were conducted. It was suggested by Stachowiak and Stachowiak (1993) that their tests did not induce accelerated wear in water because the test conditions of low speed and moderate load were not severe enough. However, Scott (1985) found that low speed (1.33-10.5 mm s⁻¹) experiments indicated poor wear resistance by PSZ in wet conditions. Stachowiak and Stachowiak (1993) also suggested that the interpretation of wear data under lubricated conditions can be difficult due to the interaction of hydrodynamic effects and tribochemical reactions.

The sensitivity of YTZP to high temperature aqueous environments has caused concern, and led to the development of the ZrO₂-CeO₂ alloy system (Stevens, 1986). In this system, the tetragonal phase field is larger than that of the zirconia-yttria system, with a solubility limit of about 18 mol. % CeO₂ in tetragonal ZrO₂. In addition, the t→m transformation temperature is lowered.
Near 15% CeO₂ addition the transformation temperature is below room temperature. This means that it is possible to produce a ceramic in which the tetragonal phase is more stable, compared to the ZrO₂-Y₂O₃ system.

2.3.4.2 Decrease of Wear in Water

The decrease of wear under water lubricated conditions compared to tests in air has been reported. Hydrodynamic pressure generation causing separation of the surfaces and stress redistribution causes reduced wear in water compared to air (Fischer et al., 1987, Iskigaki et al., 1987, Stachowiak and Stachowiak, 1993). This mechanism has a greater effect on wear than the chemical attack of the water molecules, since wear rose increasingly in humid conditions (Iskigaki et al., 1987). Flash temperature reduction by heat conduction into the water has been reported to decrease the wear rate (Iskigaki et al., 1987, Löffelbein et al., 1993, Stachowiak and Stachowiak, 1993).

Stachowiak and Stachowiak (1993) found that the wear coefficients for self-mated couples of TZP and PSZ were lower in liquid environments (water, ethanol and silicon oil) than in humid air. They found that the PSZ surfaces were smooth after sliding in water due to plastic deformation of a transferred layer of material. Although lower wear rates in water have been observed, it has been recognised by the authors that this is not always the case. Although the wear rate of TZP is reduced in water, wear pits were observed on its surface (Stachowiak and Stachowiak, 1993), confirming the susceptibility of TZP to wear degradation in polar environments. The chemical action of water will involve chemisorption of OH⁻ ions into the surface followed by diffusion into the bulk material. These processes are time dependent, so it was expected that wear damage in this material would be accelerated with prolonged sliding (Stachowiak and Stachowiak, 1993). Krell and Klaffke (1996) noted that although they observed a reduction in wear with increased relative humidity and
in water which was due to reduced friction and a transition to mild wear, more severe contact conditions may lead to an increase of wear in water.

2.3.4.3 Increase of Wear in Water

An increased wear rate in water is more widely published than a decreased rate and is generally associated with increased susceptibility to cracking (Ajayi and Ludema, 1987, Fischer et al., 1987, Fischer, 1990, Bundschuh and ZumGahr, 1991, Lancaster et al., 1992, Lee et al., 1993, Liang et al., 1993). Other possible explanations for the increase in wear are the reduction in stability of any protective transfer layer (Ajayi and Ludema, 1989, Bundschuh and ZumGahr, 1991) and thermal shock cracking facilitated by water (Bundschuh and ZumGahr, 1991).

Although water can cause stress corrosion cracking in zirconia by chemisorption embrittlement, no simple hydroxides of zirconia are known so it is unlikely that the Zr-O-Zr bond is weakened directly by the action of water (Fischer and Mullins, 1992). Another reason suggested for increased wear is the formation of Y(OH)$_3$, which then destabilises YTZP by Y$_2$O$_3$ depletion, producing a monoclinic nucleus (Lee et al., 1993). The individual contributions from stress corrosion and hydroxide formation are difficult to determine (Lee et al., 1993). If crack propagation is enhanced by water the possibility of three body abrasion by the wear particles occurs. Lee et al. (1993) observed grooves from such abrasive particles after sliding in water. Anderson (1992) found high wear rates in water for MgPSZ and evidence of loose debris, but concluded that with water present, loose wear debris is continuously rinsed away, preventing layer formation or three body wear.

Habeeb et al. (1987) found no reaction of MgPSZ when refluxed with water, but an increased wear rate when water was added to the lubricating oil. They
suggested that friction and wear conditions provide the necessary circumstances to cause the increased wear that they observed.

Although water increases the wear rate, it can simultaneously decrease the coefficient of friction compared to that in air (Ajayi and Ludema, 1987, Lancaster et al., 1992). This is achieved by a lubricating effect as opposed to a low shear strength layer being formed (Ajayi and Ludema, 1987). Normally, a lower coefficient of friction means a low shear stress on the surface which should produce less fracture, therefore the lower shear stress must be offset by some influence of the aqueous solution on crack propagation (Ajayi and Ludema, 1987).

2.3.4.4 Effect of Relative Humidity in Air

The effect of water molecules in the air on wear has been investigated and again, the results appear contradictory. Iskigaki et al. (1987) found that increasing the relative humidity in air increases the wear rate. They suggested that the $t\rightarrow m$ transformation is enhanced in a humid environment and also that adsorbed water enhances microcrack generation and therefore increases wear rates. This, however is not the case when water is present as liquid, and the wear rate is then found to be lower.

Sasaki (1989) also investigated the effect of relative humidity (RH) on wear at 10 N and 400 mm s$^{-1}$ and found that the wear coefficient was a maximum at 20 % RH. This was attributed to stress-induced corrosion cracking, which became less significant as the humidity was increased because the lubricative effect of the adsorbed water layer began to dominate the wear behaviour. The cracking was caused by enhanced $t\rightarrow m$ transformation in water.

Although it is known that water can enhance the $t\rightarrow m$ transformation and induce microcracking (see § 2.2.7), under conditions of sliding wear, the effect of water
depends on the contact conditions. It can either reduce wear by lubrication, or increase it by enhanced cracking following transformation.

2.4 CONCLUDING REMARKS

There is a large amount of literature published on the wear of zirconia under many environmental and contact conditions which can lead to confusion in assessing the wear performance for a particular application. Mechanisms of wear in zirconia are mainly plastic deformation and fracture, the dominance of either one depending on materials and contact conditions. The effect of water, both in the absence of wear and under sliding conditions, has been investigated by several authors. The fact that water can cause degradation of YTZPs through premature promotion of the t\(\rightarrow\)m transformation causing microcracks is widely reported, although there is still confusion over the exact mechanisms. The effect of water in sliding wear depends on the contact conditions and can be beneficial if it increases lubrication or detrimental under certain conditions. It is clear from the literature that few workers have focused on assessing wear under conditions of high speeds, which are likely to be encountered in several practical applications. In the current work, tests are conducted under both water-lubricated and unlubricated conditions at a high speed (6 m s\(^{-1}\)) that represents likely in-service conditions. The effect of speed in a high speed range (1–6 m s\(^{-1}\)) is investigated under unlubricated conditions.
Figure 2.1 Schematic representation of the zirconia polymorphs: (a) monoclinic; (b) tetragonal; (c) cubic. • = Zr, O = O, after Lee and Rainforth (1994).

Figure 2.2 Phase diagram for the zirconia rich portion of the zirconia-yttria system, after Lee and Rainforth (1994) following the original work by Scott (1975).
Figure 2.3 The monoclinic-tetragonal transformation on heating and cooling of pure zirconia through the transformation temperature showing a hysteresis on heating and cooling, after Stevens (1986).

Figure 2.4 Schematic indicating the constrained and unconstrained shapes of monoclinic ZrO₂ particles containing variants, after Evans et al. (1981).
Chapter 2: Literature Review

Figure 2.5 Dependence of the critical grain size on the yttria content, after Lange (1982(b)).

Figure 2.6 Schematic diagram of the stress-induced transformation of metastable ZrO₂ particles in the elastic stress field of a crack, after Stevens (1986).
Figure 2.7 The martensitic transformation that occurs in ZrO$_2$ (tetragonal to monoclinic at 900-1100 °C) with its 3-5 % volume expansion, develops microcracks around the ZrO$_2$ particles (a). A crack propagating into the particle is deviated and becomes bifurcated (b), thus increasing the measured fracture resistance, after Stevens (1986).
Figure 2.8  Worn zirconia surface showing network of cracks, after Dufrane (1986).
CHAPTER 3: MATERIALS AND EXPERIMENTAL TECHNIQUES

3.1 INTRODUCTION

Before conducting wear studies on ceramics, it is useful to be familiar with the microstructure and some of the properties. In this chapter the mechanical and thermal properties of the materials studied are presented, followed by a discussion of the techniques used for materials characterisation both before and after wear. The microstructures of the materials have been studied using a combination of polishing, etching, light and electron microscopy and X-ray diffractometry. Two key parameters relevant to wear performance, hardness and fracture toughness, have been assessed for the zirconia using an indentation method. Results of the characterisation of materials prior to wear are discussed in this chapter; results relating to worn surfaces are presented in chapter 5.

3.2 ZIRCONIA

The zirconia used was Technox 3000, a hot isostatically pressed yttria-stabilised tetragonal zirconia polycrystal (YTZP), supplied by Dynamic Ceramic Ltd., Crewe. It was received in the form of rods 60 or 15 mm long and 3 mm diameter in the as-pressed condition. Supplier's data for the material are shown in table 3.1.

Table 3.1 Properties of Technox 3000 TZP

<table>
<thead>
<tr>
<th>Property</th>
<th>Typical Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nominal Composition</td>
<td>95 wt. % ZrO₂, 5 wt. % Y₂O₃</td>
</tr>
<tr>
<td>Density</td>
<td>6.05 g cm⁻³</td>
</tr>
<tr>
<td>Flexural Strength 20 °C</td>
<td>1400 MPa</td>
</tr>
<tr>
<td>Flexural Strength 800 °C</td>
<td>270 MPa</td>
</tr>
<tr>
<td>Compressive Strength</td>
<td>2000 MPa</td>
</tr>
<tr>
<td>Modulus of Elasticity</td>
<td>205 GPa</td>
</tr>
<tr>
<td>Poisson's Ratio</td>
<td>0.30</td>
</tr>
<tr>
<td>Hardness (Vickers) 300 g load</td>
<td>1350 kg mm²</td>
</tr>
</tbody>
</table>
Table 3.1 Continued

<table>
<thead>
<tr>
<th>Property</th>
<th>Typical Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fracture Toughness</td>
<td>10 MPa m$^3$</td>
</tr>
<tr>
<td>Maximum Use Temperature</td>
<td>1000 °C</td>
</tr>
<tr>
<td>Thermal Expansion Coefficient</td>
<td>$10 \times 10^{-6}$ K$^{-1}$</td>
</tr>
<tr>
<td>Thermal Conductivity</td>
<td>2 W m$^{-1}$ K$^{-1}$</td>
</tr>
<tr>
<td>Thermal Shock Resistance (Downshock)</td>
<td>250 °C</td>
</tr>
<tr>
<td>(Upshock)</td>
<td>800 °C</td>
</tr>
<tr>
<td>Specific Heat Capacity</td>
<td>400 J kg$^{-1}$ K$^{-1}$</td>
</tr>
<tr>
<td>Electrical Resistivity 20°C</td>
<td>$10^8$ Ω cm</td>
</tr>
</tbody>
</table>

3.3 SILICON CARBIDE

The silicon carbide used was Hexoloy SA, a sintered silicon carbide, supplied by The Carborundum Company, Niagara Falls, NY. It was received in the form of discs 90 mm in diameter and 12 mm thick. Supplier's data for the material are shown in table 3.2.

Table 3.2 Properties of Hexoloy SA Silicon Carbide

<table>
<thead>
<tr>
<th>Property</th>
<th>Typical Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grain size</td>
<td>4-6 μm</td>
</tr>
<tr>
<td>Density</td>
<td>3.10 g cm$^{-3}$</td>
</tr>
<tr>
<td>Flexural Strength (4 point)</td>
<td>460 MPa</td>
</tr>
<tr>
<td>Flexural Strength (3 point)</td>
<td>550 MPa</td>
</tr>
<tr>
<td>Compressive Strength</td>
<td>3900 MPa</td>
</tr>
<tr>
<td>Modulus of Elasticity</td>
<td>410 GPa</td>
</tr>
<tr>
<td>Poisson's Ratio</td>
<td>0.14</td>
</tr>
<tr>
<td>Hardness (Knoop) 1000 g load</td>
<td>2800 kg mm$^2$</td>
</tr>
<tr>
<td>Fracture Toughness (Double Torsion &amp; SENB)</td>
<td>$4.60 \text{ MPa m}^3$</td>
</tr>
<tr>
<td>Maximum Use Temperature (air)</td>
<td>1650 °C</td>
</tr>
<tr>
<td>Thermal Expansion Coefficient (RT to 700°C)</td>
<td>$4.02 \times 10^{-6}$ K$^{-1}$</td>
</tr>
<tr>
<td>Thermal Conductivity RT</td>
<td>125.6 W m$^{-1}$ K$^{-1}$</td>
</tr>
<tr>
<td>200 °C</td>
<td>102.6 W m$^{-1}$ K$^{-1}$</td>
</tr>
<tr>
<td>400 °C</td>
<td>77.5 W m$^{-1}$ K$^{-1}$</td>
</tr>
<tr>
<td>Specific Heat Capacity</td>
<td>0.67 J g$^{-1}$ K$^{-1}$</td>
</tr>
<tr>
<td>Electrical Resistivity RT</td>
<td>$10^2 - 10^5$ Ω cm</td>
</tr>
<tr>
<td>1000 °C</td>
<td>0.01-0.2 Ω cm</td>
</tr>
<tr>
<td>Weibull Modulus (2 parameter)</td>
<td>10</td>
</tr>
<tr>
<td>Emissivity</td>
<td>0.9</td>
</tr>
</tbody>
</table>

*Dependent upon dopants in Hexoloy SA SiC which will decrease electrical resistivity
3.4 MATERIALS PREPARATION AND CHARACTERISATION METHODS

3.4.1 Polishing and Etching

In order to examine the microstructure of the as-received zirconia, it was necessary to polish and etch the material. Polished pins were etched either chemically or thermally. For the chemical etch, a pin was mounted in bakelite and polished on a Struers Planopol-2 polishing machine fitted with a Pedemax-2 rotating head according to the regime shown in table 3.3. This was chosen as it is a reproducible and stringent regime to eliminate any previously induced surface damage. The chemical etch was concentrated (60%) hydrofluoric acid and the sample, mounted in bakelite, was immersed for 5 minute intervals at room temperature. Between each stage it was rinsed in sodium hydroxide solution followed by water and then cleaned ultrasonically and dried. It was examined for signs of etching using a Zeiss Axiophot reflected light microscope. The total etching time was 20 minutes.

Table 3.3 Polishing Regime for Technox 3000 YTZP

<table>
<thead>
<tr>
<th>Diamond Size (μm)</th>
<th>Type of Wheel</th>
<th>Load (N)</th>
<th>Speed (rpm)</th>
<th>Lubrication</th>
<th>Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>metal bonded</td>
<td>60</td>
<td>300</td>
<td>water</td>
<td>2</td>
</tr>
<tr>
<td>20</td>
<td>metal bonded</td>
<td>60</td>
<td>300</td>
<td>water</td>
<td>5</td>
</tr>
<tr>
<td>30</td>
<td>resin bonded</td>
<td>60</td>
<td>300</td>
<td>water</td>
<td>5</td>
</tr>
<tr>
<td>10</td>
<td>resin bonded</td>
<td>60</td>
<td>300</td>
<td>water</td>
<td>5</td>
</tr>
<tr>
<td>6</td>
<td>Dur cloth</td>
<td>60</td>
<td>150</td>
<td>alcohol</td>
<td>25</td>
</tr>
<tr>
<td>1</td>
<td>Dur cloth</td>
<td>60</td>
<td>150</td>
<td>alcohol</td>
<td>10</td>
</tr>
</tbody>
</table>

For thermal etching, pins were mounted in epoxy resin and polished according to the regime shown in table 3.3. Following polishing, the pins were removed from the resin using a hack saw to cut away the majority of the resin. They were then soaked in acetone to soften any remaining resin which was subsequently removed by scraping with a sharp blade. These polished samples were then thermally etched in air by placing them in a Lenton 1850 high temperature tube furnace and rapidly heating to the required temperature, holding at temperature for the required time and then cooling. The samples
were removed from the furnace when it had reached room temperature. The temperatures and dwell times are given in table 3.4.

**Table 3.4** Temperatures and dwell times used for thermal etching.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Dwell Time (hours)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1200</td>
<td>1</td>
</tr>
<tr>
<td>1200</td>
<td>2</td>
</tr>
<tr>
<td>1300</td>
<td>1</td>
</tr>
<tr>
<td>1350</td>
<td>½</td>
</tr>
<tr>
<td>1400</td>
<td>none</td>
</tr>
<tr>
<td>1500</td>
<td>none</td>
</tr>
<tr>
<td>1500</td>
<td>½</td>
</tr>
<tr>
<td>1500</td>
<td>1</td>
</tr>
<tr>
<td>1500</td>
<td>2</td>
</tr>
</tbody>
</table>

The etched material was then examined by scanning electron microscopy. A fracture surface was also examined in order to ensure that the microstructure observed in the thermally etched samples was representative of the as-received material and that no grain growth had occurred.

### 3.4.2 Reflected Light Microscopy

A Zeiss Axiophot reflected light microscope was used to examine the surfaces of the pin and disc in the polished condition and after wear testing. Three types of contrast were used to gain the most information from each sample: bright field imaging, dark field imaging and differential interference contrast. Bright field imaging was the most useful for assessing progress during polishing, the surface being essentially two-dimensional and the polishing pull-out being easily observed as dark features as they scattered light outside the objective lens. Dark field imaging was useful for observing irregularities in the surface such as cracks or scratches. In dark field imaging the image produced has reversed contrast with respect to the bright field one. The incident light is no longer normal to the sample, but at an oblique angle such that the direct beam is reflected outside the objective lens. Surface irregularities may appear bright because the surface within the irregularity is locally tilted to such a
degree that the direct light is reflected back into the objective lens. Differential interference contrast was useful for observing differences in height of various surface features, for example grain relief of silicon carbide following wear testing. The illuminating beam is plane polarised and then split into two beams with vibrations at 90° to each other using a prism. The prism is at 45° to the crossed polars, so when light is passed through the analyser (second polariser) the two beams will have travelled different optical paths and therefore interfere. Height differences in the surface of the sample will adjust the path difference and therefore introduce contrast.

### 3.4.3 Scanning Electron Microscopy

Scanning electron microscopy was used to examine the microstructure of the zirconia in the polished condition, following etching and after wear testing. Two scanning electron microscopes were used, a Cambridge Stereoscan 250 and a Hitachi S3200N variable pressure microscope. Prior to examination in the Cambridge Stereoscan 250, samples were sputter coated with gold using an Edwards S150B coating unit with a current of 20 mA and a potential of 1 kV for a period of 2 minutes or coated with carbon using an Edwards coating unit. Operating the Hitachi S3200N in variable pressure (low vacuum) mode meant that it was possible to examine samples without coating and this was used for the wear surfaces. A pressure of 20 Pa was typical. In variable pressure mode secondary electron imaging is not possible and so only backscattered images were taken. Operating the Hitachi S3200N in normal pressure mode meant that it was either necessary to coat the samples or to use a low accelerating voltage to avoid charging. The silicon carbide discs were examined in the uncoated state both in variable pressure mode to produce backscattered electron images and in normal pressure mode at low accelerating voltage to produce secondary electron images. They were also occasionally examined after coating with carbon using an Edwards coating unit, for examination in the Cambridge Stereoscan 250. An Oxford
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Instruments Link ISIS series 300 microanalysis system using an energy dispersive spectrometer (EDS) fitted to the Hitachi S3200N SEM was used for qualitative analysis of the elements present in the samples, both before and following wear. Transfer of material to or from the pin and disc was investigated using this technique. It was best to operate the microscope in normal pressure mode when using the spectrometer because under variable pressure mode X-rays are sometimes deflected by air molecules leading to spurious results, for example from elements present in the specimen holder or other components inside the microscope. Under normal pressure operating conditions in the microscope, a low accelerating voltage was preferable to avoid charging of uncoated samples, although a high voltage gave better X-ray results. Therefore, it was often better to carbon coat the samples and operate the microscope under normal pressure conditions in order to use the spectrometer.

3.4.4 TRANSMISSION ELECTRON MICROSCOPY

Transmission electron microscopy was used to examine the microstructure of the zirconia in both the as-received and worn conditions. It was also used to examine debris collected from the disc after wear testing. The as-received material, in the form of 3 mm diameter rods, was cut into approximately 200 µm slices using a Struers Accutom-5 diamond cutting saw. These discs were then dimpled on a Southbay Technology Inc. model 515 precision dimpling instrument using a diamond impregnated brass dimpling wheel and diamond pastes, reducing in particle size down to 1 µm, to obtain an area of the sample approximately 30 µm thick. The dimpled samples were then further thinned using a Gatan model 600 ion beam thinner, voltage limited at 6 kV with a current of 1 mA, thinning from both sides at an initial incidence angle of 18° reducing to 12° for between 10 and 20 hours whilst rotating the sample. This progressive decrease in angle of incidence was used to obtain as large a thin area as possible and to avoid producing holes with steep sides.
The thin samples were then coated with carbon using an Edwards coating unit. A Philips 400T and a Philips CM200 transmission electron microscope were used to examine the samples obtained in this way. Worn TEM samples were made by cutting the worn end off a pin with a Struers Accutom-5 diamond cutting saw and then dimpling from the opposite side to the worn surface in a manner similar to that used for unworn samples. The dimpled wear surfaces were then thinned from the back only to produce a thin area similar to that for the unworn samples. Whilst in the Gatan ion beam thinner, the wear surface was protected by covering with aluminium foil to prevent deposits from building up on it.

Debris from and surrounding the wear track were collected by squirting a little acetone onto the disc surface following a wear test and placing an acetate sheet over the area of interest. This was allowed to dry overnight and then the acetate was peeled off, taking with it some of the debris particles. An area of the acetate containing several debris particles was cut out using a sharp blade and placed onto a 3 mm diameter copper grid which was resting on a metal gauze. This was placed in a beaker and acetone was poured in until it just reached the gauze, so wetting the acetate without it floating off the copper grid. This was left for two days with a lid on, topping up the acetone from time to time, so that the acetate dissolved and left the debris particles on the copper grid. The copper grid was placed on filter paper and allowed to dry. The sample was then thinned in a Gatan model 600 ion beam thinner, voltage limited at 6 kV with a current of 1 mA, thinning from both sides at an incidence angle of 13° for between 1 and 2 hours whilst rotating the sample. The sample was then carbon coated prior to examination in the transmission electron microscope. A similar acetate peeling technique was used to stick acetate to a worn pin surface. Once dried, this was peeled off to remove the surface layer and debris from the worn pin. The pin surfaces were mounted on copper grids as before and then ion beam thinned from behind.
3.4.5 **X-Ray Analysis**

X-ray diffraction traces were taken from surfaces of both polished and worn zirconia pins using a Philips PW 1049/01 X-ray diffractometer with a Philips PW 1710 diffractometer control. A monochromated copper source was used in a Philips PW 1130/00/60 X-ray generator. The wavelength of Kα X-rays produced is 0.15405 nm. The scan speed used was 1° min⁻¹.

3.4.6 **Indentation Studies**

A knowledge of how a ceramic responds to surface contact is useful in determining its potential application in tribological situations. The indentation fracture technique provides a convenient way of assessing the near surface plasticity and fracture behaviour of a brittle material when subjected to localised compressive loading in a controlled and reproducible manner, leading to hardness and fracture toughness values. The indentation fracture toughness is useful if damage due to indentation is also operative in sliding. Features common to wear and indentation processes include localised fracture, deformation and displacement of the surface material and sensitivity to pre-test preparation conditions. Hardness/wear relations are however, not always straightforward and clearly understood and caution must be exercised when using the indentation technique to gain information relating to potential wear responses. Some limitations in relating indentation behaviour to wear behaviour include for example, the different stress systems in indentation and sliding contacts, including factors due to friction and temperature generation. Also, other, more complex mechanisms including fatigue, and chemical reactions may occur during wear.

Zirconia samples for hardness and fracture toughness characterisation were mounted in bakelite before polishing according to the regime in table 3.3. The polished zirconia was indented with a Vickers profile diamond having an
included angle of 136° at loads of 98, 196, 284, 392 and 490 N. Equation 3.1 was used to calculate the hardness from the observed indentation diagonals

\[ H_v = \frac{2P \sin \left( \frac{\delta}{2} \right)}{d^2} \]  

(3.1)

where \( H_v \) is Vickers hardness, \( P \) is indentation load, \( \delta \) is the included angle of the indenter and \( d \) is the average of the two indentation diagonals. Indenting the zirconia at these loads produced radial cracks from the corners of the indentation. This is characteristic of a crack system seen in many brittle materials. It consists of two penny-shaped median cracks perpendicular to the surface, formed on loading, and lateral cracks, formed on unloading. The median crack often extends on unloading to become a half-penny shape and is seen as radial cracks from the corners of the indentation on the surface. The length of these radial cracks can be used to obtain a value of the fracture toughness for the material using equation 3.2 (modified from Anstis et al. (1981) by Ponton and Rawlings (1989) to include Vickers hardness, \( H_v \), instead of \( H \) (defined as the mean indentation pressure, given by \( P/2a_i^2 \), where \( P \) is the indenter load and \( a_i \) is the indentation half diagonal length) and therefore changing the constant from 0.016 to 0.0154)

\[ K_{IC} = 0.0154 \left( \frac{E}{H_v} \right)^{\frac{1}{2}} \left( \frac{P}{c} \right)^{\frac{3}{2}} \]

(3.2)

where \( E \) is Young’s modulus and \( c \) is the mean length of radial cracks. This equation can be used to calculate the fracture toughness, assuming that the cracks are in equilibrium after unloading and no slow crack growth effects are observed. This method of obtaining a value for the fracture toughness frequently gives a lower value than that obtained from more conventional
methods. For equation 3.2 to be valid, the cracks produced have to be sufficiently well developed, i.e. $c_r > a_r$.

### 3.5 RESULTS OF PROPERTY AND MICROSTRUCTURAL DETERMINATION

#### 3.5.1 Grain Size

The chemical etch after 20 minutes was quite severe and the material appeared over-etched, despite having not appeared to be etched at all after the previous stages. It was, however, useful for comparisons with the thermally etched samples to ensure that no grain growth was occurring in the furnace. Thermally etched samples were compared to the chemically etched sample, with each other and with fracture surfaces and it appeared that no grain growth occurred during thermal etching. The as-received material was a grey colour and on removal from the furnace following thermal etching it had changed to white. This is perhaps because of differences in the oxidation conditions between hot isostatic pressing and heating in a furnace. During hot isostatic pressing it is possible that impurity centres are formed due to oxygen deficiency. On heating in the furnace, oxygen was present in the air and the material became stoichiometric again and turned white. This effect was not investigated further. The best results for studying the microstructure were obtained from the sample heated to 1350 °C with a dwell time of 30 minutes and a scanning electron photomicrograph of this sample is shown in figure 3.1. The microstructure consists of small (~ 0.7 µm) grains, with a few larger (~ 4-5 µm) grains. The smaller grains are likely to be tetragonal and the larger grains are likely to be cubic. A scanning electron photomicrograph of a fracture surface of a zirconia pin is shown in figure 3.2 for comparison. The material appears to have fractured inter-granularly along the tetragonal grain boundaries and trans-granularly through the cubic grains. It can be seen that the grains are the same size as those in figure 3.1 and so no grain growth
occurred during thermal etching. The inter-granular fracture of tetragonal grains is shown in figure 3.3.

Figures 3.4 shows the microstructure of the silicon carbide. This is a secondary electron image of an uncoated disc taken at low accelerating voltage to avoid charging. There is a contrast between adjacent grains which reveals that they are angular and approximately 4-6 μm in size. This contrast is called channelling contrast and occurs because of differences in the backscattered electron coefficient with crystallographic orientation of the grains. Although this image is from the secondary electron detector, it contains information from the small fraction of backscattered electrons that are emitted from the sample in the direction of the detector and therefore the contrast is observed. Images obtained from the Robinson backscattered detector did not reveal this contrast because electrons were collected from a large solid angle so cancelling any orientation effects. It can also be seen that there are holes in the surface. By comparing polished surfaces to fracture surfaces such as the one shown in figure 3.5, it was established that most of the holes are processing porosity as they can be seen in both images. There is, however, some damage resulting from the polishing regime, which has not been removed by subsequent finer polishing as there are more holes in the polished surfaces compared with the fracture surfaces and these tend to be larger holes where grains have pulled out.

3.5.2 REFLECTED LIGHT MICROSCOPY

The reflected light microscope was useful for examining the degree of damage in the surface polishing between various stages but was not as useful as the electron microscopes for characterising the materials before or after wear testing. The grains were too small to be observed clearly in the reflected light microscope as the magnification was not sufficient. Using bright field illumination, it was possible to observe some of the features of the wear
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surface, but photographing them was difficult because the depth of field of the microscope was smaller than the size of the surface variation due to the wear test and this is particularly true for the unlubricated tests where severe surface disruption occurred. The progress of the wear scar across the face of each pin could, however, be monitored using a reflected light microscope.

3.5.3 Transmission Electron Microscopy

Transmission electron photomicrographs of the zirconia are shown in figure 3.6. Figure 3.6a shows the general microstructure observed including a larger cubic grain amongst the smaller tetragonal grains. Figure 3.6b is a general view of the edge of the sample, and twins are clearly seen in the grains. Figure 3.6c is a higher magnification view of the grains. Thickness fringes can be seen around the edges of the grains and in the grain at the right hand edge of the photomicrograph.

3.5.4 X-Ray Analysis

Figure 3.7 is a typical trace from the X-ray diffractometer for a polished zirconia pin. From JCPDS card number 17-923, the tetragonal peaks were indexed as shown in the figure. From the $d_{hkl}$ spacings of the 002 and 200 peaks, lattice parameters were calculated according to equation 3.3. These lattice parameters were then used to calculate $d_{hkl}$ spacings and expected $2\theta$ values, using equations 3.3 and 3.4 respectively, for other sets of planes (with different indices) that produce peaks in the diffractometer to confirm that the peaks produced were due to the tetragonal phase.

$$\frac{1}{d_{hkl}^2} = \frac{h^2 + k^2 + l^2}{a^2 + c^2}$$ (3.3)
\[ 2\theta = 2\sin^{-1}\left(\frac{\lambda}{2d_{hkl}}\right) \]  

(3.4)

Several traces were examined and the average values of the tetragonal lattice parameters were \( a = 0.5046 \) nm and \( c = 0.5126 \) nm. The approximate positions where monoclinic peaks would be expected, if this phase were present in the material, were marked on to the traces using data from JCPDS card number 36-420 (pure monoclinic). The exact positions would be slightly different, due to the presence of yttria. Most of these positions were very close to where the tetragonal peaks were, with the exception of the \( 111 \) peak which is expected at a position of \( 28.19^\circ \) \( 2\theta \) for the pure material. This peak was only present on some of the traces, for example that shown in figure 3.7, and so it is possible that only a small amount of monoclinic material was present, and only detected in the diffractometer at a particular sample position. The sample was rotated and re-positioned several times and the \( 111 \) monoclinic peak was only present sometimes. The position of the cubic peaks is also very close to the tetragonal peaks and it was not possible to resolve this phase.

### 3.5.5 Indentation Studies

The mean hardness values of the zirconia obtained from several indentations at each load are tabulated in table 3.5.

<table>
<thead>
<tr>
<th>Load (N)</th>
<th>( H_v ) (kg mm(^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>98</td>
<td>1299</td>
</tr>
<tr>
<td>196</td>
<td>1270</td>
</tr>
<tr>
<td>294</td>
<td>1268</td>
</tr>
<tr>
<td>392</td>
<td>1253</td>
</tr>
<tr>
<td>490</td>
<td>1310</td>
</tr>
</tbody>
</table>
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The values of fracture toughness obtained from 'valid' cracks are given in table 3.6.

**Table 3.6** Fracture toughness values of Technox 3000 from indentation.

<table>
<thead>
<tr>
<th>Load (N)</th>
<th>( K_{IC} ) (MPa m(^{3/2}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>196</td>
<td>4.8</td>
</tr>
<tr>
<td>294</td>
<td>4.5</td>
</tr>
<tr>
<td>392</td>
<td>4.5</td>
</tr>
<tr>
<td>490</td>
<td>4.5</td>
</tr>
</tbody>
</table>

These values are lower than expected from the manufacturer's data sheet, despite the known discrepancy between indentation fracture toughness and that measured by conventional methods (Ponton and Rawlings, 1989). The fracture toughness quoted in the manufacturer's data is 10 MPa m\(^{3/2}\) although the assessment method is not given. A possible explanation for the low indentation value is that damage caused by the cutting and grinding processes was not sufficiently removed in the polishing regime, resulting in an already transformed surface and therefore the transformation toughening mechanism was not operative. The presence of some monoclinic phase on a polished surface was confirmed by X-ray diffraction. The samples were small and the possibility of edge effects and indentation stress field interaction also arises if the indentations were too close to the edge and/or another indentation.

### 3.6 CONCLUDING REMARKS

The properties of the pin and disc materials have been given and some characterisation methods have been described. The microstructures of the zirconia and silicon carbide have been examined by scanning electron microscopy. The zirconia was also further investigated using transmission electron microscopy. The microstructure of the zirconia consists of small tetragonal grains (~0.7 μm) and larger cubic grains (~4-5 μm). The silicon carbide has a grain size of approximately 4-6 μm with a more uniform size distribution. X-ray diffractometry of polished zirconia revealed the presence of
some monoclinic phase, and the lattice parameters of the tetragonal phase are $a = 0.5046$ nm and $c = 0.5126$ nm. It was not possible to resolve the cubic phase due to the peak positions being very close to the tetragonal peaks. Indentation of the zirconia was used to provide information on the hardness and fracture toughness of the material. The hardness of the zirconia is $1282$ kg mm$^2$ and the indentation fracture toughness was measured as $4.6$ MPa m$^{1/2}$, which was lower than expected from the suppliers data.
Figure 3.1  Scanning electron photomicrograph of a thermally etched sample of Technox 3000 yttria stabilised zirconia

Figure 3.2  Scanning electron photomicrograph of the fracture surface of a zirconia pin.
Figure 3.3 Scanning electron micrograph of the fracture surface of a zirconia pin, showing intergranular fracture between tetragonal grains.

Figure 3.4 Scanning electron photomicrographs of Hexaloy SA silicon carbide disc.
Figure 3.5 Scanning electron photomicrograph of a fracture surface of a silicon carbide disc.
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(a)

(b)
Figure 3.6  Transmission electron photomicrographs of a zirconia pin.

Figure 3.7  X-Ray diffraction trace from a polished zirconia pin.
CHAPTER 4:
WEAR TESTS

4.1 INTRODUCTION

In this chapter the development of the wear testing rig is outlined and details of the final design are given. The wear tests are described in general, followed by experimental details of the individual tests.

4.2 DEVELOPMENT OF A WEAR RIG

4.2.1 BACKGROUND

A rig was required to replicate some of the conditions in the pump. Wear tests were to be conducted on small samples to minimise material costs and facilitate post-testing examination. The cylinder block in the pump rotates at 1500 r.p.m., providing an output water pressure of 14 MPa, which will be the maximum pressure between the cylinder block and the port plate. The maximum diameter of the cylinder block to be in contact with the port plate is 77 mm. The water is sea water and may contain sand particles filtered to below 1 mm in diameter. The specification of the rig is therefore to provide a rotational speed of 1500 r.p.m., or a relative sliding speed of 6 m s\(^{-1}\) (for samples of a different size to the cylinder block) and a contact pressure of 14 MPa in a water environment.

A pin-on-flat type arrangement was envisaged to be the most suitable sample set-up. Small zirconia pins sliding on silicon carbide flats were chosen. A new pin would be used for each test sliding against a fresh section of the flat.

There are several possibilities in terms of the set-up of the rig. In order for a constant speed to be maintained, the moving part should rotate rather than reciprocate and the motor driving the rotating disc must be able to overcome
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the friction force. The force application method should enable a contact pressure of 14 MPa to be reached easily. Various options were considered and the rotational speed required to achieve a relative sliding speed of 6 m s\(^{-1}\) would decrease with an increasing sample size. The further away from the centre of the disc the pin was positioned, the lower the necessary rotational speed would be. This leads to a compromise between sample size and power of motor required. A powerful motor was required that would withstand the loads involved and provide the rotational speed for reasonably sized samples.

4.2.2 EVOLUTION OF THE FINAL DESIGN

The final option was to use a lathe to provide a motor of the required power, and modify it to enable loads to be applied to a disc. A large (90 mm diameter) disc was used and its surface re-polished once there was no more room for a wear track on fresh surface. The disc was held in the chuck and one pin loaded onto it. Water could be applied to the contact via a hose pipe from a tap. The disc rotates in the vertical plane and so simple dead weights could not be used to load the pin. The pin needs to be loaded horizontally, and several possibilities using levers were considered. The option that was chosen, however, employs a simple spring mechanism connected to a small drill chuck that holds the pin and is mounted on the tool post of the lathe. The tool post can slide along the lathe runners and is positioned so that the spring is stretched when the pin comes into contact with the disc. The spring is extended and provides a load on the pin that is proportional to its displacement. A schematic diagram of the apparatus is shown in figure 4.1.

4.2.3 SIMPLE CALCULATIONS OF DISC STRESS

Some simple checks were carried out to ensure that the disc would not fail as a result of either compression in the lathe grips, or stresses generated due to the rotation. The splitting stress of a disc in compression must not be
Chapter 4: Wear Tests

exceeded in the wear tests. The equation for splitting stress in a disc compressed at two points is

\[ \sigma = \frac{w}{\pi R_d t} \] (4.1)

where \( w \) is the compressive load applied to the disc, \( R_d \) is the disc radius (45 mm) and \( t \) is the disc thickness (12 mm). For most ceramic materials the bend strength is approximately twice the tensile strength, and the lower bend strength of the silicon carbide quoted by the manufacturer is 460 MPa. For the splitting stress not to exceed 230 MPa in the disc, the compressive load must not exceed 390 kN. It was envisaged that this was easily possible while still holding the disc securely in the chuck.

In addition to the stresses generated by compression of the chuck, stresses arise from the rotation of the disc. The equations for radial and tangential stress in a rotating disc are

\[ \sigma_r = \frac{\rho \omega^2}{8} \left[ (3 + \nu)(R_d^2 - r^2) \right] \] (4.2a)

\[ \sigma_t = \frac{\rho \omega^2}{8} \left[ (3 + \nu)R_d^2 - (1 + 3\nu)r^2 \right] \] (4.2b)

where \( \rho \) is material density, \( \omega \) is angular velocity, \( \nu \) is Poisson's ratio, \( R_d \) is disc radius and \( r \) is a radial co-ordinate. The radial and tangential stresses must not exceed the strength of the disc material. Using the material properties in table 3.2, the radial and tangential stresses were calculated to be less than 0.07 MPa at a rotational speed of 1500 r.p.m. and 0.23 MPa at a rotational speed of 2890 r.p.m. (the maximum possible on the lathe) and were therefore not considered to be likely to cause problems.
4.3 EXPERIMENTAL DETAILS
4.3.1 GENERAL COMMENTS ON WEAR TESTS

Water-lubricated and dry sliding wear of YTZP and silicon carbide couples was investigated using the rig described in § 4.2.2. The pin loading assembly was positioned so that the pin would contact the disc at the desired radius. The rotational speed of the disc was adjusted until it was rotating at the pre-calculated speed to provide the required sliding velocity. For water lubricated tests, the water flow rate was adjusted until it was pouring steadily at a rate of 2 l min⁻¹. The pin was then brought into contact with the rotating disc and the load increased to the required value by rapid extension of the spring. During the water-lubricated tests the position of the spring was constant because the linear wear of the pin was small. During the dry tests, minor manual adjustment to the position was necessary to keep the load constant as the pin wore.

The pin was marked with a horizontal line so that it could be re-positioned in the chuck of the pin loading assembly in the same orientation after removing between stages of an interrupted test. This was done in the first instance with a pencil as this was not removed by cleaning in acetone. However, during the early water-lubricated tests it became apparent that the mass of the pencil line was of the same order of magnitude to that of the worn mass. If any of the pencil line was rubbed off during the test or cleaning stage, then this could affect the results significantly. A permanent marker was found that was not completely removed in acetone and the mass of the line could not be detected on an AND HA-202M balance that was capable of reading to 0.01 mg. The balance used for weighing the pins and disc after the first dry wear test and the early water-lubricated tests was a Stanton balance, capable of reading to 0.1 mg. Upon further investigation it was found that considerable fluctuations were occurring in the mass measurement of pins that were stored in a desiccator in the same laboratory as the balance and weighed at intervals. All
mass measurements after these tests were made on the AND HA-202M balance that was capable of measuring the mass of the pins to 0.01 mg. Before further wear tests were conducted, the consistency of mass measurements made on this balance was checked by weighing several pins at intervals. The fluctuations were found to be on the order of 0.02 mg and this was considered satisfactory.

The geometry of the pins is such that all tests were carried out with a flat area of the pin in contact with the disc. It is believed that a flat-on-flat contact condition is more representative of a real situation than a spherical on flat contact and that the nominal contact pressure is a useful parameter in describing the wear tests. Wear test results are therefore given in this work with respect to nominal contact pressure as they are, for example, in the work by Birkby et al., 1995.

4.3.2 Specimen Preparation

4.3.2.1 Flat Ended Pins

Preparation of the zirconia pin specimens involves cutting them to the correct length. The cutting action can be considered as a type of wear process with a consequent introduction of surface damage. In order to study the wear in the pin caused during the wear test, it is desirable to start with a surface which is undamaged. Therefore the surfaces of the pins to be in contact with the disc during the wear test were polished to remove as much of the surface damage induced by machining (cutting) as possible and to provide a consistent and known initial surface for conducting the wear tests. To allow comparisons between tests, the initial state of the surface of each pin should be the same. It was important to ensure that the polish was achieved at right angles to the length of the pin in each case, providing as flat a surface as possible for the wear interface and thus an even stress distribution on the pin.
Chapter 4: Wear Tests

The pins that were 60 mm long when received were cut to lengths of approximately 15 mm using a Struers Accutom-5 cut-off saw fitted with a circular diamond impregnated blade and using a water-based lubricant. The flat face to be wear tested was polished and this part of the pin specimen preparation technique evolved during the course of the experimental work. Initially, the pins were polished by mounting them vertically in epoxy resin and then polished according to the regime shown in table 3.3. Following polishing, the pins were removed from the resin as described in § 3.4.1 for the pins that were thermally etched. Finally the pins were ultrasonically cleaned, rinsed and dried. During subsequent wear tests using some of these pins for interrupted water-lubricated tests, chipping occurred during the first 30 s of contact with the disc. This may have been as a consequence of the wear process or due to a flaw developing in the pin during removal from the epoxy resin. The wear data of tests for which this occurred had to be disregarded.

Later pin specimens were polished in-situ on the rig to ensure surface conformity between the pin and disc and to reduce the possibility of introducing flaws during the preparation procedure. This was achieved using various grades of silicon carbide paper stuck to a brass disc, in a manner similar to a conventional polishing machine. A polishing regime was developed which resulted in the surface of the pin being parallel to the disc surface and this is given in table 4.1.

<table>
<thead>
<tr>
<th>SiC Paper Grit Size</th>
<th>Particle Diameter (μm)</th>
<th>Load (kg)</th>
<th>Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>500</td>
<td>30</td>
<td>5</td>
<td>until flat (~2)</td>
</tr>
<tr>
<td>800</td>
<td>22</td>
<td>5</td>
<td>2</td>
</tr>
<tr>
<td>1200</td>
<td>14</td>
<td>3</td>
<td>3x2 (3 fresh papers)</td>
</tr>
<tr>
<td>2400</td>
<td>8</td>
<td>3</td>
<td>1½</td>
</tr>
<tr>
<td>4000</td>
<td>5</td>
<td>3</td>
<td>1½</td>
</tr>
</tbody>
</table>

(The grit size of the silicon carbide indicates the number of meshes per linear inch in a sieve through which the particles will pass completely)
This did not produce a completely flat surface as easily as was achieved with the conventional polishing machine, as the surface contained small grooves in the direction of sliding. This is because the samples are not rotated as they are polished. The polishing regime did, however, achieve a consistent and flat surface with a surface finish at least as smooth as that which was produced in the water-lubricated tests.

4.3.2.2 Tapered Pins

Some pins had an area of their wear surface ground away at an angle, to reduce the area in contact with the disc and make it easier to produce a larger nominal contact stress. The final shape of these tapered pins is shown in figure 4.2. This was achieved by rotating the tool post through an angle (in this case 45°) and polishing pins as before on silicon carbide paper. The first stage used a coarse silicon carbide (120 grit) to grind away material and form the tapered shape and two further stages were introduced to polish down to the 500 grit paper which was used as the initial stage for the flat ended pins. The tapers were polished to the same finish as the flat ended pins. It was difficult to monitor the progression of the initial stage and therefore the size of the taper varied from pin to pin. It was possible to calculate the area of the flat end from equation 4.3 (Zwillinger, 1996), having first measured the height of the segment, \( h_s \), using a reflected light microscope

$$
A = R_p^2 \cos^{-1} \frac{R_p - h_s}{h_s} - (R_p - h_s) \sqrt{2R_p h_s - h_s^2}
$$

(4.3)

where \( A \) is the area of the segment, \( R_p \) is the radius of the pin and \( h \) is the height of the segment. This equation was only used if \( h_s < R_p \). If the area ground away was less than half of the circular area of the pin end, equation 4.3 was used to calculate the area removed which was then subtracted from the total circular area to give the area of the wear surface.
4.3.2.3  Silicon Carbide Discs

The silicon carbide discs were received from the Carborundum Company in the polished condition with a surface of finish 0.1 µm $R_s$ and they were used for wear testing in this condition. When there was no more room on a disc for further wear tracks, it was sent to Agate Products, London, to grind away 1 mm of material from the surface, and so remove any material affected by the wear test. This was followed by subsequent lapping and polishing to a 0.1 µm $R_s$ surface finish.

4.3.3  WATER-LUBRICATED TESTS
4.3.3.1  Polished Pins

The early water-lubricated tests were conducted as described in § 4.3.1 for intervals of 30 s at a time at a nominal contact pressure between pin and disc of 14 MPa and a relative sliding speed of 6 m s$^{-1}$. The mass change was measured between each stage following removal of the pin, cleaning ultrasonically, rinsing in acetone and drying. The pin was then re-positioned in the rig and the process repeated. This was to monitor wear as it occurred in the early stages. Between the first few stages it was possible to follow the progress of the wear by visual examination. By comparing the size of the wear scar to that of the polished area, it was observed that the wear scar progressed across the polished surface as the test proceeded. The first two water-lubricated tests were conducted under these, nominally identical, conditions. Continuous tests were then conducted for an hour each in total. During the first of these the lathe developed a problem with the bearing, possibly leading to a reduction in speed towards the end of the first stage and the test had to be stopped after just under half an hour. The pin was weighed at this stage and the test resumed after the lathe had been repaired. The continuous test was repeated using another pin for the whole hour.
Due to the inaccuracies mentioned in § 4.3.1, the first two water-lubricated interrupted tests were repeated using the more accurate balance and a marker pen to locate the pins. They were ultrasonically cleaned in soapy water in case any oil from the lathe was transferred to their surfaces during removal from the loading assembly and then rinsed in acetone and dried. Two runs were completed at 30 s and 60 s intervals.

4.3.3.2 Pins Polished in-Situ

Interrupted and continuous uninterrupted wear tests were conducted on pins polished in-situ on the rig as described in § 4.3.2.1 at a nominal contact pressure of 14 MPa and a speed of 6 m s⁻¹.

4.3.3.3 Tapered Pins at Increased Contact Pressures

Pins with tapered ends as described in § 4.3.2.2 were used for further water-lubricated tests at nominal contact pressures up to 70 MPa to investigate the effects of increased pressure on the breakdown of the lubrication regime. First, tests were conducted at 14 MPa for comparison with previous tests on pins polished flat in-situ on the rig. Secondly, the nominal contact pressure was increased to 3 times the original pressure (to 42 MPa) and the tests repeated. Thirdly, the pressure was increased to five times the original value (70 MPa) and the tests repeated. In order to determine the pressure at which the lubrication regime was broken down, further tests were conducted at nominal contact pressures of 60 and 65 MPa. Three further tests at 70 MPa were then conducted.
4.3.4 UNLUBRICATED TESTS
4.3.4.1 Polished Pins

Several interrupted wear tests were conducted on pins mounted in epoxy resin and polished according to the regime in § 3.4.1 and then removed from the resin. These tests were conducted at a nominal contact pressure of 14 MPa and a relative sliding speed of 6 m s\(^{-1}\).

4.3.4.2 Pins Polished In-Situ

Two further unlubricated tests were conducted under the same load and speed conditions on pins polished in-situ on the rig according to the regime in table 4.1.

4.3.4.3 Varying Load and Speed Conditions

Interrupted wear tests were conducted on pins polished in-situ on the rig under different conditions of relative sliding speed and nominal contact pressure as marked by an x in table 4.2. Where there is a c in the table, a longer, continuous test was also conducted.

Table 4.2 Test conditions for unlubricated tests on pins polished in-situ.

<table>
<thead>
<tr>
<th>Nominal contact pressure (MPa)</th>
<th>2.1</th>
<th>3.5</th>
<th>6</th>
<th>14</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 relative sliding speed (m s(^{-1}))</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>x</td>
<td></td>
<td></td>
<td>x</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td></td>
<td></td>
<td>x</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>c</td>
<td></td>
<td>x</td>
</tr>
<tr>
<td>4</td>
<td>c</td>
<td></td>
<td></td>
<td>x</td>
</tr>
<tr>
<td>6</td>
<td></td>
<td></td>
<td></td>
<td>x</td>
</tr>
</tbody>
</table>
4.4 CONCLUDING REMARKS

In this chapter the wear testing rig has been described. Details of the sample preparation techniques have been given and these were: flat-ended pins polished on a machine; flat-ended pins polished on the rig, and tapered pins (with a smaller flat area) polished on the rig. The wear tests that were conducted with both water-lubrication and unlubricated have been described. Under water-lubricated conditions, the sliding speed was 6 m s\(^{-1}\) and the nominal contact pressure was varied from 14 to 70 MPa. Under unlubricated conditions, the sliding speed was varied between 1 and 6 m s\(^{-1}\) and the nominal contact pressure was varied between 2.1 and 14 MPa. The results of the tests described in this chapter will be presented in chapter 5.
Figure 4.1 Schematic diagram of the wear testing rig.

Figure 4.2 Shape of tapered pins.
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CHAPTER 5:
RESULTS

5.1 INTRODUCTION

In this chapter the results of experiments described in chapter 4 are presented along with a preliminary discussion which includes calculation of wear coefficients. The results of analyses of worn surfaces and debris are also presented, followed by X-ray diffraction results.

5.2 WATER-LUBRICATED WEAR TESTS
5.2.1 Polished Pins

During the water-lubricated tests there was occasional chatter between the pin and disc. Overall the noise generated from the contact was low. On one plot the results of the first four water-lubricated tests with polished pins are shown in figure 5.1; two were interrupted with short time intervals, one had two long intervals and one was continuous. As reported in § 4.3.1 the balance used for the mass loss measurements during these initial tests was not as accurate as was required. However, the low wear rate that was measured for the continuous (■) test appears valid because on visual observation of the pin, no wear scar was observed and the surface still appeared polished. The results of two further tests conducted using a more accurate balance are shown in figure 5.2. Figure 5.3 shows the results of the interrupted tests on one plot. These tests were carried out under nominally the same contact conditions. It was expected that, by conducting experiments under nominally identical conditions, the scatter in the results would reveal any experimental errors in mass loss and time measurements. It is clear that there is quite a large amount of variation in these results and it appears that the variation in the results between different pins is much greater than could be expected from
experimental errors. However, the general shape of each curve is similar, beginning with an initial mass loss as the pin wears and then the change in mass loss reduces as no more measurable wear is occurring. It was important to establish whether the variation in mass loss values between different pins was due to actual material variations or testing conditions such as pin alignment. Possible alignment problems (exaggerated) are illustrated in figure 5.4 which shows the possible orientations of the pins that were polished on the polishing machine. Either the surface was flat and perpendicular to the length of the pin but the misalignment was caused by the set up of the drill chuck load application mechanism in relation to the disc in the lathe chuck (a), or the end was flat but not polished so that the surface was perpendicular to the length of the pin (b). In order to investigate which of these was the case, the pins were polished in-situ as described in § 4.3.2.1 and table 4.1 and wear tests were repeated.

5.2.2 Pins Polished In-Situ

The results of the interrupted tests conducted on pins polished in-situ on the rig are presented in figure 5.5. Note that the ordinate scale is much smaller than for figure 5.1 and that variations in mass loss are both positive and negative. From these results, and observation of the pin surfaces using a reflected light microscope, it was obvious that no measurable wear was occurring. Ensuring that there was a conformal contact between the pin and the disc had reduced the wear rate to zero. It is most likely that the pin and disc were separated by a layer of water, that is hydrodynamic lubrication (HDL) was achieved. This means that the load is supported by the hydrodynamic film pressure. From figure 5.5 it appears that hydrodynamic lubrication is achieved from the very beginning of the test, i.e. there is no running in period. Longer, uninterrupted tests were conducted on these pins, in case wear was occurring, but at a very low rate. However, no wear was measured, confirming the occurrence of HDL.
5.2.3 **TAPERED PINS**

Pins with tapered ends were used in order to achieve a higher nominal contact pressure and investigate HDL breakdown. Pins of this geometry were also investigated at a nominal contact pressure of 14 MPa and results of these tests are shown in figure 5.6. The general shape of the curves is similar to that seen for the pins polished on the polishing machine, i.e. initial wear followed by no further mass loss. The initial running-in period occurs because the pin and disc surfaces are not suitably aligned for hydrodynamic lubrication to be achieved until a certain amount of wear has altered the shape of the contact. In creating the taper on the pins the toolpost had to be moved through 45° and then back to the original position. The pin end was polished before the edge was ground away and the taper made. Although the angle of the toolpost is marked, altering its position may have meant that on returning to the original position the pin was not exactly aligned in its polishing position with respect to the disc. This would be enough to cause the initial wear observed, as in the first tests, before HDL was achieved in the system. The absolute values of mass loss are different for each pin. This is because the degree of misalignment is different and so a different volume is worn away before the conditions for HDL can be achieved.

The results for the three experiments on tapered pins at a contact pressure of three times the original pressure (42 MPa) are given in figure 5.7. The shape of the curves is similar to those already obtained for tests at 14 MPa, i.e. there is still an initial running-in period despite the pins being polished after making the taper to eliminate misalignment problems that could arise through moving the toolpost. This suggests that the alignment problem may be due to very slight 'play' in the position of the drill chuck in relation to the disc. This could not be prevented without changing the load application mechanism completely and it was considered that meaningful results could nevertheless be gained from the rig both on the lubrication regime and the wear mechanisms during
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running-in. The effect of increasing the nominal contact pressure on the breakdown of the lubrication regime was further investigated bearing in mind that there may be an initial running-in period.

The results of increasing the nominal contact pressure to five times the original pressure (70 MPa) are shown in figure 5.8. From figure 5.8(a) it appears that hydrodynamic lubrication is again achieved after a running-in period. However, from figure 5.8(b), which was obtained under the same contact pressure and speed conditions it is clear that the lubrication has broken down and that wear occurred for this pin. This wear was not thought to be a running-in period as the magnitude of the mass loss is much greater than that previously observed and was measured after a period of no wear. The breakdown of the lubrication regime at this pressure was confirmed by examination of the pin by scanning electron microscopy. In order to further verify the pressure at which hydrodynamic lubrication was broken down, additional water-lubricated experiments were conducted at nominal contact pressures of 60 and 65 MPa. The results of these tests are shown in figures 5.9 and 5.10. Again, hydrodynamic lubrication was achieved after an initial running-in period. Therefore it was concluded that the lubrication began to break down at a contact pressure of 70 MPa. Three further water-lubricated tests were conducted at 70 MPa, the results of two of which are shown in figure 5.11. Both pins broke during the tests and so the tests were shorter than previous tests. However, it can be seen that wear is occurring. The other pin tested under these conditions failed to show any change in mass at all for the 120 s of contact (four 30 second intervals). It was concluded that the onset of hydrodynamic lubrication breakdown is beginning to occur at a contact pressure of 70 MPa. This nominal contact pressure can be supported by hydrodynamic lubrication if the exact pin alignment is favourable. This depends on slight 'play' in the position of the testing rig, which cannot be controlled. When hydrodynamic lubrication is broken down, the wear rate is rapid compared to that measured during running-in under HDL conditions.
5.3 UNLUBRICATED WEAR TESTS

5.3.1 Polished Pins

Wear tests conducted under unlubricated conditions on pins polished on the polishing machine prior to wear testing resulted in several of the pins breaking. The fracture occurred towards the back face (away from the wearing interface) and the mass loss results did not represent a wear rate in these cases. The results of a test on a pin that did not break are shown in figure 5.12. There appears to be a short initial period where the wear rate of the pin is less than the steady state, which is reached after about 60 s. This test created a lot of noise, heat and sparks, and after the last interval a large crack had appeared in the disc, perhaps due to thermal shock, and so the test was concluded. The total wear was 0.0832 g and this corresponds to a reduction in length of 1.95 mm of the 3 mm diameter pin. It is suggested that during the first 60 s of the test, there was a misalignment problem and the whole surface of the pin was not in contact with the disc and this was confirmed by the fact that the wear scar only covered some of the pin surface. The pin wore across the surface from the edge, causing the increase in wear rate once the wear scar covered the whole pin surface and so wear was occurring over the maximum surface area.

5.3.2 Pins Polished In-Situ

As some alignment problems had come to light during the water-lubricated tests as described in § 5.2.1 it was possible that there was a similar problem in the unlubricated tests. The problems with the balance are not as significant here because the amount of mass loss is much greater, although wear tests from this point onwards were conducted using the 5 figure balance. Results for unlubricated tests on pins polished in-situ on the rig are given in figure 5.13. On comparison with figure 5.12 it is clear that tests on pins polished in-situ on the rig produced a lower wear rate. The test rig vibrated much more
during these tests than the previous unlubricated test and both of the tests for which results are shown were stopped because the pins chipped in the rig, one at the wearing face and the other at the back face. As well as polishing the pins *in-situ*, another factor that could have contributed to this difference was that between the first and second sets of unlubricated tests the discs were re-polished. Although the same surface finish was specified (0.1 μm R_a) a better finish was achieved after re-polishing as determined by higher reflection on visual examination. This difference in surface finish was difficult to quantify because the finish is so smooth, although an attempt was made using a confocal laser scanning microscope. These differences in geometry and the surface finish of the two components between the first and second sets of tests may have caused the differences in the amount of wear.

Examination of the surface of the disc after testing revealed approximately regularly spaced areas of zirconia transfer to the wear track. This periodic transfer may have been caused by a stick-slip motion of the pin on the disc. This may account for the vibration of the rig. The high degree of conformity and the smooth surface finish of the pin and disc led to higher adhesive forces between the two components than for the previous tests on pins that were not polished *in-situ*. This pattern of zirconia transfer was not observed for all unlubricated tests. The overall wear rate was lower for this pin, than for one polished on the polishing machine, but this could be because of the lower initial pressure and not related to the stick-slip phenomenon. The surface area initially in contact was different for the pins polished on the polishing machine and those polished on the rig. For the pins polished on the polishing machine, the pin was initially only in contact at one edge so the contact pressure was high, leading to fracture and material removal locally. This running-in period was important in establishing the wearing surfaces. As the test proceeded, the wear scar extended to cover the whole face of the pin. At this stage the surface of the pin was already damaged and not smooth, and so further asperity contact caused a steady wear rate. For the pins polished on the rig,
the surfaces of the pin and disc were conformal and so the initial contact pressure was lower, leading to the lower wear rate. The surface of the pin was polished and so larger areas were in contact which favoured a stick-slip pattern of wear, due to high adhesive forces. If the pins had not broken and it had been possible to continue the later tests beyond the first few intervals, the stick-slip regime may have changed to continuous contact as parts of the pin surface wore. It is clear that the surface finish and the exact geometry of the two components in the tribological system is crucial to determining whether the pin wears at a steady rate or in a less uniform manner due to the occurrence of stick-slip motion.

5.3.3 VARYING LOAD AND SPEED CONDITIONS

The results of the unlubricated tests on pins under different speed and load conditions as described in § 4.3.4.3 are presented here. Figure 5.14a shows the results from all of the tests for comparison and figure 5.14b is an expanded view of the area of low wear rate. The results are presented according to test conditions in figures 5.15 with tests conducted at the same speed plotted on the same axes. Results from tests conducted at different speeds for the same time intervals are not directly comparable because the sliding distance is different. Comparison is easier when considering the wear coefficients as these are normalised for sliding distance, § 5.4.

The results of tests conducted at a speed of 1 m s⁻¹ are shown in figure 5.15a and the effect of contact pressure is difficult to establish at this speed. Figure 5.15b shows the results of tests conducted at a speed of 2 m s⁻¹ and it is suggested that the amount of wear is greater for a contact pressure of 3.5 MPa compared to 2.1 MPa. The amount of wear at a contact pressure of 6 MPa is very similar to that at 3.5 MPa for the interval of test conducted. If it had been possible to continue the test, a clearer result may have been obtained. The results of tests conducted at 3 m s⁻¹ are shown in figure 5.15c
and the effect of contact pressure is clearer, although there is a large difference between the two tests at 6 MPa, despite the fact that they begin the tests at very similar levels of mass loss. Figure 5.15d shows the results of tests conducted at 4 m s\(^{-1}\). The gradient of each plot, and therefore the wear rate, increases with contact pressure. One of the pins tested at 3.5 MPa broke and so there is a discontinuity in mass loss although the gradient is steady. The value of mass loss in the results following the pin breakage have been reduced to show the likely plot had the pin not broken (open circles).

The trend that would be expected from these wear tests is an increase in mass loss with increasing contact pressure for a given sliding speed. This trend is observed for some of the wear tests, but discrepancies do exist, especially at low speeds. The absolute value of mass loss per given time interval is expected to be lower at lower speeds, as the sliding distance is less. It is therefore possible that the difference arising from varying the pressure will be more significant at higher speeds. If there is any scatter due to experimental error, this will be larger in percentage terms at lower speeds, making determination of the effect of pressure more difficult at lower speeds than for higher speeds. The mass loss is normalised for sliding distance in the calculation of wear coefficients in § 5.4.

However, the results of tests at 3 m s\(^{-1}\) and 6 MPa reveal that there is a large difference between the two sets of results for different pins tested under these conditions. This suggests that there was some variable between the two tests that is not being controlled. During the test for which the lower wear rate was recorded, there was a lot of vibration in the rig and following this test some screws had to be tightened. This may explain the lower wear rate if vibration was causing the pin contact conditions to vary. This highlights the importance of minor chatter and vibration in the rig, which is difficult to control from test to test.


5.4 WEAR COEFFICIENTS

A wear coefficient was calculated for each of the water-lubricated and un lubricated tests according to equation 5.1.

\[ K = \frac{V}{Ls} \]  

where \( K \) is the volumetric wear coefficient \( (\text{mm}^3 \text{ N}^{-1} \text{ m}^{-1}) \), \( V \) is the worn volume \( (\text{mm}^3) \), \( L \) is the applied load \( (\text{N}) \) and \( s \) is the total sliding distance \( (\text{m}) \). This wear coefficient is frequently quoted in the literature as a useful parameter in assessing wear and comparing amounts of wear for different materials and from different test situations. However, the amount of wear can depend on parameters not included in the equation such as surface finish, the shape of the contact and the sliding speed. Lubrication also has a large effect as has been seen from the results presented in this chapter, therefore caution should be used when making comparisons from wear coefficients alone.

In order to calculate the wear coefficient for a water-lubricated test, a straight line was drawn through the results for the period when wear was occurring, i.e. before hydrodynamic lubrication was achieved. The gradient was then converted from grams per second to cubic millimetres per metre (by dividing by density and speed). This was then normalised by dividing by the applied load to give the wear coefficient. Examples are given in figures 5.16a and b. The resulting wear coefficient will therefore apply to the 'running-in' period. It should be noted that for tapered pins, the applied load varied from pin to pin in order to maintain the same nominal contact pressure. This is because the area of the flat end of a tapered pin varied, so normalising with respect to applied load would not necessarily give consistent wear coefficients for pins worn under nominally the same conditions. It was subsequently noted, however, that variations in values of wear coefficient were greater than could
be explained by this (relatively small) variation in applied load. Wear coefficients for water-lubricated tests are given in table 5.1. Figures 5.17a and b show the wear coefficient, $K$, for the water-lubricated tests plotted on log axes against (a) load and (b) nominal contact pressure. From these figures, there is no clear dependence of wear coefficient on load (or pressure).

### Table 5.1 Wear coefficients for water-lubricated tests

<table>
<thead>
<tr>
<th>Nominal Contact Pressure (MPa)</th>
<th>$K$ ($\text{mm}^3 \text{N}^{-1} \text{m}^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>14</td>
<td>5.36x10^-8</td>
</tr>
<tr>
<td>14</td>
<td>1.24x10^-9</td>
</tr>
<tr>
<td>14</td>
<td>1.61x10^-9</td>
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<td>14</td>
<td>7.06x10^-9</td>
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<td>14</td>
<td>4.67x10^-9</td>
</tr>
<tr>
<td>14</td>
<td>9.29x10^-10</td>
</tr>
<tr>
<td>14</td>
<td>3.53x10^-9</td>
</tr>
<tr>
<td>42</td>
<td>5.72x10^-9</td>
</tr>
<tr>
<td>42</td>
<td>1.33x10^-9</td>
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<td>42</td>
<td>1.24x10^-9</td>
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<td>70</td>
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<td>1.30x10^-9</td>
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<td>7.95x10^-8</td>
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<td>60</td>
<td>1.85x10^-8</td>
</tr>
<tr>
<td>60</td>
<td>9.01x10^-10</td>
</tr>
<tr>
<td>65</td>
<td>1.72x10^-10</td>
</tr>
</tbody>
</table>

For the unlubricated tests, the wear coefficient was calculated in a similar manner, by drawing a straight line through most of the results to give as good a steady state wear coefficient as was possible. This sometimes meant leaving out the first one or two mass loss results if there was a larger or smaller increase in mass loss during the initial stages, compared to the rest of the test. Examples are shown in figures 5.18 a and b. Interrupted tests were used, as continuous tests were not conducted under all conditions and they resulted in a lower mass loss for a given contact time than an interrupted test. This lower mass loss may have been because for interrupted tests, the pin was subjected to repeated cycles of heating and cooling as it was removed for weighing. During the continuous tests the pin was subjected to only one cycle of this type.
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For the unlubricated tests under varying load and speed conditions, the applied load was the same for each nominal contact pressure as the pin area was always the same. The wear coefficients are given in table 5.2 and shown plotted against load and speed in figure 5.19.

Table 5.2  Wear coefficient, $K$ (mm$^3$ N$^{-1}$ m$^{-1}$) for unlubricated tests.

<table>
<thead>
<tr>
<th>Load (N)</th>
<th>Pressure (MPa)</th>
<th>speed (m s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>14.7</td>
<td>2.1</td>
<td>1.4x10$^{-8}$</td>
</tr>
<tr>
<td>24.5</td>
<td>3.5</td>
<td>1.7x10$^{-8}$</td>
</tr>
<tr>
<td>42.2</td>
<td>6</td>
<td>2.6x10$^{-8}$</td>
</tr>
<tr>
<td>98.1</td>
<td>14</td>
<td>5.1x10$^{-8}$</td>
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<td></td>
<td></td>
<td>2.0x10$^{-8}$</td>
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</tr>
<tr>
<td></td>
<td></td>
<td>3.7x10$^{-6}$</td>
</tr>
</tbody>
</table>

The wear coefficients calculated from the unlubricated test results show two clear trends. There is an increase in wear coefficient with an increase in either nominal contact pressure (or load) or speed. The increase of wear coefficient with nominal contact pressure could be related to the increase in the severity of the contact, leading to a larger amount of material removal. The increase with speed is less obvious as the wear coefficient is normalised with respect to total sliding distance, although it may be related to increased temperature generation. Temperature generation at the sliding interface is discussed in § 6.3.4.3 and § 6.4.3.4.

During the initial stages of a test, in some cases, the wear scar did not cover the whole pin surface and it developed as the test progressed. This resulted in a short period of initial wear that was not steady state. In some cases, this initial period resulted in a higher wear rate (mass loss/time) than the steady state (for example pin polished in-situ and worn at 2 m s$^{-1}$ and 2.1 MPa, figure 5.18b), and in some cases it resulted in a lower wear rate than the steady state (for example pin polished on machine worn at 6 m s$^{-1}$ and 14 MPa, figure 5.18a). There are two factors to consider. First, the area in contact during the initial stages is smaller than the total pin surface area, and so for a given pressure, the actual mass loss would be expected to be lower than if the same
pressure was acting on the whole surface and causing wear. Second, the actual pressure acting on the smaller area is greater than the nominal contact pressure, and it is possible that this increases the wear rate. The relative magnitude of the effects of these two factors governs whether the initial wear rate is greater or less than the steady state. The effect of the higher pressure on the wear can be deduced from the dependence of mass loss (or wear coefficient) on pressure. At low nominal contact pressures, the pressure dependence of mass loss is higher than at high pressures. So at low pressures during the initial stages, a higher pressure on part of the surface will produce a higher mass loss than the steady state, even though the area being worn is initially less. This is because the fact that only part of the surface is wearing is not as important to the overall mass loss as the increase in pressure. Conversely, at high pressures, during the initial stages, an even higher pressure on part of the surface will produce a lower mass loss than the steady state, as the size of the area being worn is more significant to mass loss than the variation in pressure, at higher pressures.

5.5 WORN SURFACE AND DEBRIS ANALYSIS

5.5.1 Pins from Water-Lubricated Tests

It was important to try to ensure that, in examining the surface, especially at high magnifications, representative areas of the surface were chosen. This was achieved by examining several areas of a worn pin surface and comparing them. There were three main features of interest in the surfaces of pins worn under water-lubricated conditions; plastic deformation, intergranular fracture and a network of cracks both parallel and at right angles to the sliding direction. Microscopy revealed that as the nominal contact pressure was increased, the wear mechanism became more severe and the areas showing intergranular fracture increased.
Microscopy of the surfaces of flat polished pins worn at a nominal contact pressure of 14 MPa revealed that although there was no measured mass loss, grooves had been worn in the surface, indicating that material is being displaced rather than lost. These grooves did not cover the whole surface and an example is shown in figure 5.20. Although the tapered pins worn at this contact pressure after being polished on the rig did undergo a mass loss, the mechanism appeared mild. The surface contained a few scratches and grooves, although these did not cover the whole of the worn surface. The wear scar covered approximately three-quarters of the pin surface. Examples are shown in figures 5.21a and b.

As the nominal contact pressure was increased to 42 MPa, the wear mechanism appeared more severe. The surface contained evidence of the three apparent mechanisms of damage mentioned above. A pin was examined following 30 s and 390 s of wear. The type of damage observed on the surface did not appear to have changed much with increased time, but the wear scar had grown. The various surface features are shown in figures 5.22 a-f.

Examination of surfaces of pins worn at 70 MPa revealed a damage mechanism which was obviously more severe. Pins from tests where hydrodynamic lubrication had broken down were examined and revealed that the wear scar contained much larger areas of intergranular fracture and there was evidence of plastic deformation, giving rise to surface smearing (figures 5.23 a-d), although the grooves and crack networks previously seen were also observed (figures 5.24 a-c). There were some areas that appeared grooved and smeared (figure 5.25). Figure 5.26 shows a relatively low magnification view of the border between areas consisting mainly of smearing and grooves (upper right) and an area consisting mainly of material removal by what appears to be intergranular fracture (lower left). In this case the wear scar covered the whole pin surface and at the time the photomicrograph was taken.
it appears as though the material that had been smeared and grooved was yet to be removed.

From these images it appears that the material in contact with the disc is worn by abrasive grooving and plastic deformation of the surface (manifested by smearing). This then leads to material removal in layers as intergranular fracture at a depth of a few micrometres below the surface links up with the crack networks observed in the surface. It is suggested that these crack networks could be generated by thermal shock, caused by high temperature generation in the interface. This is discussed further in § 6.3.4.

5.5.2 Pins from Unlubricated Tests

In general, the surfaces of pins worn under unlubricated conditions exhibited much more severe damage than those worn under water-lubricated conditions. However, some similar features were observed, particularly towards the milder end of the wear testing conditions, i.e. grooves and smearing, networks of cracks parallel and at right angles to the direction of sliding and material removal by what appears to be intergranular fracture, in layers from the surface. The wear scar on the pin worn at 1 m s⁻¹ and a nominal contact pressure of 2.1 MPa contained areas of material removal by intergranular fracture and smeared areas. Increasing the nominal contact pressure at this speed to 3.5 and 6 MPa meant that the wear scar then contained a larger area showing grains, suggesting material removal by intergranular fracture, and cracks similar to those observed in water-lubricated worn pins were observed as well (figure 5.27).

For wear tests that were conducted at greater speeds, the time intervals and total times of sliding contact were the same which meant that the total distance was higher, the greater the speed. The surface of a pin worn at 2 m s⁻¹ and a nominal contact pressure of 2.1 MPa is shown in figure 5.28. It shows islands
of material not yet removed from a layer (figure 5.28a) and grooves and cracks in the material of the new surface following material removal (figure 5.28b). A pin worn under similar conditions but uninterrupted was examined by reflected light microscopy and figure 5.29 shows features of a crack network, grooves and material removal (dark areas).

Figure 5.30a shows an area of the worst damage on the surface of a pin worn at 3 m s\(^{-1}\) and a nominal contact pressure of 2.1 MPa. It can be seen that flakes of material have been removed from the surface in patches following deformation by grooves and smearing. The material in the newly created surface contains cracks (figure 5.30b). The trailing edge of the wear scar of this pin exhibited milder damage such as that seen on pins worn under less severe conditions, namely grooves and smearing, with some material removal in patches. The surface of a pin worn at 3 m s\(^{-1}\) and a nominal contact pressure of 3.1 MPa, showed similar features to those already described and examples are shown in figures 5.31 a-b.

Pins worn at 4 m s\(^{-1}\) and a nominal contact pressure of 3.5 MPa were examined after 390 s of wear and an example of the damage on the surface is shown in figures 5.32a-c. A pin was worn for a further 60 s and examined before ultrasonic cleaning and as figure 5.33 shows, small particles of loose debris were observed on the surface. There were also more lifted plates of material, which would presumably be removed by ultrasonic cleaning. A pin worn under these conditions for an uninterrupted 390 s was examined (figure 5.34) and the surface appeared very similar to those examined from interrupted tests. It is interesting to note that on examination of this pin, the central area showed the most severe wear, with the leading edge being smeared while the trailing edge clearly contained more grooves, suggesting that the grooves are caused by pin material removed from the contact.
Pins worn at 6 m s\(^{-1}\) and a nominal contact pressure of 14 MPa showed much more severe wear than those previously described, as would be expected from their wear rates. Figure 5.35 is a reflected light photomicrograph after 10 s of wear under these conditions showing the network of cracks and grooves in the direction of sliding. After 120 s sliding the damage was more severe with large flakes lifted up from the surface (figure 5.36). This pin was examined in the scanning electron microscope after a total of 176 s wear and photomicrographs are shown in figures 5.37 a-c. It is clear that the whole surface is severely worn and material is removed in flakes.

The height difference between areas of intergranular fracture and flakes was measured using an axiophot reflected light microscope to focus on the different features in adjacent areas and was found to be between 2-5 \(\mu\)m.

A pin worn at 4 m s\(^{-1}\) and a nominal contact pressure of 3.5 MPa for 390 s was placed in a vacuum chamber and a 9.2 weight % solution of gold chloride in diethyl ether was introduced so that it might infiltrate cracks seen on the surface. It was then left for approximately 1 hour at atmospheric pressure in the solution, removed and placed in a drying oven for 2 hours at 60 °C to remove the diethyl ether. The sample was then broken open and the sections examined in the scanning electron microscope. Some areas of the surface contained what appeared to be a layer of material, partially separated by a crack from the underlying material. Examples of this type of feature are shown in figures 5.38 a-b. The depth of the crack below the surface is approximately 3 \(\mu\)m. X-ray mapping revealed that gold chloride particles were seen on the sample to a depth of approximately 40 \(\mu\)m below the surface. This can only be considered as a general estimate of the depth of penetration of the gold chloride solution because the particles were quite spread out, there was not a clear border between areas containing gold chloride and those not. Assuming the gold chloride was not transferred to the sectioned surface during
preparation, this depth can be taken as an estimate of the depth of cracks from the surface of the pin.

5.5.3 **Discs**

The discs were also examined following wear tests and the main features were grooves, transferred zirconia and grain relief. Figure 5.39 is a reflected light photomicrograph using differential interference contrast showing grooves and transferred zirconia (lighter). Figure 5.40 shows some grooves caused by a loose zirconia particle which has then become stuck in the disc surface. Figure 5.41 is a scanning electron photomicrograph of the disc surface showing zirconia particles trapped in the holes in the surface. Figure 5.42 shows that the grooves are of two sizes, with larger 'waves' and smaller grooves. Figures 5.43 a-b are reflected light micrographs using differential interference contrast to show grain relief. It is possible that this occurs because the grains are oriented in different directions and wear rate is dependent on crystallographic direction. The features observed on the worn surface of the disc were similar for all tests, with the amount of transferred zirconia greater for the unlubricated tests. An energy dispersive spectrometer (EDS) was used to examine the extent of zirconia transfer. Discrete particles of zirconia were seen to have transferred to the disc surface and become trapped, either in holes, or at the end of grooves they had made. The transferred zirconia did not cover the whole of the wear track.

5.5.4 **Transmission Electron Microscopy of Worn Pin Surfaces and Debris Analysis**

A worn surface was prepared as described in § 3.4.4 and examined by transmission electron microscopy. In this limited TEM study, only one such sample was examined. It was from a pin worn at 2 m s⁻¹ and a nominal contact pressure of 2.1 MPa under unlubricated conditions. The sample
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contained several cracks, although these may have occurred during preparation. Twins were observed, figure 5.44 a-c and were seen to be at different orientations in adjacent grains. The presence of twins indicates that the monoclinic phase was formed. The cracks go through the twins, indicating that it is likely that the cracks formed after the twins, perhaps in sample preparation.

A pin surface was removed by sticking an acetate sheet to the surface using acetone and peeling it off once this had dried as described in § 3.4.4. Areas of the surface layer were removed with the acetate and it is suggested that they contained debris and delaminated flakes such as those shown in figure 5.38. The surface was removed from a pin following wear at 4 m s\(^{-1}\) and a nominal contact pressure of 3.5 MPa. Examination in the TEM revealed that the surface consisted of very small grains, approximately 10-30 nm, figure 5.45.

Debris was collected from the wear track of a disc following a wear test at 2 m s\(^{-1}\) and a nominal contact pressure of 2.1 MPa as described in § 3.4.4. Examination in the TEM revealed that the debris was sub-micrometre size, approximately 0.25-0.5 \(\mu\)m (figure 5.46a-c). Electron diffraction patterns of this sample were taken and were of the spotty ring type, indicating that the debris was crystalline, but it was not possible to determine the crystal structure with any certainty due to the closeness of the rings and a pattern from the copper supporting grid superimposed on the sample pattern.

5.6 X-RAY DIFFRACTION

Worn pin surfaces were analysed in the X-ray diffractometer as described in § 3.4.5. There was no clear \(\overline{1}11\) monoclinic peak at about 28° (2\(\theta\)) in any of these traces and so the X-ray work was inconclusive in determining the role of the phase transformation on wear. As demonstrated in § 3.5.4, a sample that
contained some monoclinic phase would only reveal this in certain orientations. Absence of a monoclinic peak suggests that a large volume percentage of monoclinic phase is not present, but small amounts of monoclinic phase could be present but undetected. Debris was collected from the disc following a dry test using sellotape and an X-ray trace produced from this which did not show any characteristic zirconia peaks. It is thought that this is because it was not possible to collect sufficient debris by this method for investigation with the X-ray diffractometer.

5.7 CONCLUDING REMARKS

In this chapter the results of the wear tests have been presented. It was found that under water-lubricated conditions, wear depended on the exact geometry of the contact. With flat ended pins polished in-situ on the rig, hydrodynamic lubrication (HDL) was achieved and no wear was recorded. With tapered pins (with a reduced flat area in contact) there was generally a running-in period and then HDL was maintained up to a nominal contact pressure of around 70 MPa. Under unlubricated conditions a geometry dependence also existed, with a lower wear rate recorded for pins polished in-situ on the rig compared to those polished on a polishing machine. Differences in the surface finish of the disc may also have played a part in the lower wear rate, with a stick-slip motion being observed. Wear rates were measured under unlubricated conditions with different speeds and nominal contact pressures in the range 1-6 m s\(^{-1}\) and 2.1-14 MPa. Wear coefficients (K) were calculated for the tests conducted. For the water-lubricated tests, K was calculated for the period of the test when wear was occurring. For the unlubricated tests, K was calculated for a period when the wear rate was at a steady state. The wear coefficient showed large scatter for the water-lubricated tests, attributed to variations in lubrication conditions. For the unlubricated tests, the wear coefficient increased with both speed and nominal contact pressure, with no sudden transitions observed.
Examination of the worn surfaces revealed three main types of damage mechanism: grooves and surface smearing; material removal in flakes/layers by intergranular fracture and a network of cracks in the surface parallel and normal to the sliding direction. These features were observed on most of the surfaces where a wear rate was recorded, the severity of the mechanism increasing with the severity of the contact. Transmission electron microscopy revealed the formation of twins, which indicates transformation to monoclinic phase, although XRD was inconclusive in this respect. The surface of a worn pin was found to contain very small grains (10-30 nm). The wear debris was microcrystalline and approximately 0.25-0.5 μm in size.

These results are discussed further in the following chapter in which the wear coefficients are compared to literature values. The surface features which are common to worn pins from both water-lubricated and unlubricated tests, and possible mechanisms of formation, are discussed individually. This leads to a possible physical model for wear.
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Figure 5.1 Results of preliminary water-lubricated wear tests on polished pins.

Figure 5.2 Results of two interrupted water-lubricated tests on polished pins, using a balance capable of measuring to 10 µg.
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Figure 5.3 Results of interrupted water-lubricated wear tests on polished pins.

Figure 5.4 Schematic diagram showing possible misalignments (exaggerated) of pin and disc for pins polished on a polishing machine.
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Figure 5.5 Water-lubricated wear test results for two pins tested after polishing in-situ on the rig.

Figure 5.6 Water-lubricated wear test results for tapered pins at 14 MPa contact pressure.
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(a)

(b)
Figure 5.7 (a-c) Results of water-lubricated tests on tapered pins at 42 MPa.
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Figure 5.8 (a-b) Results of water-lubricated tests on tapered pins at 70 MPa.
Figure 5.9  Results of water-lubricated tests on tapered pins at 60 MPa.

Figure 5.10  Results of water-lubricated tests on a tapered pin at 65 MPa.
Figure 5.11  Results of further water-lubricated tests on tapered pins at 70 MPa.
Figure 5.12  Results of unlubricated test at 14 MPa on a polished pin

Figure 5.13  Results of unlubricated tests on pins polished *in-situ* on the rig.
Figure 5.14  Results of unlubricated tests under various conditions of speed and nominal contact pressure (a) complete data sets; (b) detail of low mass loss region.
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(a) 1 m s\(^{-1}\)

(b) 2 m s\(^{-1}\)
Figure 5.15  Results from unlubricated wear tests under various conditions of speed and nominal contact pressure (a) 1 m s\(^{-1}\); (b) 2 m s\(^{-1}\); (c) 3 m s\(^{-1}\); (d) 4 m s\(^{-1}\).
Figure 5.16 Examples of gradients for wear coefficient calculation for two different water-lubricated tests. (a) 14 MPa (flat ended pin polished on machine); (b) 60 MPa (tapered pin polished in-situ).
Figure 5.17 Wear coefficient $K$ plotted against (a) load; and (b) pressure for water-lubricated tests.
Figure 5.18  Examples of gradients used for wear coefficient calculation for two unlubricated tests (a) 14 MPa, 6 m s\(^{-1}\) (pin polished on machine); (b) 2.1 MPa, 2 m s\(^{-1}\) (pin polished \textit{in–situ}).
Figure 5.19 Variation in wear coefficients for unlubricated tests with speed and nominal contact pressure.
Figure 5.20  Scanning electron photomicrograph of the surface of a flat polished pin worn under water-lubricated conditions at 14 MPa showing grooves covering some of the surface.
Figure 5.21 (a) Scanning electron photomicrograph of the surface of a tapered pin worn under water-lubricated conditions at 14 MPa showing grooves and (b) higher magnification image of a similar area.
Figure 5.22 (a) Scanning electron photomicrograph of the surface of a tapered pin worn under water-lubricated conditions showing grooves and a band of more severe damage and (b) higher magnification view of a, showing the area of worst damage where material has been removed by intergranular fracture.
Figure 5.22 Scanning electron photomicrograph of the surface of a pin worn under water-lubricated conditions at a pressure of 42 MPa (c) showing grooves and a network of cracks parallel and normal to the direction of sliding (d) showing three types of surface damage: grooves in the direction of sliding; material removal by intergranular fracture and cracks parallel and normal to the sliding direction.
Figure 5.22 Scanning electron photomicrograph of the surface of a tapered pin worn under water-lubricated conditions at a pressure of 42 MPa (e) showing grooves and the network of cracks (f) showing cracks and grooves.
Figure 5.23  Scanning electron photomicrograph of the surface of a tapered pin worn at 70 MPa under water-lubricated conditions (a) showing surface smearing and (b) material removal by intergranular fracture.
Figure 5.23  Scanning electron photomicrograph of the surface of a tapered pin worn under water-lubricated conditions at 70 MPa (c) showing smeared surface and an area of material removal (d) showing an area where a layer of material has been partially removed revealing grain relief in the lower layer and cracks in the remaining upper layer.
Figure 5.24 Scanning electron photomicrograph of the worn surface of a tapered pin tested under water-lubricated conditions at 70 MPa showing (a) grooves and cracks in the smeared surface (b) higher magnification view of an area of figure 5.23 a showing surface cracks and small grooves.
Figure 5.24 (c) Reflected light photomicrograph (dark field) of the surface of a tapered pin worn under water-lubricated conditions at a pressure of 70 MPa showing a network of cracks in the surface.

Figure 5.25 Scanning electron photomicrograph of the worn surface of a tapered pin tested under water-lubricated conditions at 70 MPa showing an area that was grooved and smeared.
Figure 5.26 Scanning electron photomicrograph of the worn surface of a tapered pin tested under water-lubricated conditions at 70 MPa showing the border between an area of grooves and surface smearing (upper right) and an area where material has been removed in a layer by intergranular fracture (lower left).
Figure 5.27 Scanning electron micrograph of the surface of a pin worn under unlubricated conditions at 1 m s\(^{-1}\) and 3.5 MPa showing cracks parallel and normal to the direction of sliding.
Figure 5.28 Scanning electron micrograph of the surface of a pin worn at 2 m s\(^{-1}\) and 2.1 MPa. (a) showing material removal in a layer, leaving islands and cracks in the new (lower) surface. (b) showing grooves and cracks in the surface created after material was removed in a layer.
Figure 5.29  Reflected light micrograph of the surface of a pin worn uninterrupted under unlubricated conditions at 2 m s⁻¹ and 2.1 MPa showing grooves, cracks and material removal (dark areas).
Figure 5.30 Scanning electron micrographs of the surface of a pin worn under unlubricated conditions at 3 m s⁻¹ and 2.1 MPa showing an area of the most severe damage where flakes of material have been removed in layers from the surface. Cracks are seen in the upper and lower layers of material.
Figure 5.31 Scanning electron micrographs of the surface of a pin worn under unlubricated conditions at 3 m s^{-1} and 3.1 MPa showing an area where a layer of material has been removed.
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(a)  

(b)
Figure 5.32 Scanning electron micrographs of the surface of a pin worn under unlubricated conditions at 4 m s\(^{-1}\) and 3.5 MPa. (a) showing flakes lifted from the surface (b) and (c) areas of material removal in layers.

Figure 5.33 Scanning electron micrograph of the surface of a pin worn under unlubricated conditions at 4 m s\(^{-1}\) and 3.5 MPa before ultrasonic cleaning showing small particles of debris on the surface.
Figure 5.34  Scanning electron micrograph of the surface of a pin worn uninterrupted under unlubricated conditions at 4 m s\(^{-1}\) and 3.5 MPa.

Figure 5.35  Reflected light photomicrograph of the surface of a pin worn under unlubricated conditions at 6 m s\(^{-1}\) and 14 MPa for 10 s showing crack networks and grooves in the direction of sliding.
Figure 5.36  Reflected light photomicrograph of the surface of a pin worn under unlubricated conditions at 6 m s⁻¹ and 14 MPa showing severe damage and flakes of material lifted up from the surface.
Figure 5.37 Scanning electron photomicrograph of the surface of a pin worn under unlubricated conditions at 6 m s\(^{-1}\) and 14 MPa (a) revealing the severe wear mechanism of material removal in flakes (b) higher magnification view of figure 5.36 a (c) another area of the worn surface.
Figure 5.38 (a) Scanning electron photomicrograph of the cross section of the surface of a pin worn under unlubricated conditions at 4 m s⁻¹ and 3.5 MPa showing a flaked surface and cracks parallel to the surface (b) higher magnification view of figure 5.38 a.
Figure 5.39  Reflected light photomicrograph (differential interference contrast) of the surface of a disc wear track showing transferred zirconia (lighter) and grooves in the sliding direction.

Figure 5.40  Reflected light photomicrograph (differential interference contrast) of the surface of a disc wear track showing a trapped zirconia particle and the grooves it caused in the disc surface.
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Figure 5.41  Scanning electron photomicrograph of the worn surface of a disc showing zirconia particles (lighter) trapped in the holes in the disc.

Figure 5.42  Reflected light photomicrograph (differential interference contrast) of the surface of a worn disc showing large and small grooves in the sliding direction.
Figure 5.43 Reflected light micrographs (differential interference contrast) of the surface of a worn disc showing grain relief.
Figure 5.44  Transmission electron photomicrographs of a back thinned pin surface (a) showing cracks and twins (b) showing that the twins are at different orientations in different grains.
Figure 5.44 (c) Higher magnification view of figure 5.44b.

Figure 5.45 Transmission electron photomicrograph of a worn pin surface removed by acetate and back thinned showing very small grains.
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(a)

(b)
Figure 5.46  Transmission electron photomicrograph of debris collected from the disc following an unlubricated test. The debris particles are 0.25-0.5 μm size.
CHAPTER 6: DISCUSSION

6.1 INTRODUCTION

In the previous chapter, results of water-lubricated and unlubricated sliding wear tests of YTZP were presented. It was shown that under water-lubricated conditions, wear was extremely geometry dependent and with a pin polished in-situ on the rig, hydrodynamic lubrication could be achieved and maintained at a sliding speed of $6 \text{ m s}^{-1}$ to a nominal contact pressure of 70 MPa, where the lubrication regime began to break down. Under unlubricated conditions, the wear rate depended on sliding speed and nominal contact pressure, increasing with increases in either. The amount of mass loss was an order of magnitude greater for the unlubricated tests than for the water-lubricated tests under the same contact conditions. Examination of worn surfaces from these tests revealed some degree of commonality in terms of the surface features. Three main mechanisms of surface disruption were observed: abrasive grooves and surface smearing; intergranular fracture leading to material removal; and a network of cracks parallel and normal to the sliding direction. These features were seen in varying proportions on the worn surfaces suggesting that, despite the differences in wear rates, the two types of test (water-lubricated and unlubricated) have common mechanisms of wear.

In this chapter, the results of the wear tests and analyses are discussed in more detail. The wear coefficients are compared to values from the literature. The surface features mentioned above are discussed individually and conclusions about their formation are drawn. The effect of the wear tests on the silicon carbide disc is discussed. A physical model for the wear mechanism is proposed, covering both water-lubricated and unlubricated conditions.
6.2 WEAR COEFFICIENTS

6.2.1 REPORTED VALUES FOR YTZPs

There are several authors who publish wear data either as a wear coefficient, or in a form that can easily be converted to a wear coefficient using equation 5.1. It is useful to make comparisons between results from this study and published data. However, it is not necessarily straightforward to make comparisons between the results from different authors because of the variation in testing conditions and environments, material compositions and processing routes. Wear coefficients can vary throughout a test and it is not always clear whether the wear coefficient relates to the total wear for a given period or to an average value. Therefore, the variability of material and testing conditions, alongside the inherent variability of a single test, leads to a broad range of wear coefficient values in the literature.

Table 6.1 is a table of wear coefficients from the literature for YTZP worn self-mated or against another ceramic at room temperature either with water-lubrication or unlubricated. Only data acquired for tests at room temperature are included, for useful comparison with the current work. If the wear coefficient was not quoted, but sufficient information was included for its calculation, this is shown in the table with †. Where the contact was reciprocating not unidirectional, this is indicated with ↔ and where a speed is indicated, it is the average sliding speed.

Table 6.1 Wear Coefficients for YTZPs from the Literature.

<table>
<thead>
<tr>
<th>Reference</th>
<th>Materials</th>
<th>Contact Conditions</th>
<th>Speed (m s⁻¹)</th>
<th>Load (N)</th>
<th>Wear Coefficient (mm³ N⁻¹ m⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Scott (1985)</td>
<td>YTZP-YTZP</td>
<td>↔ hemispherical pin on flat</td>
<td>0.00133</td>
<td>4.9</td>
<td>1.1x10⁻⁹</td>
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<tr>
<td>Fischer et al.  (1987)</td>
<td>YTZP-YTZP</td>
<td>hemispherical pin on disc</td>
<td>0.001</td>
<td>9.8</td>
<td>2x10⁻⁷-2x10⁻⁶</td>
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<tr>
<td>Ishigaki et al. (1987)</td>
<td>YZTP-YTZP</td>
<td>flat ended pin on disc</td>
<td>0.546 0.41 0.20</td>
<td>5</td>
<td>8x10⁻⁶ 10⁻⁶ 5x10⁻⁶</td>
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## Table 6.1 Continued

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<th>Reference</th>
<th>Materials</th>
<th>Contact Conditions</th>
<th>Speed (m s⁻¹)</th>
<th>Load (N)</th>
<th>Wear Coefficient (mm N⁻¹ m⁻³)</th>
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<tr>
<td>Sasaki (1989)†</td>
<td>YTZP-YTZP</td>
<td>pin on disc</td>
<td>0.1</td>
<td>50</td>
<td>1x10⁻⁵</td>
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<tr>
<td></td>
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<td>8x10⁻⁶</td>
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<td>0.4</td>
<td></td>
<td>6x10⁻⁶</td>
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<td>Bundschuh and Zum Gahr (1991)</td>
<td>YTZP-YTZP</td>
<td>block on ring</td>
<td>0.78</td>
<td>10</td>
<td>3x10⁻³</td>
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<tr>
<td>Lee et al. (1993)†</td>
<td>YTZP-YTZP</td>
<td>ball on 3 flats</td>
<td>0.0019-0.57</td>
<td>2-380</td>
<td>5x10⁻⁵-5x10⁻⁴</td>
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<td>Liang et al. (1993)†</td>
<td>YTZP-YTZP</td>
<td>hemispherical pin on disc</td>
<td>0.01</td>
<td>9.8</td>
<td>10⁻⁴</td>
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<td>Krell and Klaffke (1996)</td>
<td>Al₂O₃-YTZP</td>
<td>↔ ball on flat</td>
<td>20Hz</td>
<td>10</td>
<td>2x10⁻⁷</td>
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### Unlubricated Tests

<table>
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<th>Reference</th>
<th>Materials</th>
<th>Contact Conditions</th>
<th>Speed (m s⁻¹)</th>
<th>Load (N)</th>
<th>Wear Coefficient (mm N⁻¹ m⁻³)</th>
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<tbody>
<tr>
<td>Scott (1985)</td>
<td>YTZP-YTZP</td>
<td>↔ hemispherical pin on flat</td>
<td>0.00133</td>
<td>4.9</td>
<td>8.8x10⁻⁹</td>
</tr>
<tr>
<td>Fischer et al. (1987)</td>
<td>YTZP-YTZP</td>
<td>hemispherical pin on disc</td>
<td>10⁻³</td>
<td>9.8</td>
<td>4x10⁻⁷</td>
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<tr>
<td>Ishigaki et al. (1987)</td>
<td>YTZP-YTZP</td>
<td>flat ended pin on disc</td>
<td>0.545-0.41-0.20</td>
<td>5</td>
<td>7x10⁻⁴-5x10⁻³-3x10⁻⁴</td>
</tr>
<tr>
<td>Ajayi and Ludema (1989)†</td>
<td>TZP-TZP</td>
<td>flat ended pin on disc</td>
<td>0.25</td>
<td>13.7</td>
<td>7x10⁻⁴ (pin) 3x10⁻⁴ (pin) 9x10⁻⁴ (flat) 3x10⁻⁴ (flat)</td>
</tr>
<tr>
<td>Fischer et al. (1989)</td>
<td>YTZP-YTZP</td>
<td>hemispherical pin on disc</td>
<td>10⁻³</td>
<td>9.8</td>
<td>4x10⁻⁷</td>
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<tr>
<td>Sasaki (1989)†</td>
<td>YTZP-YTZP</td>
<td>pin on disc</td>
<td>0.4</td>
<td>10</td>
<td>8x10⁻⁴</td>
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<tr>
<td>Stachowiak and Stachowiak (1989)</td>
<td>YTZP-YTZP</td>
<td>↔ flat ended pin on plate</td>
<td>0.08</td>
<td>3.7</td>
<td>1.6x10⁻⁶</td>
</tr>
<tr>
<td>Bundschuh and Zum Gahr (1991)</td>
<td>YTZP-YTZP</td>
<td>block on ring</td>
<td>0.78</td>
<td>10</td>
<td>5x10⁻⁴</td>
</tr>
<tr>
<td>Lee et al. (1993)†</td>
<td>YTZP-YTZP</td>
<td>ball on 3 flats</td>
<td>0.0019-0.57</td>
<td>2-380</td>
<td>5x10⁻⁷-2.5x10⁻⁴</td>
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<tr>
<td>Liang et al. (1993)†</td>
<td>YTZP-YTZP</td>
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<td>0.01</td>
<td>9.8</td>
<td>4x10⁻⁴</td>
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<td>Wang et al. (1993)</td>
<td>YTZP-YTZP</td>
<td>ball on disc</td>
<td>0.0125</td>
<td>17.8</td>
<td>3.68x10⁻³</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>26.7</td>
<td>1.12x10⁻⁵</td>
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<td></td>
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<td></td>
<td></td>
<td>35.6</td>
<td>2.32x10⁻⁵</td>
</tr>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>44.5</td>
<td>2x10⁻⁵</td>
</tr>
<tr>
<td>Zum Gahr et al. (1993)†</td>
<td>YTZP-YTZP</td>
<td>block on ring</td>
<td>0.78</td>
<td>10</td>
<td>4x10⁻⁴-4x10⁻³</td>
</tr>
<tr>
<td></td>
<td></td>
<td>↔ ring on block</td>
<td>0.02</td>
<td>100</td>
<td>6x10⁻⁵-10⁻⁴</td>
</tr>
<tr>
<td>Ajayi et al. (1994)</td>
<td>ZrO₂-ZrO₂</td>
<td>↔ hemispherical pin on flat</td>
<td>0.05</td>
<td>50</td>
<td>3x10⁻⁵</td>
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</table>
Table 6.1 Continued

<table>
<thead>
<tr>
<th>Reference</th>
<th>Materials</th>
<th>Contact Conditions</th>
<th>Speed (m s⁻¹)</th>
<th>Load (N)</th>
<th>Wear Coefficient (mm² N⁻¹ m⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kim, Kim and Hsu (1994)</td>
<td>ZrO₂-ZrO₂</td>
<td>ring on ring</td>
<td>0.02</td>
<td>735</td>
<td>5.6x10⁻⁵</td>
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<td></td>
<td></td>
<td></td>
<td>980</td>
<td>7.1x10⁻⁶</td>
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<tr>
<td>Tucci and Esposito (1994)</td>
<td>YTZP-Al₂O₃</td>
<td>hemispherical alumina pin on disc</td>
<td>0.3</td>
<td>33.47</td>
<td>1.6x10⁻³</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.7</td>
<td>1</td>
<td>1.5x10⁻³</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3</td>
<td>3x10⁻⁴</td>
</tr>
<tr>
<td>Kirkby et al. (1995)</td>
<td>YTZP-YTZP</td>
<td>flat ended pin on disc</td>
<td>0.24</td>
<td>4.8</td>
<td>7x10⁻⁶ - 3.2x10⁻⁶</td>
</tr>
<tr>
<td>He et al. (1996)</td>
<td>SiC-YTZP</td>
<td>↔ sphere on plate</td>
<td>0.08</td>
<td>8</td>
<td>10⁻⁶-8x10⁻⁶</td>
</tr>
<tr>
<td>Krell and Klaffke (1996)</td>
<td>Al₂O₃-YTZP</td>
<td>↔ ball on flat</td>
<td>20Hz</td>
<td>10</td>
<td>2x10⁻⁶-1.5x10⁻⁶</td>
</tr>
<tr>
<td>Adachi et al. (1997)</td>
<td>ZrO₂-ZrO₂</td>
<td>pin on disc</td>
<td>0.01-2.3</td>
<td>2-100</td>
<td>10⁻⁷-10⁻³</td>
</tr>
<tr>
<td>He et al. (1997)</td>
<td>SiC-YTZP</td>
<td>↔ sphere on plate</td>
<td>0.08</td>
<td>8</td>
<td>1.08x10⁻⁶, 5.18x10⁻⁶</td>
</tr>
<tr>
<td>Esposito et al. (1998)</td>
<td>Al₂O₃-YTZP</td>
<td>hemispherical pin on disc</td>
<td>0.3</td>
<td>32.83</td>
<td>2x10⁻⁶</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>0.7</td>
<td>3</td>
<td>3x10⁻⁶</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1</td>
<td>10⁻⁴</td>
</tr>
<tr>
<td>Rainforth and Stevens (1998)</td>
<td>YTZP-ZTA⁺</td>
<td>flat ended pin on disc</td>
<td>0.24</td>
<td>19</td>
<td>1.8 x 10⁻⁴</td>
</tr>
</tbody>
</table>

* Zirconia Toughened Alumina

6.2.2 COMPARISON WITH LITERATURE VALUES

In order to make comparisons between the current work and the literature, it is more convenient to represent the wear coefficient data graphically. Generally, wear tests in the current work have been conducted at much higher sliding speeds than those reported in the literature and this must be borne in mind when comparing values plotted against load. Figures 6.1a and b are plots of the wear coefficients presented in table 6.1 (from the literature) and tables 5.1 and 5.2 (from the current work) obtained under water-lubricated and unlubricated conditions, respectively. Where a range of values is given in table 6.1, upper and lower values are plotted as individual points.
From figure 6.1a, although there are very few literature data points at comparable loads, the trend suggests that the K values from this study are lower than would be expected. In most cases for the current work, these wear coefficients were calculated for the running-in period, before hydrodynamic lubrication started. The loads applied are towards the higher end of the scale compared to those quoted in the literature. This means that the worn volume is divided by a larger load. Although wear was occurring at this stage of the test, it is thought that the surfaces may have been lubricated for some of the time and wore by occasional contacts until the surfaces were sufficiently conformal for full hydrodynamic lubrication to begin. The high speeds used will have helped the water layer to support the high loads and reduce the wear rate. The effect of speed on lubrication is not taken into account by the wear coefficient as speed is simply converted to a total sliding distance. Therefore, during the running-in period, the water has a lubricating effect at the high speed used, but the surfaces are not separated by a fluid film all of the time. The overall effect is more complex than can be described by a wear coefficient alone.

From figure 6.1b it is clear that the values of wear coefficient for unlubricated sliding obtained in the current work agree well with literature values. This is somewhat surprising given that the speeds employed were generally higher and there have been reports of increased wear at high speeds (Woydt and Habig, 1988 and Woydt et al., 1991). It highlights the difficulty in making comparisons by using only wear coefficients. Whether wear is in a severe or mild regime cannot be determined from the wear coefficient alone, although it can provide a useful starting indication. The mechanisms of wear are more readily determined by examination of the worn surfaces and wear debris and these will be discussed further in section 6.3.

In conclusion, the wear coefficient can be a useful parameter to make an initial comparison between wear rates from different tests, but care must be taken to
account for factors that are not included in the wear coefficient calculation, for example the effect of sliding speed. In the water-lubricated case, under conditions of the current work, the high speed causes a degree of lubrication even during the running-in period. Therefore a low wear coefficient is recorded. From the wear coefficients plot, it appears as though a low value is obtained at high loads and this could lead to misinterpretation in the absence of further testing details. In the unlubricated case, the wear coefficient values fit well into the literature values and it is now interesting to examine the wear mechanisms.

6.3 PHENOMENA OBSERVED ON THE WORN SURFACES

6.3.1 INTRODUCTION

The three main features observed on the worn surfaces at various stages in the wear process will be discussed in more detail in the following sections. They are permanent deformation of the surface by smearing and abrasive groove formation, fracture and material removal in flakes (delamination) and a network of cracks parallel and normal to the sliding direction. These features have been observed on worn zirconia surfaces from a wide spectrum of testing conditions, including both water-lubricated and unlubricated conditions. Generally, as the severity of the contact is increased (i.e. increased speed and nominal contact pressure and removal of lubrication), the surface disruption and large scale material removal increases, moving from groove formation to moderate plastic deformation and surface smearing and then to delamination and fracture. The difference in features observed under water-lubricated and unlubricated conditions depend on whether hydrodynamic lubrication was achieved immediately or after running-in, and on the nominal contact pressure and sliding speed. Under certain unlubricated sliding conditions, there are similarities to surfaces worn with water lubrication, for example compare figures 5.22e and 5.27; 5.22f and 5.28b; and 5.23d and 5.30b. The presence of water reduces the severity of the wear mechanism, compared to the
unlubricated case. Similar features are seen under unlubricated conditions to those seen at higher speed and load combinations with water present. Mechanisms of formation of surface features and their contribution to wear will be considered in the following sections. Their interaction and how this leads to the development of a wear mechanism is presented in § 6.5.

6.3.2 ABRASIVE GROOVES/SURFACE SMEARING

Grooves were observed in the worn surfaces of several pins and these varied in width from less than a micrometre (e.g. figures 5.20, 5.21) to several micrometres (e.g. figures 5.29, 5.30a). They tended to be larger under more severe contact conditions. It is possible that the small grooves have been formed by small debris particles or asperities and the larger ones by larger debris particles, before they are broken up in the contact. The debris was examined as described in § 5.5.4 and found to consist of small sub-micrometre particles approximately 0.25-0.5 μm. This corresponds with the size of some of the small grooves formed on the worn surfaces. The mechanism of small groove formation is considered to be associated with mild conditions, because when it is the only observed surface feature, wear rates are low as very little, if any, actual material loss occurs. For example, for flat-ended pins polished in-situ on the rig, no measurable wear occurred and the only surface modification after the wear tests were abrasive grooves. When the contact conditions were more severe and wear occurred, additional features were observed on the surface. These additional features were not observed in isolation and abrasive grooves or surface smearing were always present under these circumstances. It is not surprising, therefore that plastic deformation is the most widely reported observation following sliding wear tests on zirconia.

Plastic deformation or displacement of material in the surface does not necessarily lead to wear if material is not removed. However, repeated plastic
deformation can lead to initiation of fatigue cracks (Amov, 1987 (a)) and the build up of plastic strain may be released by fracture, for example as suggested in the delamination theory of wear (Suh, 1973) which is discussed in § 6.3.3.2. Therefore, although grooves in the surface do not contribute to the wear rate directly, they are the first stage in the process that leads to material removal.

Another surface feature that indicates plastic deformation is smearing, see for example figures 5.23a-c. From figures such as these, it looks as though the silicon carbide surface has caused deformation in the direction of sliding by flattening any roughness on the zirconia surface or debris trapped in the contact. Once again, this does not necessarily cause material removal and contribute to the wear rate, but is likely to contribute to a build up of plastic strain that will eventually lead to fracture. In this way, the features of abrasive grooves and surface smearing are related to surface fracture.

6.3.3 FLAKES OF DELAMINATED MATERIAL

6.3.3.1 Introduction

As mentioned in § 6.3.2, the onset of fracture is related to the amount of deformation in the surface. Fracture is the element of the wear mechanism that causes material removal. In the current work, one form of fracture occurs parallel to the surface, causing the delamination of flakes of material (see figure 5.23d). It is postulated that the surface has been subjected to repeated sliding contact by silicon carbide asperities and debris in the contact and these have caused a permanent deformation of the surface, which is manifested in the form of smeared areas and abrasive grooves. Above a certain critical strain, it is possible that the zirconia will not be able to accommodate this permanent deformation and the plastic strain may be released by fracture. The layer of material under the deformed layer is, at this stage, relatively undamaged. Events such as these can lead to a delamination wear
mechanism for which a theory has been proposed and this will be discussed in
the following section.

6.3.3.2 The Delamination Theory of Wear

The delamination theory of wear was first published in 1973 (Suh, 1973) and
was revised in 1977 (Suh, 1977). In the theory it is proposed that wear occurs
by delamination of flat plate-like wear particles that are formed on sliding due
to crack nucleation and propagation in a layer below the surface. It was based
on metallic materials but can apply to all materials in which sub-surface crack
nucleation and propagation mechanisms are operative. The four stages of the
process are:
1. Surface traction deforms the material plastically. Under repeated loading,
   plastic deformation accumulates.
2. Cracks nucleate within the plastically deformed material beneath the
   surface around inclusions and second phase particles. In single phase
   materials these could be formed by dislocation pile-ups, at grain
   boundaries or twin intersections.
3. Once cracks are present (they may pre-exist), further loading and
   deformation causes them to propagate and coalesce with adjacent ones.
   The cracks tend to propagate parallel to the surface at a depth governed
   by material properties, applied load and the coefficient of friction.
4. The cracks shear to the surface at certain weak positions and long thin
   sheets of material delaminate to form wear particles when the strength of
   the cracked sub-surface layer is less than the shear stress applied at the
   surface.

The high compressive stress from the contact means that cracks would not be
nucleated very near the surface, but at a distance below it. Surface traction
affects the delamination process and it depends on the physical and chemical
nature of the surfaces. It was noted that as the contact loads increased, the
depth at which cracks nucleated was greater. Once the cracks are nucleated (or if there are pre-existing voids), the crack in front of the slider is closed (in compression) while the crack behind the slider is opened since the stress is tensile. This leads to crack extension as an asperity passes.

Although this mechanism was developed for metals, it can apply to ceramic materials as sub-surface crack nucleation and propagation mechanisms are operative, although whether they are initiated solely by plastic deformation is uncertain. Indeed, flaws are likely to exist prior to wear. Dislocations were observed by Rainforth and Stevens (1998) in a region 1-3 μm below the surface of a worn zirconia, some of which had formed loose tangles or pile-ups at grain boundaries. It is possible that dislocation motion and plastic deformation play a part in sub-surface crack initiation, although other factors such as the t→m phase transformation are also important as discussed in the following section.

6.3.3.3 Delamination of Zirconia Reported in the Literature

Several authors have referred to the delamination theory of wear when describing the surface of a worn zirconia (He et al., 1996, Hooper and Morgan, 1989) and some others have observed that the wear occurs by removal of material as delaminated sheets (Stachowiak and Stachowiak, 1989, Wang et al., 1993, Esposito et al., 1998, Ajayi and Ludema, 1987, Tucci and Esposito, 1994 and Bundschuh and Zum Gahr, 1991), which may consist of primary surface, or compressed debris.

Hooper and Morgan (1989) noted that the delamination process observed in grinding PSZ was initiated by plastic deformation and crack nucleation by dislocation interaction in line with the theory of Suh (1973, 1977), although a detailed analysis was not presented. He et al. (1996) observed that for TZPs with a grain size greater than 0.9 μm wear occurs by delamination. Instead of
plastic deformation, they suggested that the stress induced $t\rightarrow m$ transformation occurred at the surface, causing a compressive surface layer, but the development of a tensile stress beneath this layer formed internal stresses in local areas. These internal stresses promote microcrack nucleation at, for example, pores and grain boundaries. They noted that as the degree of $t\rightarrow m$ transformation increases with grain size, so does the wear rate. Stress discontinuity due to phase transformation was also proposed as the mechanism of formation of thin plates by Bundschuh and Zum Gahr (1991). They observed delaminated plate-like wear particles on YTZP specimens of low porosity (0.1%). High porosity (12.4%) resulted in granular wear debris. They suggested that the particles were plastically deformed and fatigue cracked. Fatigue cracks caused by plastic deformation leading to delamination were observed also by Ajayi and Ludema (1987).

Stachowiak and Stachowiak (1989) and Tucci and Esposito (1994) observed deformation of the surface and compaction of wear debris which made up the deformed layer that was removed as flat particles by delamination. Another factor in the removal of delaminated plates of material following plastic deformation was proposed by Esposito et al. (1998) as the propagation of thermal shock cracks resulting from large thermal gradients.

Several authors have reported that wear of zirconia can occur by delamination of material from the surface, causing high wear rates, but there is no one clear mechanism. It appears that the combined effect of contact stresses and pre-existing flaws may lead to sub-surface cracks and eventual delamination, but the mechanism may be further complicated by the $t\rightarrow m$ transformation and cracking due to thermal shock.
6.3.3.4 Observation of Delamination in the Current Work

From scanning electron photomicrographs of the worn zirconia surfaces presented in chapter 5, it appears that some material is removed from the surface as delaminated flakes due to cracks parallel to the surface (see for example figures 5.23d, 5.30a-b, 5.32, 5.33). Cross-sections of the surface have shown shallow cracks parallel to it (figures 5.38 a,b). This delamination is associated with the most severe wear rates. In the water-lubricated case this is at the breakdown of hydrodynamic lubrication and in the unlubricated case it is at the higher end of the load and speed conditions. From the cross-section micrographs, an approximate estimate of the depth of the cracks below the surface is 3 µm, or a few tetragonal grain diameters. It is not clear whether the delaminating material is deformed debris reattached to the surface, or deformed primary surface. In some cases it appears to cover a large portion of the pin surface (figure 5.34), and in others it appears as isolated islands of material (figure 5.28a). The removal of material continues with time and it may be that these two figures are taken at different stages of the removal cycle, and so different proportions of the surface layer have been removed. It is possible that a combination of reattached debris and deformed primary surface are removed by delamination. The surface layer was removed by an acetate peeling technique as described in § 3.4.4 and observations from the transmission electron microscopy are discussed in § 6.3.5.

The observed mechanism of material removal in the current work is consistent with the delamination theory of wear. The cracks may be formed due to plastic deformation at the surface, such that and at a certain point, no more plastic strain can be accommodated, and fracture ensues. The applied stress involves tensile and shear components, as well as compressive forces, which will enhance delamination crack propagation. It would seem to be most likely that a combination of mechanical, thermal and, potentially, transformation stresses are the cause of the delamination. If the $t \rightarrow m$ transformation
occurred at the surface during the test, it is likely that the delamination crack would form at the boundary between transformed and untransformed material, due to the discontinuity in stress. The depth of the delaminated layer in the current work is approximately 3 μm (§ 5.5.2). Garvie et al. (1982) measured the transformation depth from fracture surfaces of Mg and Ca PSZ to be 0.4-4.2 μm. For Y$_2$O$_3$ stabilised zirconia the transformation depths were between 1.5 and 1.7 μm (Kosmac et al., 1981). These depths are of the same order of magnitude as the depth of delamination cracks in the current work. If these cracks form at the boundary between transformed and untransformed material, then the layer of delaminated material should contain a substantial proportion of monoclinic phase.

6.3.4 NETWORK OF CRACKS

6.3.4.1 Introduction

A feature that has been observed on many of the worn zirconia surfaces is an approximately rectangular network of cracks that intersect the surface and are parallel and normal to the sliding direction (see for example, figure 5.22c). It is not clear at what stage in the process they form, but they can be seen at the surface and below a layer of delaminated material (for example figure 5.30b). From this it appears possible that they are formed before delamination cracks form and the surface layer has been removed. These crack networks may or may not lead to material removal, and so contribute to the wear mechanism, depending on whether they link up with any cracks that have formed parallel to the worn surface. This cracking has been tentatively assigned to be due to thermal shock and in the following section similar observations from the literature are described. This is followed by an estimate of temperatures generated by the sliding interface and a discussion on the relative susceptibility of zirconia and silicon carbide to thermal shock.
6.3.4.2 Similar Features Observed in the Literature

This type of cracking, in a network parallel and normal to the sliding direction, has been detected by other workers. For example, Breznak et al. (1985), Dufrane (1986), Dufrane and Glaeser (1987), Dufrane (1989), Chen (1990), Woydt et al. (1991), Ravikiran and Pramila Bai (1995) and Tucci and Esposito (1994), all observed similar cracking in various zirconia samples, and Esposito et al. (1998) saw this phenomenon in zirconia toughened alumina. Most of these workers assigned this damage to thermal shock, with various hypotheses as to why this should be the case.

Dufrane (1986), Dufrane and Glaeser (1987) and Dufrane (1989) presented micrographs of worn zirconia (MgPSZ and YTZP) surfaces which showed cracks very similar to those observed in the current work (see for example figure 2.8). It was suggested that these cracks were associated with hot spots caused by thermo-elastic instability (as discussed in § 2.3.2.3). This occurs when frictional heat causes local areas of the surface to expand. They therefore carry a higher proportion of the load. If heat in these areas is not dissipated fast enough, they continue to expand and so carry most of the load. These areas are then subjected to wear, and regress such that other, adjacent regions become hotter. It was thought that the temperatures generated were sufficient to cause thermal shock and this resulted in the crack network and spalling.

The worn surfaces of self-mated MgPSZ presented by Woydt and co-workers (Woydt and Habig, 1988, Woydt and Habig, 1989 and Woydt et al., 1991) contain cracks of a similar nature to those observed in the current work. In this case they were attributed to surface stresses caused by all monoclinic and tetragonal phases transforming to cubic due to hot-spot temperatures (up to 2200 °C) and micro-asperity pressures (up to 60 GPa). So although the authors recognised that temperature plays a part in the crack formation, their
opinion was that it caused the m→c and t→c phase transformations and the cracking is not strictly due to thermal shock. Chen et al. (1990) also presented a worn surface containing cracking similar to that observed here and they too attributed it to the t→c phase transformation caused by the increase in surface temperature.

Ravikiran and Pramila Bai (1995) also presented similar micrographs showing this type of cracking. They attributed it to thermal shock or tensile cracking and suggested that flat plate-like wear particles were formed when these cracks link up.

From the micrographs in the literature, approximate estimates of the spacing between cracks can be made and these are given in Table 6.2. The values in the table are only approximate as they have been estimated from one or two published micrographs, but they are of the same order of magnitude as those observed in the current work and so potentially caused by a similar mechanism. The notion that these cracks are due to thermal shock will be investigated in more detail in the following discussion.

Table 6.2 Spacings of crack networks in the literature

<table>
<thead>
<tr>
<th>Reference</th>
<th>Materials</th>
<th>Lubrication</th>
<th>Contact Severity</th>
<th>Speed</th>
<th>Crack spacing (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dufrane (1986)</td>
<td>YTZP-YTZP</td>
<td>mineral oil</td>
<td>9 N/mm</td>
<td>500-1000 rpm</td>
<td>~60</td>
</tr>
<tr>
<td>Dufrane and Glaeser (1987)</td>
<td>MgPSZ-MgPSZ</td>
<td>mineral oil</td>
<td>9-25 N/mm</td>
<td>500-1000 rpm</td>
<td>~40</td>
</tr>
<tr>
<td>Ravikiran and Pramila Bai</td>
<td>YTZP-steel</td>
<td>none</td>
<td>15.5 MPa</td>
<td>4 m s⁻¹</td>
<td>~30</td>
</tr>
<tr>
<td>Current Work</td>
<td>YTZP-SiC</td>
<td>water/none</td>
<td>2.1-70 MPa</td>
<td>1-6 m s⁻¹</td>
<td>20-40</td>
</tr>
</tbody>
</table>
In order to explore the hypothesis that thermal shock was the cause of severe wear, the method of Dufrane (1986) is adopted as discussed in § 2.3.2.3. The value of $v_{cr}$ (from equation 2.3), the critical velocity to cause thermo-elastic instability, for the current work is calculated and estimates are presented in table 6.3. The experimental variables in this model are the coefficient of friction and the width of the slider. In the current work, however, the coefficient of friction was not measured, but $v_{cr}$ can be calculated for a range of $\mu$ values. The effect of hydrodynamic lubrication would be to decrease the coefficient of friction. A typical value for $\mu$ under conditions of hydrodynamic lubrication is 0.01 (Dufrane, 1986). The critical velocity is then increased considerably, compared to when there is no hydrodynamic lubrication, although it is still below speeds used in some experiments in the current study. The silicon carbide counterface has a lower thermal expansion coefficient and higher thermal diffusivity and conductivity than the TZP, and using the properties of SiC in equation 2.3, critical velocities to induce thermal shock damage on the SiC surface can be calculated.

Table 6.3 $v_{cr}$ values for different contact conditions

<table>
<thead>
<tr>
<th>Materials</th>
<th>$\mu$</th>
<th>$v_{cr}$ (m s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>YTZP 0.85</td>
<td>0.85</td>
<td>0.00068</td>
</tr>
<tr>
<td>YTZP 0.5</td>
<td>0.5</td>
<td>0.00196</td>
</tr>
<tr>
<td>YTZP 0.01</td>
<td>0.01</td>
<td>4.89</td>
</tr>
<tr>
<td>SiC (RT props)</td>
<td>0.85</td>
<td>0.056</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>0.16</td>
</tr>
<tr>
<td></td>
<td>0.01</td>
<td>407.6</td>
</tr>
<tr>
<td>SiC (400°C props)</td>
<td>0.85</td>
<td>0.035</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>0.10</td>
</tr>
<tr>
<td></td>
<td>0.01</td>
<td>251.6</td>
</tr>
</tbody>
</table>

According to this model, all of the experiments conducted under unlubricated conditions in the present study are above the critical velocity for zirconia and so the pins are susceptible to thermal shock. Under conditions of hydrodynamic lubrication the coefficient of friction will be of the order of 0.01 and according to the model $v_{cr}$ is 4.89 m s$^{-1}$. However, if hydrodynamic
lubrication is achieved, the surfaces are not in contact and so thermal shock will not be a problem until contact occurs and the model is limited in this respect. Once surface contact occurs, the coefficient of friction will rise. The lubricative and cooling effects of the lubricant are not covered by the model. The values of $v_{cr}$ for silicon carbide indicate that it would also be susceptible to thermal shock under conditions of some of tests in the current study. However, the critical velocity is two orders of magnitude lower than for the zirconia and so the silicon carbide is far less likely to suffer from thermal shock. The critical velocity model does not give an accurate prediction of the velocity at which a material is likely to be susceptible to thermal shock due to thermo-elastic instability, but indicates a relative order of merit. In the current work, some of the worn zirconia surfaces did contain networks of cracks, with no evidence of them on the silicon carbide surface.

This concept provides a useful starting point for estimating whether certain experimental conditions will lead to severe wear by thermal shock, although the effect of a lubricant will be more significant to thermal shock than merely reducing the coefficient of friction.

### 6.3.4.3 Estimation of Temperatures Generated by Sliding

In order to investigate whether the materials had been subjected to thermal shock conditions during the wear tests, it was useful to have an estimate of the temperatures generated at the interface and a computer program was used for this purpose. In order to calculate temperatures, several approximations were made and so the values are only estimates. However, the values compare well with other estimates from the literature (§ 6.3.4.4).

When two surfaces in contact slide against each other, work is done against friction. Almost all of the energy appears as heat, generated at the surfaces. This leads to a local increase in temperature which influences the friction and
the wear rate. There are two temperatures of interest, the bulk surface temperature, $T_b$, and the local flash temperature, $T_f$. The bulk surface temperature is the surface temperature that would be reached if the frictional heat was injected uniformly across the nominal contact area. It is a good estimate of the temperature a few tens of micrometres below the actual surface. The flash temperature is higher than the bulk temperature, because in reality, the heat enters the surface at the small asperities where contact is actually made. These temperatures are of interest because the wear mechanisms when the surfaces are hot are different to when they are cold, due to the effect of temperature on material properties and chemical reactions as well as the possibility of thermal shock fracture.

Approximate estimates of the flash and bulk temperatures generated during the unlubricated tests in the current work were made with the computer program 'T-Maps version 4.0' by Ashby et al. (1992). The results of the computed calculations are presented as temperature maps in the program, showing temperature contours for different values of sliding velocity and load. Temperature values were read off these maps for certain load and speed combinations in order to present them in tabular form in the current work.

In order to obtain estimates of temperatures generated using the computer program, several assumptions were needed, both about material properties and contact conditions. For example, heat diffusion distances, from the interface to the heat sink, which are modified by poor thermal contact with the sink are only estimates. In the current work, the heat sinks for the pin and disc are the drill chuck and the lathe. The pin is in constant contact with the disc for a test interval and so heat flow into it will reach a steady state, whereas heat flow into the disc is nearly always transient as new, cold material comes into contact with the pin as the disc rotates. This will have an effect on the effective heat diffusion distance. The coefficient of friction was required by the program, but was not measured in the current work. Typical unlubricated
values from the literature are in the range 0.2-1 (Breznak et al., 1985 and Amin and Nag, 1995).

As it was necessary to make approximations for some input variables, the output can only be thought of as approximate and the method was not refined many times. The thermal conductivity of silicon carbide decreases with increasing temperature and a value at 200 °C was used initially.

Some of the results from the program are presented in table 6.4 for two extreme values of coefficient of friction. Bulk temperatures are given first and flash temperatures are in brackets.

Altering the value for thermal conductivity of silicon carbide to its 400 °C value of 77.5 W m⁻¹ K⁻¹ raises the bulk and flash temperatures at 6 m s⁻¹ and 14 MPa to ~130 °C and 1700 °C respectively and at 6 m s⁻¹ and 70 MPa to 520 °C and 1950 °C (for μ=1.0). Values were calculated at 70 MPa and 6 m s⁻¹ for comparison, although in reality these tests were water-lubricated which would reduce the temperature.

**Table 6.4 Temperatures calculated by T-Maps 4.0 (Ashby et al., 1992)**

<table>
<thead>
<tr>
<th>Pressure (MPa)</th>
<th>Speed (m s⁻¹)</th>
<th>Bulk Temperature (°C)</th>
<th>Flash Temperature (°C)</th>
</tr>
</thead>
<tbody>
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<td>2.1</td>
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<tr>
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<td>&lt;50 (170)</td>
<td>&lt;50 (300)</td>
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<tr>
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<td></td>
<td>2</td>
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<td>&lt;50 (300)</td>
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<td>70</td>
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<td>&lt;50 (180)</td>
<td>&lt;50 (300)</td>
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<table>
<thead>
<tr>
<th>Pressure (MPa)</th>
<th>Speed (m s⁻¹)</th>
<th>Bulk Temperature (°C)</th>
<th>Flash Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
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<thead>
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<th>Flash Temperature (°C)</th>
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<td>&lt;50 (275)</td>
<td>&lt;50 (500)</td>
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</tbody>
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<tr>
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<th>Bulk Temperature (°C)</th>
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</tr>
</thead>
<tbody>
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<tr>
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<tr>
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<td>14</td>
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<td>&lt;50 (275)</td>
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</tr>
<tr>
<td>70</td>
<td></td>
<td>&lt;50 (275)</td>
<td>&lt;50 (500)</td>
</tr>
</tbody>
</table>

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It is apparent from the above discussion that these are only approximate estimates of the bulk and flash temperatures reached during unlubricated sliding, but they give a first indication of the temperatures that could be attained. They compare reasonably well with some values in the literature, reported in the next section, and experimental observations. After unlubricated tests, the discs were too hot to touch and thus had probably attained a temperature of the same order of magnitude as those predicted.

6.3.4.4 Reported Estimates of Temperatures Generated During Sliding

Estimates of actual bulk and flash temperature rises in the literature are rare, although several authors refer to thermal shock as part of the wear mechanism. Some of the estimates that are available are presented below. Estimates can be made by using heat generation equations and various approximations, by analysing observed microstructural changes, or by direct measurement at a distance away from the sliding interface and all of these methods are covered in the literature.

Lee et al. (1993) suggested that the flash temperature rise at an asperity tip could be 500-800 °C depending on the speed and load conditions. They noted that at high speeds the asperity flash temperature is a significant factor and that thermal shock induced brittle fracture may be a cause of wear. They noted that under water-lubricated conditions, excess heat build-up at the interface is prevented. Liang et al. (1993) estimated the maximum flash temperatures to be 60 °C at sliding speeds of 1 cm s⁻¹ and loads up to 44.5 N. Woydt et al. (1991) calculated the flash temperature for a self-mated MgPSZ couple as a function of speed and load for a contact area of 0.1 mm² and 10 micro-contacts. For a load of 10 N and a speed of 3 m s⁻¹, the flash temperature was calculated to be 2200 °C above ambient. Griffioen et al. (1985) measured the flash temperature generated during unlubricated sliding
of sapphire and silicon nitride to be up to 2700 °C concentrated in areas of 100 μm in diameter for sliding speeds of 1.53 m s⁻¹ and loads of 8.9 N. The bulk pin temperature was 96 °C, measured with a thermocouple 1 mm from the contact face. Breznak et al. (1985) measured the bulk temperature of 3Y-TZP sliding unlubricated and self-mated to be up to 327 °C for a flat on flat sample configuration after about 15 minutes of operation.

Birkby et al. (1995) noted that high interface temperatures lead to thermal shock cracking similar to that caused by thermo-elastic instability and suggested that the frictional heating would have been sufficient to cause flash temperatures in excess of 2000 °C. Rainforth and Stevens (1998) found no evidence of melting at the surface (melting would have resulted in wear debris with a rounded morphology) and concluded therefore the surface temperature was <1900 °C. No microstructural change was observed to have occurred at a depth of >10 μm, and so they suggested a reasonable upper limit on temperature at this depth to be 1600 °C.

Chen et al. (1990) measured the bulk temperature 1 mm from the sliding interface of PSZ on steel and found it to be 50 °C at a sliding speed of 10 m s⁻¹ and a load of 5 N, and noted that the surface temperature would be considerably higher due to the low thermal conductivity of zirconia. They analysed wear debris and found it to consist only of cubic phase, indicating a high interface temperature.

From the preceding discussion and the approximate calculation of temperatures generated under the conditions of the current work it appears likely that very high flash temperatures are generated during unlubricated sliding. The effect of water in the contact, as well as providing lubrication, will be to contribute to heat dissipation so reducing the likelihood of thermal shock. The susceptibility of zirconia to thermal shock will be discussed in the following section.
6.3.4.5 Susceptibility to Thermal Shock

From the previous section, it appears that high temperatures are generated at the sliding interface, particularly at high speeds. The effect of these temperatures on a material will depend on its resistance to thermal shock which will be explored in this section for zirconia and silicon carbide in order to investigate whether it is reasonable to expect to see thermal shock cracks on the silicon carbide surface as well.

Thermal shock refers to the thermal stresses developed in a component as a result of a temperature difference between the surface and interior of a component, or between various regions of the component. Thermal shock failure usually occurs on cooling since the more rapidly cooled surface develops a tensile stress relative to the interior. Thermal shock resistance is an important property for ceramics in applications involving sliding wear contact as high temperatures can be generated.

Thermal shock resistance, like fracture, can be divided into two parts: resistance to crack initiation and resistance to crack propagation. The two parts have different material property requirements. For engineering ceramics, thermal shock resistance parameters usually describe the resistance of a material to crack initiation under thermal shock conditions. Fracture initiation occurs when the level of stress in a body reaches the failure stress. So a material with a high thermal shock resistance will have properties which keep the thermal stress induced to a minimum. In general, this requires materials with low elastic modulus and thermal expansion coefficient, with high tensile strength, thermal conductivity and thermal diffusivity. For resistance to crack propagation, materials should have high Young's modulus and low strength. This is in direct opposition to the requirements for crack initiation.
Chapter 6: Discussion

Thermal stresses arise in a component when it is constrained and heated or cooled, and generally if a thermal gradient exists in an unconstrained body. In the case of an infinitely fast quench, a maximum tensile stress develops at the surface as it is constrained from contracting by the bulk. The maximum stress develops when the temperature of the surface of the specimen reaches that of the quenching medium instantaneously and the centre of the specimen does not have time to conduct any heat away. The magnitude of this stress is given by:

\[ \sigma_{ts} = \frac{E\alpha \Delta T}{(1-\nu)} \]  \hspace{1cm} (6.1)

where \( \sigma_{ts} \) is the thermally generated tensile stress at the surface, \( E \) is Young's modulus, \( \alpha \) is the coefficient of thermal expansion, \( \nu \) is Poisson's ratio and \( \Delta T \) is the temperature difference. This is the maximum thermal stress that can be produced by quenching.

As well as sudden changes in temperature, a steady rate of temperature change can also lead to temperature gradients and thermal stresses, because the thermal conductivity is finite. For example when a plate is cooled at a constant rate, the surfaces are at a lower temperature than the average temperature of the body and are thus in tension. This results in a temperature distribution in the body. Because ceramics are weaker in tension than in compression, failure under these conditions of constant heating and cooling occurs at the surface during cooling. The maximum stresses occur at the surface and at the centre.

For more complicated (practical) heating and cooling conditions, it is important to consider the surface heat transfer coefficient of the system, \( h \), and the thermal conductivity of the material, \( k_{th} \). A useful ratio involving these parameters is the Biot modulus, \( \beta \):

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where \( b \) is a characteristic specimen dimension (e.g. component half-width). The Biot modulus represents the severity of the shock, hence a high Biot modulus is indicative of a severe shock. So, for example, using a material with a higher thermal conductivity would decrease the susceptibility to thermal shock (everything else being equal). Decreasing the surface heat transfer coefficient, so decreasing the rate of cooling at the surface, will also decrease \( \beta \) and so the stress in the material will be reduced, compared to an infinitely fast quench. The stress in the material compared to the maximum stress achievable (i.e. with an infinitely fast quench), is reduced by a stress reduction factor, \( \psi \), equation 6.3.

\[
\psi = \frac{\sigma_{\text{real}}}{\sigma_{\text{max}}} \tag{6.3}
\]

i.e.

\[
\sigma_{\text{real}} = \frac{\psi E \alpha \Delta T}{(1 - v)} \tag{6.4}
\]

The amount the stress is reduced by depends on \( \beta \), although the relationship between \( \beta \) and \( \psi \) is not straightforward. The resistance of a material to thermal shock damage can therefore be expressed in terms of a combination of these properties. Hasselman (1970) has defined thermal stress resistance parameters for various heat transfer conditions and conditions of crack initiation versus crack growth. Some of these are given in table 6.5.
Table 6.5 Thermal stress resistance parameters (after Hasselman, 1970).

<table>
<thead>
<tr>
<th>Parameter designation</th>
<th>Parameter type</th>
<th>Parameter</th>
<th>Thermal environment. The appropriate parameter is used to compare:</th>
</tr>
</thead>
<tbody>
<tr>
<td>R</td>
<td>Resistance to fracture initiation</td>
<td>( \frac{\sigma_f (1 - \nu)}{E\alpha} )</td>
<td>Maximum ( \Delta T ) allowable for steady heat flow</td>
</tr>
<tr>
<td>R'</td>
<td>Resistance to fracture initiation</td>
<td>( \frac{\sigma_f (1 - \nu) k_m}{E\alpha} )</td>
<td>Maximum heat flux for steady flow</td>
</tr>
<tr>
<td>R''</td>
<td>Resistance to fracture initiation</td>
<td>( \frac{\sigma_f (1 - \nu) k}{E\alpha} )</td>
<td>Maximum allowable rate of surface heating</td>
</tr>
<tr>
<td>R'''</td>
<td>Resistance to propagation damage</td>
<td>( \frac{E}{\alpha (1 - \nu)} )</td>
<td>Minimum in elastic energy at fracture available for crack propagation</td>
</tr>
<tr>
<td>R''''</td>
<td>Resistance to propagation damage</td>
<td>( \frac{E_Y}{\sigma_f^2 (1 - \nu)} )</td>
<td>Minimum in extent of crack propagation on initiation of thermal stress fracture</td>
</tr>
<tr>
<td>R_{sl}</td>
<td>Resistance to further crack propagation</td>
<td>( \left( \frac{\gamma}{E\alpha} \right)^2 )</td>
<td>Maximum ( \Delta T ) allowed for propagating long cracks</td>
</tr>
</tbody>
</table>

In comparing materials resistance to thermal shock, calculation of the appropriate thermal shock resistance parameter can be useful. The value of the relative thermal shock resistance parameter changes significantly, depending on which parameter is specified. Parameter R relates to very rapid quenches. It expresses the maximum temperature drop that a body can withstand. The parameter R' is simply the product of R and the thermal conductivity of the material. It is a more complex parameter than the first, and also more useful because it relates to a more widespread range of practical conditions and is a useful figure of merit. Some values are given in table 6.6.

Note that for zirconia, the tensile strength will depend whether the region arresting a crack is at a sufficiently low temperature for transformation to occur (in addition to particle size effects etc.). Using the suppliers data for strength at 800 °C gives R as 92 °C.
Table 6.6  Thermal shock resistance parameters for some common ceramic materials.

<table>
<thead>
<tr>
<th>Material</th>
<th>YTZP†</th>
<th>SIC†</th>
<th>Al₂O₃‡</th>
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</thead>
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<tr>
<td>E (GPa)</td>
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<td>410</td>
<td>379*</td>
</tr>
<tr>
<td>α (x10⁻⁶ K⁻¹)</td>
<td>10</td>
<td>4.02</td>
<td>7.4*</td>
</tr>
<tr>
<td>σ (MPa)</td>
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<td>460</td>
<td>344.5*</td>
</tr>
<tr>
<td>ν</td>
<td>0.3</td>
<td>0.14</td>
<td>0.22*</td>
</tr>
<tr>
<td>kₘ (W m⁻² K⁻¹)</td>
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<td>125.8 (RT)</td>
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<tr>
<td>κ (m² s⁻¹)</td>
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<td>6 x 10⁻⁵</td>
<td>9.2 x 10⁻⁸</td>
</tr>
<tr>
<td>R (K)</td>
<td>476</td>
<td>240</td>
<td>96</td>
</tr>
<tr>
<td>R' (W m⁻¹)</td>
<td>956</td>
<td>30144</td>
<td>2779</td>
</tr>
<tr>
<td>R'' (K m² s⁻¹)</td>
<td>4 x 10⁻⁴</td>
<td>0.015</td>
<td>8.8 x 10⁻⁴</td>
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* calculated from κ=κₒ/ρx
† suppliers data
‡ Richerson (1982)

Comparing the R' thermal shock resistance parameter of the materials reveals that zirconia is much more susceptible to thermal shock than silicon carbide or alumina, even when its room temperature strength is used. The susceptibility to thermal shock will also depend on the size of the component. In the current situation, the disc is much larger than the pin, but heat is only generated over a small fraction of the surface. This, combined with the higher resistance to thermal shock of silicon carbide means that although it is part of the same sliding couple and therefore subjected to the same interfacial temperatures, thermal shock cracks will not necessarily be initiated in the silicon carbide, even if they are in the zirconia. In the current work, no crack networks were observed on the silicon carbide surface. Only on one occasion, following an unlubricated test, was a large crack observed in the disc which was thought to be caused by thermal shock. Under the more severe of the unlubricated conditions in the current work, some of the pins were found to have broken in the rig at the end of a test interval. This could be due to thermal shock if the bulk temperature of the pin was sufficient to cause thermal shock cracking on removing the pin from the sliding contact due to rapid cooling. From this analysis, it seems that the temperatures generated at the interface are sufficient to cause thermal shock in the zirconia, in the case of unlubricated sliding but are not sufficient to cause cracks in the silicon carbide. The crack
networks were observed on water-lubricated worn pins as well, although the magnitude of the effect of water on flash temperature generation is not known.

In order to investigate further whether the surface cracks observed after wear were due to thermal shock, the side edges of some pins were examined by electron microscopy. If the cracks were due to thermal shock because of a large thermal gradient, they might be observed at the edge near the sliding surface, as well as actually on it. From § 5.5.2 the cracks were expected to be of the order of 40 μm long and the area this close to the surface was examined. However, no evidence of cracking was seen on the curved face of the pins, close to the sliding surface.

The thermal shock behaviour was investigated further by rapid quenching into water at room temperature after heating. Two heating methods were employed: a hot plate and a bunsen burner. The hot plate temperature was measured by a thermocouple to be 234 °C. The pin was placed with its flat face in contact with the hot surface and left for approximately 2 minutes. It was then rapidly removed and quenched in water at 18 °C (ΔT=216 °C). The surface was subsequently examined using both reflected light and scanning electron microscopy. No evidence of surface cracking was found. The end of another pin was held in the hot part of a bunsen flame (approximately 850 °C) for approximately 1 minute, by which time the end was glowing orange/red. It was then quenched in water and examined as before. The surface contained a random network of several large cracks, typical of those seen in ceramics quenched in this type of experiment. Therefore zirconia is susceptible to thermal shock under these conditions, when ΔT is approximately 832 °C, but the thermal environment is different under conditions of sliding wear, with fluctuating temperatures generated from contacting asperities on a smaller scale than this experiment. Perhaps this could explain why the cracks observed after sliding were smaller than those observed after the quenching experiment. From the temperature estimates and the known susceptibility of
zirconia to thermal shock, it is possible that the asperity flash temperatures cause a local 'small scale' thermal shock. When an asperity is in contact, its temperature rises and causes thermal expansion. When another asperity in a different area of the pin surface becomes load bearing, due to wear of the original asperity, the area close to the original contacting asperity is no longer in contact and cools to the bulk temperature. This is one possibility for thermal shock crack initiation and it depends on the difference between the flash and bulk temperatures being sufficient to cause thermal shock as the pin is in contact with the disc for all of each test interval. Another possibility for the crack formation is when the test ends and the pin is removed from the disc. This was the case in all tests; the pin was removed from the rotating disc, rather than allowing the disc to stop before removing the pin. This will have caused a sudden cooling of the hot surface. In the unlubricated case, the surface was cooled by air, and for the water-lubricated case by water. This is similar to a quenching experiment on the surface of the pin. However, the observation of the crack network below the delaminated layer seems to suggest that it was formed before delamination occurred and so was not formed by macro-thermal shock at the end of a testing interval, but during the period when the pin is in contact with the disc.

Despite these arguments, it would appear difficult to offer conclusive proof that these cracks are due solely to thermal shock. The pattern of the cracks is, in most cases, very regular. This is in common with literature findings. This periodic nature suggests that the tensile component of the contact stress may be playing a part. It must be noted that although these cracks are on the pin specimen which is in continuous contact for the duration of each test interval, different asperities on the pin surface will be in contact as the test proceeds, so each area of the pin will see changing contact conditions. Tensile stresses will therefore exist on the pin surface during sliding, behind the contacting asperities.
Chapter 6: Discussion

The cracking is likely to be due to a combination of local thermal shock (perhaps enhanced at the end of each test interval by removal of the pin from the disc), reduced toughness due to the non-operation of the transformation toughening mechanism at the high induced surface temperatures, and tensile stresses induced by the contact.

6.3.5 Near-Surface Microstructural Changes

In section 5.5.4 a brief description of the TEM study was presented. By comparing these observations to those of other workers, notably Rainforth and co-workers, who have conducted more detailed TEM studies, conclusions can be drawn on mechanisms and microstructural change. To re-cap the observations in the current work from § 5.5.4, a TEM specimen from the worn surface revealed microcracks and twin formation within grains. This confirms that some transformation to the monoclinic phase occurred. The exact depth below the surface from which the sample came is unknown, but it was back-thinned (i.e. from one side only) and so should come from very close to the surface. Back thinning was also used by Rainforth (1996) to examine a 3YTZP surface worn against a steel disc and he observed occasional transformation to monoclinic. Most of the grains, however, were tetragonal exhibiting residual strain effects. In the current work, several grains contained twins and the sample also contained cracks, although it is not possible to say whether they were formed during wear, or in making the TEM sample.

The outer worn near surface region, removed using acetate (and likely to have been removed by fracture along delamination cracks), was likely to have come from nearer the surface than the cut-off surface sample. The layer of delaminated material was approximately 3 μm thick and it is suggested that this is what was removed by the acetate. In making the cut-off surface sample, it is possible that the delaminated layer became detached (for example during dimpling), so the observations made of this sample were from
a greater depth than the acetate removed sample. The sample removed by acetate revealed a very fine crystallite size (of the order of 10-30 nm). The formation of small crystallites has been observed by other workers. Rainforth and Stevens (1998) observed fine equiaxed tetragonal grains formed in a YTZP. Their grain size was approximately 50 nm although it tended to decrease towards the surface and it seemed likely that microcrack coalescence was the formation mechanism as microcracks were observed along grain boundaries. In a region below the small grains, elongated tetragonal grains were observed by the authors and it is interesting to note that the small grain size was similar to the minimum thickness of the elongated grains. In the current work, the TEM study was not so extensive and no dislocations were observed, so the mechanism of intragranular microcrack coalescence is not contradicted and could have caused the grain size reduction.

Analysis of debris collected from the wear track and surrounding area of the disc revealed that it consisted of small, sub-micrometre particles (0.25-0.5 μm). A spotty ring type diffraction pattern revealed that they were crystalline, but resolution of the phase was not possible.

Breval et al. (1986) found similar 5-50 nm size wear debris particles after sliding YTZP against itself, and 1 μm size (and occasionally smaller) particles after sliding YTZP on SiC. They found these particles to be exclusively tetragonal by electron diffraction with no evidence of SiC in the debris. Birkby et al. (1995) however, found that electron diffraction revealed the small crystalline wear debris from YTZP to be monoclinic although a significant amount of tetragonal phase was detected by X-ray diffraction. This apparent discrepancy was attributed to the difference in size distribution of tetragonal and monoclinic wear debris. X-ray diffraction will only generate discrete peaks if the particle size is ~50 nm or greater while electron diffraction can generate characteristic patterns from crystals an order of magnitude smaller.
Microcrystalline wear debris with a grain size of the order 50-100 nm was also reported by Rainforth et al. (1989) for a YTZP worn against ZTA. This was attributed to recrystallisation indicating a large temperature rise at the interface, which also led to some of the debris being amorphous. No amorphous debris was found in the current work, and a high dislocation density is required to drive a recrystallisation mechanism, which was not observed.

It is possible that the wear debris was formed by delamination of sheets of material as described in § 6.3.3.2 and then subsequently crushed in the contact to form the small particles observed on the TEM. Whether any subsequent recrystallisation occurred is uncertain but cannot be ruled out, due to the high interfacial temperatures.

6.4 DISC WEAR

The silicon carbide disc wear was not measured for each test. This was because the accuracy of the balance was reduced as the mass of the disc was over 100 g and at this level, no wear was recorded. The surface was examined following testing and found not to have undergone a severe wear mechanism. The main features on the worn disc surface, as mentioned in § 5.5.3, were grooves, transferred zirconia in holes in the disc surface and a grain relief which was revealed by examining the disc in a reflected light microscope using differential interference contrast.

There are two sizes of grooves in the surface of the silicon carbide (see figure 5.42). Small, sub-micrometre sized grooves are likely to be caused by loose debris in the contact (for example figure 5.39) as their size corresponds to the 0.25-0.5 μm debris observed (described in § 5.5.4). Larger ridges and troughs are likely to be caused by larger debris particles removed from the zirconia pin. No evidence of silicon carbide was found on the pin surfaces and so it is likely
that these grooves were caused by ploughing or plastic deformation. Some of the debris causing the grooves subsequently became trapped in the holes in the disc surface (for example figure 5.40).

The grain relief (figures 5.43a and b) showed that adjacent grains had worn by different amounts, as revealed by their height difference shown by differential interference microscopy. This type of grain relief has been observed in ceramic materials before. For example Scott (1985) noted the anisotropy of wear as a function of crystal orientation in an MgPSZ. The reason for this anisotropy could be due to the difference in relative ease of plastic deformation on different crystal planes and in different directions as, for example, in alumina (Hockey, 1971, 1972). Rainforth (1996) observed differential wear in adjacent grains of MgPSZ worn against steel. In this case the wear mechanism was tribochemical involving dissolution of zirconia into the iron oxide transfer layer. He attributed the grain relief to variation in tribochemical reaction rates as a function of crystallographic orientation.

In the current work no evidence of chemical reaction between the zirconia and silicon carbide was found and so it is more likely that the anisotropic wear behaviour is due to differences in mechanical properties and likelihood of plastic deformation compared to fracture with crystal orientation.

6.5 WEAR MECHANISM MODEL

6.5.1 INTRODUCTION

Following on from the discussion in the previous sections, a wear mechanism is proposed which operates under both water-lubricated and unlubricated contact conditions. The extent of each aspect of the mechanism depends upon the nominal contact pressure, the speed and the lubrication regime. The model describes qualitatively what happens to the surface as wear proceeds. Such a model is useful in that it describes the events that lead to material
removal. A fundamental understanding at this level can then be applied to sliding wear of zirconia under different conditions by considering the likely effect of changing testing conditions on each event that makes up the wear process.

### 6.5.2 Wear Mechanism

It is suggested that the following events occur in the surface of the zirconia which lead to material displacement and removal and therefore wear. If hydrodynamic lubrication is achieved, there is no further asperity-asperity contact and therefore no more wear. However, during running-in, or if the lubrication regime is broken down, the events that occur in the surface are similar to those that occur in unlubricated tests, at lower nominal contact pressures and speeds. This is because the presence of water in the contact is likely to reduce the interfacial temperatures and therefore the thermal shock in the surface, and may also affect the stress distribution in the contact.

A schematic illustration of the possible sequence of events leading to the observed surface features is given in figure 6.2. Upon asperity-asperity contact, the surface is placed under a large compressive stress locally and undergoes plastic deformation which manifests itself as grooves and smearing. In the current work, these grooves varied in size, from sub-micrometre to several micrometres. The repeated plastic deformation leads to the build up of strain which reaches a limit that can no longer be accommodated by the material. This results in cracking which is parallel to the surface and at a depth of approximately 3 micrometres. This mechanism may be further complicated by mechanically or thermally induced phase transformations. A tensile stress is generated in the zirconia surface behind each sliding silicon carbide asperity and transformation to monoclinic phase may occur in this region (if the local temperature is low enough). The delamination crack may form as transformation occurs, or following
transformation due to internal stresses generated at the boundary between transformed and untransformed material. If microcracking accompanies the transformation this may link delamination cracks to the surface. However, flash temperatures were potentially high, and could have suppressed this transformation and even caused transformation to the cubic phase. On cooling the c→t and possibly then t→m transformation would occur to depths of a few micrometres. If the local temperature is too high for the t→m transformation to occur, the delamination mechanism may occur independently (as is observed in non-transforming materials) due to the nature of the contact. Once a crack has formed, this would release the stress needed to drive the transformation and transformation is unlikely to occur after delamination cracking. Twins were observed in the surface of a worn sample, indicating that some material did transform to the monoclinic phase. Material removal occurs when the delamination cracks link up to the surface, which may occur due to microcracks in the top layer, or if the delamination cracks link up with the network of cracks that are parallel and normal to the sliding direction.

At some stage in the wear process, a network of cracks is formed on the surface, parallel and normal to the sliding direction. They are approximately 40 μm deep into the material and approximately 20-40 μm apart. Frictional heat is generated at the interface and large flash temperatures are generated at asperities. As the distribution of asperities in contact varies throughout the test, rapid cooling to the bulk temperature occurs as asperities cease to be in contact. This means that the material is subjected to thermal shock locally. It is thought that thermal shock of the whole pin surface due to its sudden removal of from the contact is also a possible mechanism. Tensile stresses in the contact are also a potential cause. The effect of these cracks will be to increase the wear rate, if they link up with delamination cracks to cause material removal. The mechanism of formation of these cracks remains controversial.
The removed material is either flung out from the contact by the rotating disc, or caught in the contact between the two components. Material caught in the contact could be broken up to form the small wear debris particles (0.25-0.5 μm) that were observed. Material removed from a worn pin surface by an acetate peeling method contained small (10-30 nm) crystallites which may have been formed from crushed debris or primary surface. The debris particles also cause further grooves in the pin surface. As material is removed from the contact in this way, fresh surface is exposed which is then subjected to a similar process.

The effect of increasing nominal contact pressure will increase the load to which each asperity is subjected. According to the above model, this means that the extent of plastic deformation and perhaps cracking parallel to the surface will increase, leading to increased wear. Increasing the speed will increase the likelihood of thermal shock.

6.6 CONCLUDING REMARKS

The model proposed in the preceding section presents a series of events that lead to wear and the formation of the observed surface phenomena. The mechanisms in this model are not contradicted by experimental findings although supporting evidence is not always conclusive. For example, the mechanism of formation of the network of cracks remains controversial and in § 7.2 (further work) suggestions will be made to further investigate this aspect of the wear mechanism.
Figure 6.1 Graphical representation of wear coefficients from the current work in relation to values in the literature (a) water-lubricated; (b) unlubricated.
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(a) asperity contact causes large local stresses

(b) plastic deformation of the surfaces causes grooves in the direction of sliding

(c) plastic strain builds up in a layer at the surface

(d) plastic strain is released by cracks parallel to the surface due to tensile stresses behind silicon carbide asperities

(e) phase transformations contribute to cracking and may link cracks to the surface

(f) meanwhile heating/cooling cycles cause a network of thermal shock cracks in the surface / tensile cracks form

(g) thermal shock/tensile and sub-surface cracks link up and cause material removal and expose new surface to be subjected to the same process again.

(h) the material that is removed is broken up in the contact and forms small particles of wear debris. This then causes further grooves on the pin and disc surfaces.

(i) some wear debris re-attaches to the surface and further plastic deformation of this debris and the original surface causes a smeared appearance.

Figure 6.2 Schematic diagram of the wear mechanism.
7.1 CONCLUSIONS

The aim of this study was to elucidate the wear mechanisms of YTZP at the high speeds and loads which are likely to be encountered in a practical situation. This aim has been met and, as an outcome of this work, a number of conclusions have been drawn which are outlined in this section.

A wear testing rig (based on a lathe) has been designed, and wear tests have been conducted successfully. The method of sample preparation was developed in response to early experimental observations and subsequently pins were polished in-situ on the rig. The wear rate of YTZP sliding against silicon carbide depends on the lubrication conditions and is lower under water-lubricated conditions than in air. The exact alignment of the pin in relation to the disc is important in determining the lubrication regime which in turn affects the wear rate. With pins polished in-situ, hydrodynamic lubrication (HDL) is achieved for nominal contact pressures up to 70 MPa; around this pressure the HDL begins to be broken down. There may be an initial running-in period before HDL is achieved. The wear rates during the running-in period are low (e.g. $1.7 \times 10^{-6}$ g s$^{-1}$) compared to those obtained once the lubrication has been broken down (e.g. $4.96 \times 10^{-4}$ g s$^{-1}$). The wear rates under unlubricated conditions are much larger than with water lubrication under similar contact conditions (e.g. $4.2 \times 10^{-4}$ g s$^{-1}$ compared to $1.2 \times 10^{-6}$ g s$^{-1}$).

Wear coefficients, $K$, have been calculated for the running-in period and the period of HDL breakdown of water-lubricated tests and for unlubricated tests. For water-lubricated tests, $K$ ranges from $4.7 \times 10^{-11}$ to $1.1 \times 10^{-9}$ mm$^3$ N$^{-1}$ m$^{-1}$ and for unlubricated tests, $K$ ranges from $1.4 \times 10^{-6}$ to $5.1 \times 10^{-5}$ mm$^3$ N$^{-1}$ m$^{-1}$.
Chapter 7: Concluding Remarks

For the water-lubricated tests, these values are slightly lower than would be expected from the literature at similar loads. For the unlubricated tests, these values are consistent with findings from the literature. No clear dependence of \( K \) on nominal contact pressure or load was observed for water-lubricated tests. Wear coefficient increased as both sliding speed and nominal contact pressure increased for the unlubricated tests. The increase in sliding speed is likely to lead to an increased temperature generation at the interface which may be linked to the higher wear rate.

The surfaces of worn pins revealed that a broad spectrum of testing conditions led to similar features. Under mild conditions the only surface modification was the formation of grooves in the direction of sliding. This is indicative of plastic deformation of the surface. As testing conditions became more severe (reduced lubrication or increased pressure or speed) the observed damage was accordingly more severe. The three main features observed on the surfaces were deformation (in the form of grooves or smearing of the surface or debris), a network of cracks parallel and normal to the sliding direction and removal of material in flakes. Material removal was by a delamination mechanism in which intergranular cracks running parallel to the surface at a depth of a few micrometres were observed. These cracks linked up with the network of cracks parallel and normal to the sliding direction and led to material removal. A physical model has been proposed, based on the phenomena observed, that links the events that lead to material removal.

High temperatures are generated in the contact, with the maximum estimate of flash temperature being 1650 °C. At this temperature, the monoclinic phase should not exist, but it may be formed on cooling. Due to its low thermal conductivity and diffusivity, zirconia is susceptible to damage by thermal shock cracking. Therefore it is likely that thermal shock plays a part in the formation of the crack networks, perhaps on removing the pin from the contact at the
end of a testing interval. Tensile stresses in the contact may also contribute. The details of the formation mechanism, however, remain unclear.

Flakes of material are formed by delamination and this mechanism may be further complicated by mechanically or thermally induced phase transformations. The flakes of material that are removed from the pin surface and remain in the contact are subject to grinding and form particles of wear debris with a grain size of approximately 0.25-0.5 \(\mu m\).

The outer surface of the pins consist of debris and compacted surface and exhibit a reduced grain size (10-30 nm) compared to the unworn material (\(~0.7\ \mu m\)). This is likely to be caused by microcrack coalescence.

The wear of the silicon carbide disc is mild in comparison to the zirconia and the mechanisms are possibly plastic deformation and grain relief. The grooves observed on the disc surface were caused by ploughing by asperities and trapped debris. The grain relief was caused by anisotropic wear due to differences in mechanical properties and likelihood of plastic deformation in different orientations. Zirconia was transferred to the disc surface and became trapped in holes in the surface.

\section*{7.2 SUGGESTIONS FOR FURTHER WORK}

\subsection*{7.2.1 INTRODUCTION}

The work described in this study has led to the proposition of a physical model for the wear of YTZP sliding against a silicon carbide counterface. The wear mechanism is complex and involves many processes, some of which are related, and work is still required to increase understanding. Some areas that are worth further consideration are given in the following sections.
7.2.2 **NETWORK OF CRACKS**

The cause of the observed network of cracks and how they contribute to the wear mechanism remains controversial and more work is required in this area. It would be interesting to reverse the sample sizes, i.e. a silicon carbide pin sliding on a YTZP disc and investigate whether the crack network formed on either surface. Low speed, higher load tests could be conducted to investigate any tensile stress effects on the crack network formation in the absence of high temperature generation that occurs at high speeds.

7.2.3 **ROLE OF TRANSFORMATION**

The extent of the tetragonal to monoclinic transformation should be examined further, and the part it plays in the wear mechanism investigated, in particular the part it plays in the delamination cracking which leads to material removal. It is likely that transmission electron microscopy can be used to gain this information.

7.2.4 **EFFECT OF SEA WATER**

The lubricant in the pump would be sea water and the effects of this (compared to the tap water used in the current study) should be investigated. It is envisaged that chemical effects would be minimal compared to the effect of organic material, for example enhancing lubrication. The application may also involve the introduction of sand particles into the contact and this could be investigated further, although may require a different sample geometry.

7.2.5 **EFFECT OF PROLONGED EXPOSURE TO WATER**

The enhanced degradation of YTZP in water at temperatures of approximately 200 °C has been well documented in the literature. The effect of any
degradation occurring due to long exposures to sea water (low temperature) on subsequent wear properties would be of interest for the proposed application but has not been considered in this study. The relative rate of degradation compared to material removal rate may be of importance once any degraded material has worn away.
REFERENCES


References


References


