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The Effect of Surface Transformation on the Wear Behaviour of Zirconia TZP Ceramics

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Abstract

The effect of transformation toughening on the wear behaviour of tetragonal zirconia polycrystals (TZPs) has been evaluated. Trials were conducted using wire drawing dies and automotive cam followers fabricated from both 2 and 3 mol% Y_2O_3 *TZPs, sliding under lubricated conditions against steel counterfaces. The worn surfaces were analysed by scanning electron microscopy and X-ray diffraction techniques. A mechanism for the wear of TZP ceramics is presented which provides a qualitative relationship with the degree of transformability, the composition of the as-received powder and the preferred orientation effects occurring in the surface layers of ceramic wear components.*

Der Effekt der Umwandlungsverstärkung auf das Verschleißverhalten von tetragonalem polykristallinem Zirkonoxid (TZP) wurde untersucht. Versuche wurden mit einer Durchzugmatrize und einer Exzenterrolle, jeweils aus 2 und 3 mol.% Y_2O_3*–TZP, durchgeführt. Das Gegenmaterial für die Verschleißversuche war in beiden Fällen Stahl, der mit einem Schmiermittel versehen war. Die geschädigten Flächen wurden mit REM und XRD untersucht. Ein Mechanismus für das Abriebsverhalten von TZP wird aufgezeigt, für einen qualitativen Zusammenhang zwischen dem Grad der Transformierbarkeit, der Zusammensetzung der Ausgangspulver und den bevorzugten Orientierungseffekten in den Oberflächenschichten der keramischen Abriebskomponenten.*

On a évalué ici l'effet du renforcement par transformation sur le comportement à l'usure de polycristaux de zircone tétragonale. Les essais ont été effectués à l'aide de filières de tréfilage et d'excentriques d'arbres automobiles en TZP (contenant 2 ou 3% molaires d'oxyde d'yttrium), glissant sur des contreparties métalliques lubrifiées. Les surfaces usées ont été analysées par microscopie électronique à balayage et par diffraction X. Un mécanisme est proposé pour l'usure des céramiques TZP; celui-ci fournit un rapport qualitatif avec le degré de transformabilité, la composition de la poudre de départ et les effets d'orientation préférentielle apparaissant dans les couches superficielles des composants anti-usure.

1 Introduction

In pursuit of increased efficiency and reduced 'downtime', designers and engineers are continually searching for materials which enable them to approach their goal of 'zero wear'.

Frequently, superior wear resistance has been equated with a high hardness and, although this is a simplistic correlation, it is nevertheless a commonly observed relationship. A logical progression of this argument would therefore suggest the use of engineering ceramics in critical components, since these materials, as a consequence of their interatomic bonding and fine-grained microstructure, display high values of hardness and elastic modulus.

A limitation of the more general application of ceramics is the lack of ductility displayed by these materials, which renders them difficult to handle and prone to catastrophic brittle failure. However, since transformation toughening was first described by Garvie *et al.*,[1] zirconia-based ceramics have done much to overcome such limitations. The toughness

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values which may now be obtained with zirconia ceramics, in conjunction with their hardness and chemical inertness, point to a multitude of structural and wear applications. Examples of their wear-resistant applications are cylinder liners in automotive engines, conveyor belt scraper blades for the mining industry and dies for the hot extrusion of copper.[2-4] In addition to mechanical strength, the applications listed above call for substantial wear resistance. However, a basic understanding of the behaviour of zirconia ceramics in sliding wear applications is not an area which has received extensive coverage in the scientific literature.

The aim of the present work has been to investigate the wear of tetragonal polycrystalline zirconia (TZP) and the microstructural features and environmental factors which affect this. In particular, the effect of the mechanism of transformation toughening on the wear process was evaluated. The mechanism of transformation toughening and the properties attainable with TZP ceramics are not discussed in depth as a comprehensive review is already available.[5] The results obtained from field trials with wire drawing dies and automotive cam followers are described, together with scanning electron microscope and X-ray diffraction analyses of the worn surfaces. As a consequence of this work a new wear mechanism for toughened ceramics is postulated.

2 Experimental Methods

The wear behaviour of TZP ceramics has been investigated under conditions of lubricated sliding by conducting field trials with

(1) wire drawing dies,
(2) automotive cam followers.

Drawing dies were produced by uniaxial die pressing of zirconia powders containing 2 and 3 mol% Y_2O_3 (2Y-TZP, 3Y-TZP) produced by the Tosoh Corporation, Japan. The compacts were then sintered at 1575°C for 2 h (2Y-TZP) and at 1450°C for 6 h (3Y-TZP).

These sintering schedules produced two materials, both with essentially tetragonal grain structures, but with different mechanical and physical properties as shown in Table 1. The densities of both ceramic compositions were close to theoretical.

Table 1. Mechanical and physical properties of TZPs

	2Y-TZP	*3Y-TZP*
Grain size (μm)	0·85	0·35
Hardness (HV20)	1 300	1 450
Modulus of rupture (3 pt bend) (MPa)	920	1 020
Fracture toughness (MPa m$^{1/2}$)	9·4	5·2

The 2Y-TZP with the larger grain size and lower stabiliser content has been shown to be more transformable than the 3Y-TZP. The transformability of the 3Y-TZP was reduced further by utilising a 6 h dwell at the sintering temperature which homogenised the distribution of the stabiliser within the structure. An example of the microstructure is shown in Fig. 1.

Following diamond machining to the correct profile and polishing to the required surface finish, the dies were encased within En.8 steel (Fig. 2) and subjected to an interference fit of 0·038 mm, which generated a compressive pre-stress at the bore of the die of ~360 MPa. The dies were used on the final stage of a five-stage cold drawing machine under the conditions given in Table 2.

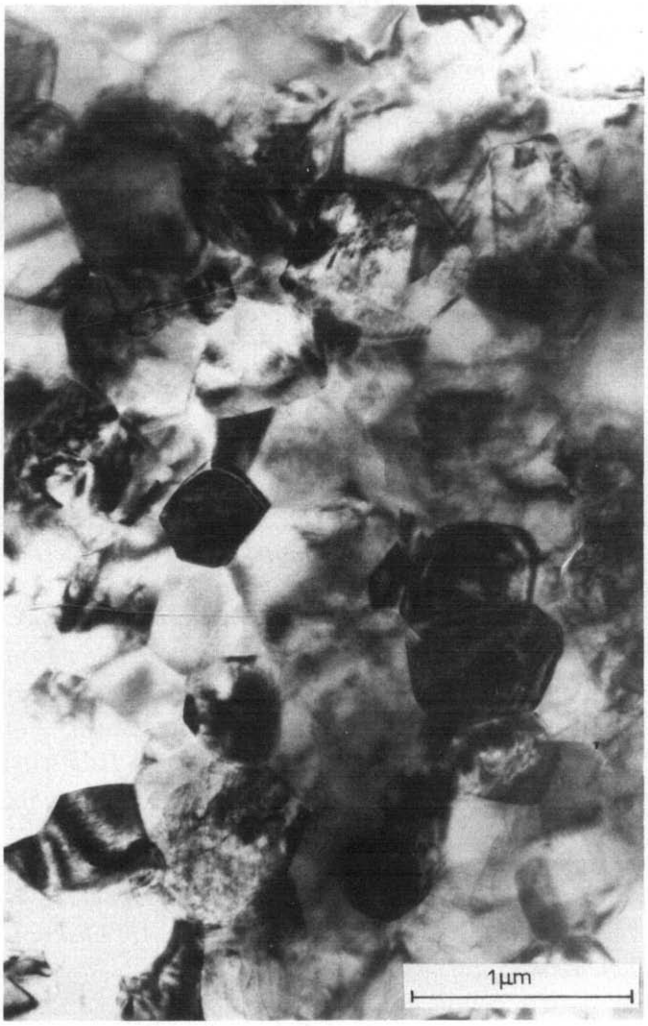


Fig. 1. TEM micrograph of a 3 mol% Y-TZP sintered at 1450°C for 6 h to give a grain size of 0·4 μm.

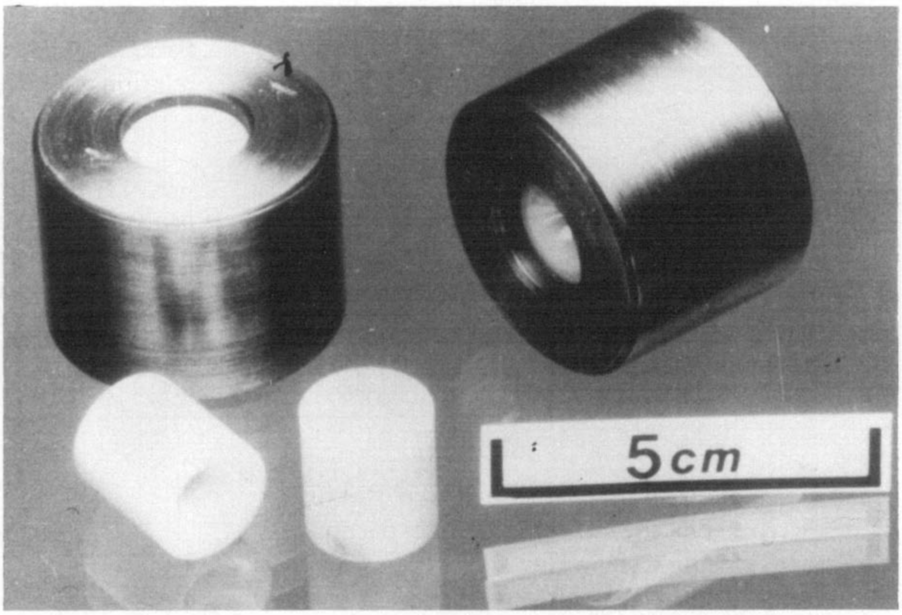


Fig. 2. Cased and uncased drawing dies.

Upon removal from the drawing machine the dies were extracted from their cases, sectioned along the bore and examined by scanning electron microscopy.

Cam followers for an automotive engine test apparatus were also fabricated from 2Y-TZP in the form of circular discs by die pressing and sintering to give a similar microstructure to the 2Y-TZP drawing dies. The discs were then secured into a recess within the top of the body of the cast-iron follower using a suitable cement as shown in Fig. 3.

Each of the followers was run for 160 h at 1200 rev/min against a hardened steel cam. The followers were allowed to rotate freely about their central axis under the action of contact with the cam. After removal the worn discs were examined by scanning electron microscopy and X-ray diffraction. In an attempt to gather further information concerning the relative extent of transformation which had occurred on the worn disc, a similar unworn disc was annealed at a temperature of 1100°C for 30 min and a further disc was subjected to surface grinding. Only 2Y-TZP discs were subject to testing due to lack of apparatus testing time.

Although several authors have attempted an exact quantitative phase analysis of the zirconia system by XRD,[6-8] each of these studies has presented equations which are only directly applicable to the specific powders examined. The reasons for this are complex. Addition of a different cation to the unit

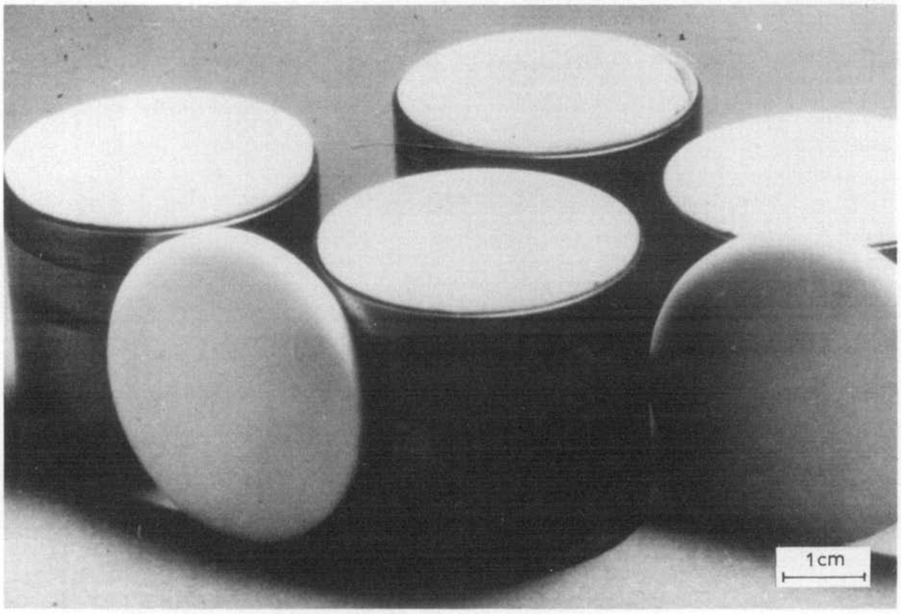


Fig. 3. Automotive cam followers.

Table 2. Wire drawing conditions

Drawn wire	*Werkstoff steel grade 4370*
Drawn wire dia. (mm)	2·95
Feed wire dia. (mm)	3·26
Area reduction (%)	18·1
Wire hardness (HV10)	400
Drawing angle (degree)	12
Drawing speed (m/s)	3·5
Bearing length (mm) (length of die initially in contact with wire)	1·15
Wire temperature at die exit (°C)	130
Mass of drawn wire (kg)	400

cell (as occurs with the addition of a stabilising oxide) causes an alteration in lattice parameters leading to a peak shift in the XRD trace. A more important effect however, is the distortion of the unit cell, which then affects the structure factor. The intensity of a specific peak can then be changed considerably.

The zirconia–yttria system has been investigated systematically,[9] and the change in lattice parameter can be explained in terms of Y^{3+} substitution of Zr^{4+} with a corresponding change in anion vacancy concentration. Recent work by Paterson and Stevens[10] has also highlighted the modification of the monoclinic phase in the fracture surfaces of these materials, in addition to a preferred orientation of the monoclinic $(11\bar{1})$ reflection.

In the present study, the volume fraction of monoclinic phase was calculated from the modified Garvie and Nicholson equation,[8] as suggested by Paterson and Stevens,[10] using the following relationships:

$$I_T = 1{\cdot}255 I(111) + 0{\cdot}833 I(11\bar{1})$$

where I_T is the corrected intensity of the monoclinic peaks $[I(111)_m + I(11\bar{1})_m]$ measured by planimetry.

The volume fraction of the monoclinic phase (V_m) is then calculated from the equation of Toraya *et al.*:[7]

$$V_m = \frac{PX_m}{1 + (P-1)X_m}$$

where

$$X_m = \frac{I_T}{I_T + I(111)\text{ tetragonal}}$$

and P (= 1·31) is the experimental constant for these systems.

3 Results

During the cold drawing of 400 kg of the steel wire the die produced from the 2Y-TZP displayed an increase in bore diameter of 0·04 mm (1·4%). The 3Y-TZP displayed no measurable increase in bore dimension. The nominal die exit temperature measured by infra-red pyrometry was of the order of 130°C.

Micrographs of a section through the diameter of the bores of both materials, shown in Figs 4 and 5,

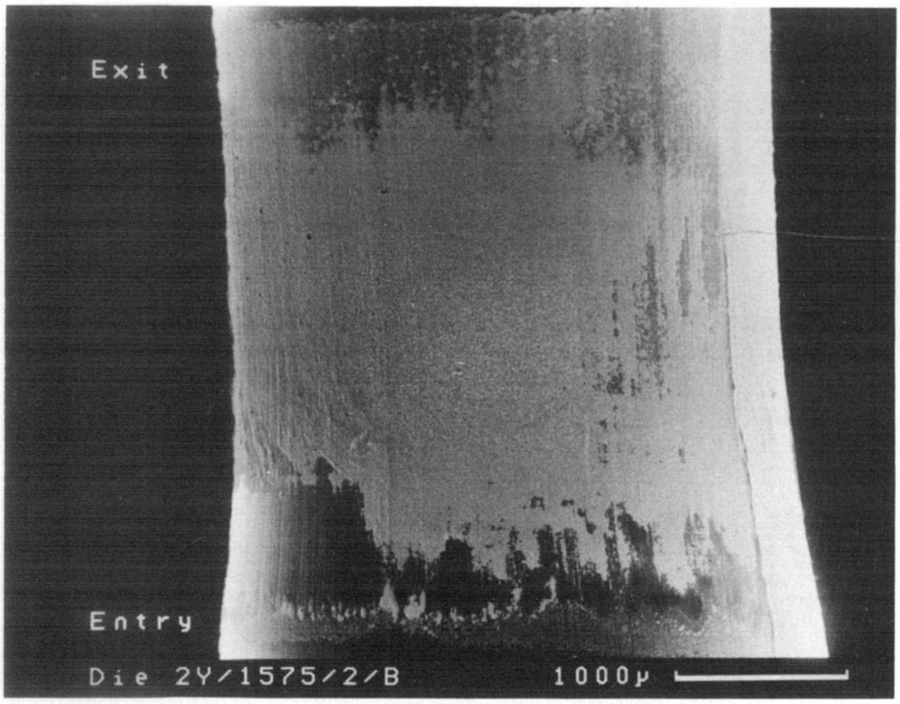


Fig. 4. 2Y-TZP drawing die bore (drawing direction up the page).

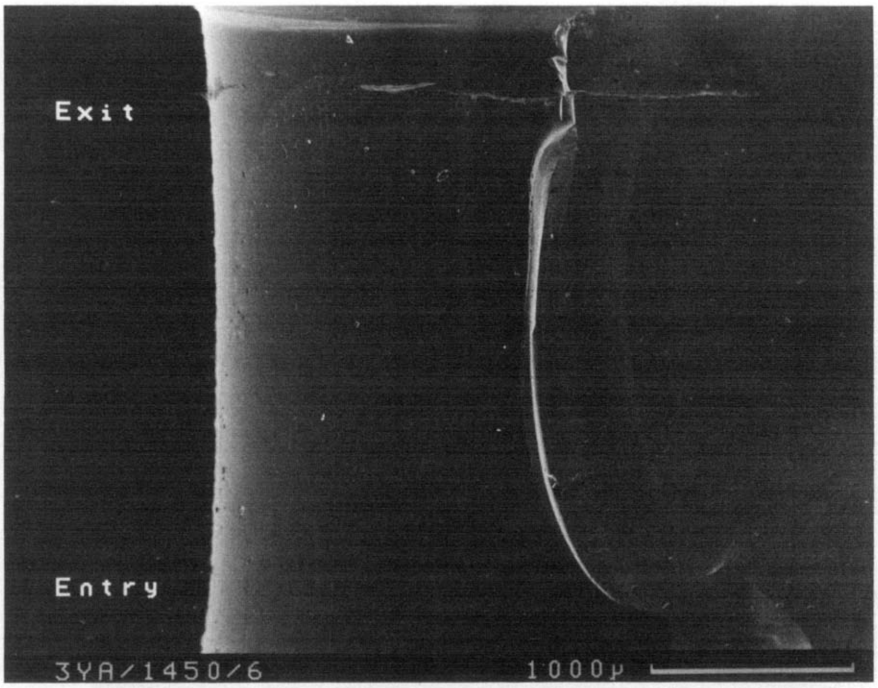


Fig. 5. 3Y-TZP drawing die bore (drawing direction up the page).

reveal a substantial difference in the surface appearance even at low magnifications. Higher magnifications reveal the granular structure of the worn 2Y-TZP die as opposed to the striated, 'plastically' deformed surface of the 3Y-TZP die (Figs 6, 7 and 8). None of the severe wear regions found with the 2Y-TZP die were observed on the 3Y-TZP die.

During the testing of the 2Y-TZP cam followers the surfaces wore excessively in automotive terms and the test was terminated after 4 h. The worn surface was similar to that found in the mild wear regions of the 2Y-TZP drawing die, with some evidence of 'plastic' or permanent non-elastic deformation (Figs 9 and 10).

X-ray diffraction traces illustrating the development of the monoclinic phase from the as-sintered surface to the worn surface of the 2Y-TZP material are shown in Fig. 11 (a, b and c). It is interesting to note the greater development of the monoclinic $(11\bar{1})$ peak relative to the monoclinic (111) peak.

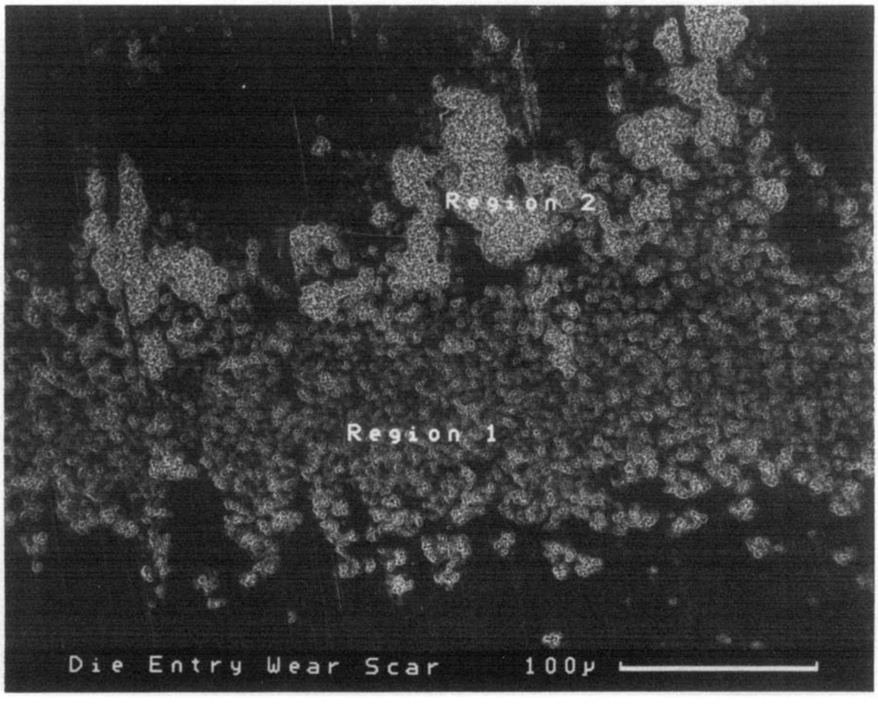


Fig. 6. 2Y-TZP drawing die (1) mild and (2) severe wear regions.

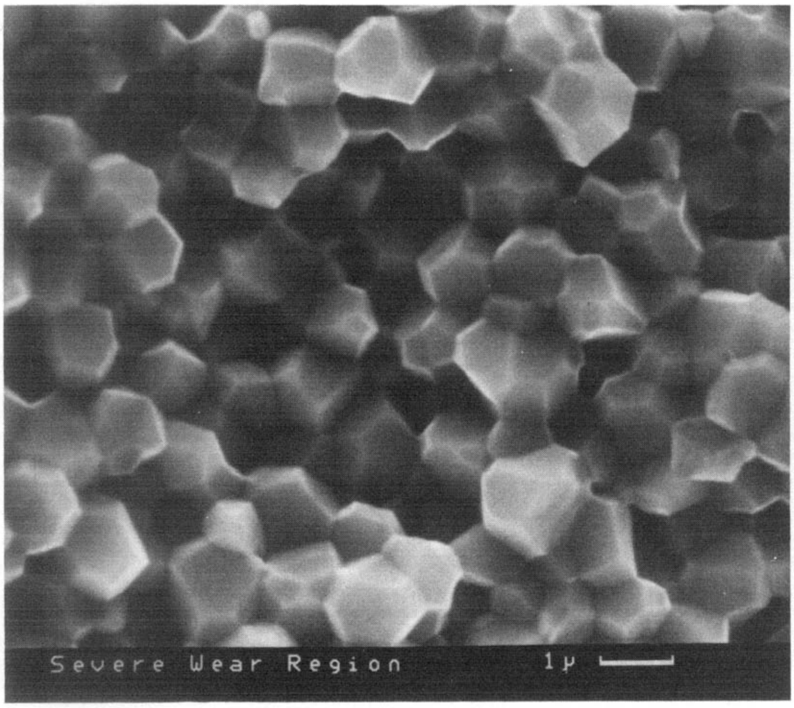


Fig. 7. 2Y-TZP drawing die severe wear regions.

4 Discussion

Of the wear mechanisms which may occur in hard materials, abrasive wear has been reported to develop as a consequence of both permanent deformation and fracture.[11] However, with polycrystalline ceramics the amount of 'plastic' deformation that can occur is strictly limited by the available slip systems and twinning modes. Consequently, abrasive wear is aided by fracture mechanisms operative as a result of the brittle nature of the material. A schematic microstructural representation of the fracture systems operative during the abrasive wear of brittle materials is shown in Fig. 12. On a smaller scale than the cracking shown in Fig. 12 (i.e. $<1\,\mu$m grain diameter) 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. Frequently, with engineering ceramics, it is the propagation of the sub-surface lateral cracks which gives rise to the removal of material when

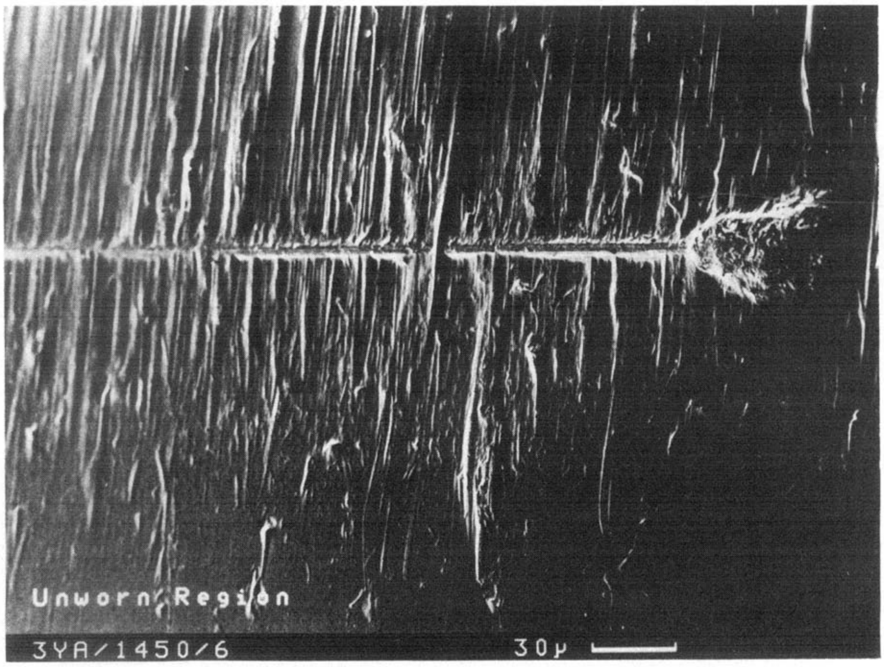


Fig. 8. 3Y-TZP drawing die.

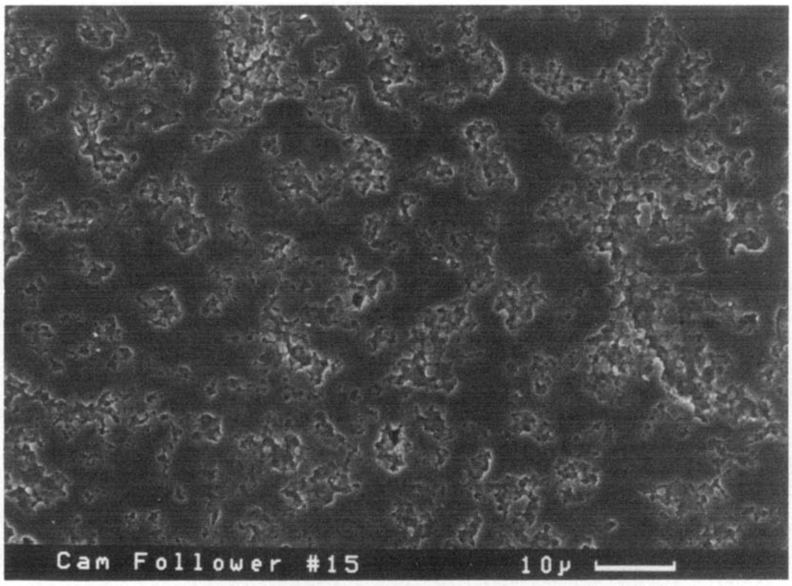


Fig. 9. 2Y-TZP cam follower worn surface.

these cracks change direction and intersect with the free surface of the body.

With ductile materials the mechanism of adhesive wear is often reported. This mechanism is attributed to the cold welding of asperity junctions upon sliding.[12] Further sliding leads to the fracture of these junctions and hence material removal and the formation of new junctions. In the case of brittle materials where the interface is ceramic/ceramic, any shearing of junctions generally leads to fracture which is irregular in nature. This results in surface roughness, gouging and ploughing. However, it must be noted that adhesive wear is less likely to occur with ceramic pairs due to the covalent/ionic nature of the bonding in these materials. In the case of ceramic/metal pairs adhesive wear can occur and is due to the high interface temperatures, which can lead to the formation of an adhesive transfer film of metal onto the ceramic surface. Subsequent contact with the metal counterface may then lead to adhesive wear, as the bulk metal adheres to the transfer film.

From the micrographs of the worn surfaces produced in this study, it is apparent that the highly transformable 2Y-TZP surfaces do not display typical abrasive or adhesive wear characteristics. Rather they wear by an extensive grain removal mechanism with no evidence of trans-granular fracture which is typical with the occurrence of the former type of wear. Interestingly, the surface of the relatively stable 3Y-TZP (Figs 5 and 8) appears to indicate a plastic deformation process with no

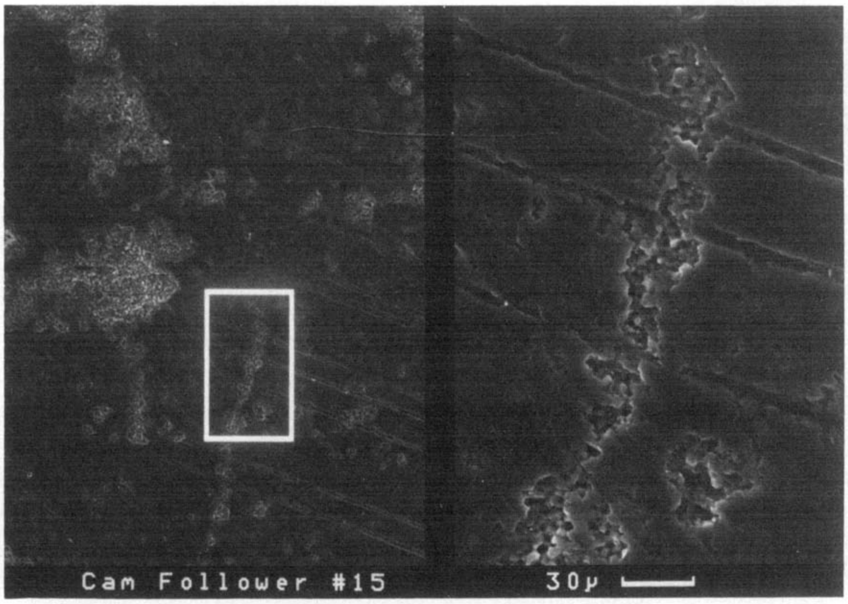
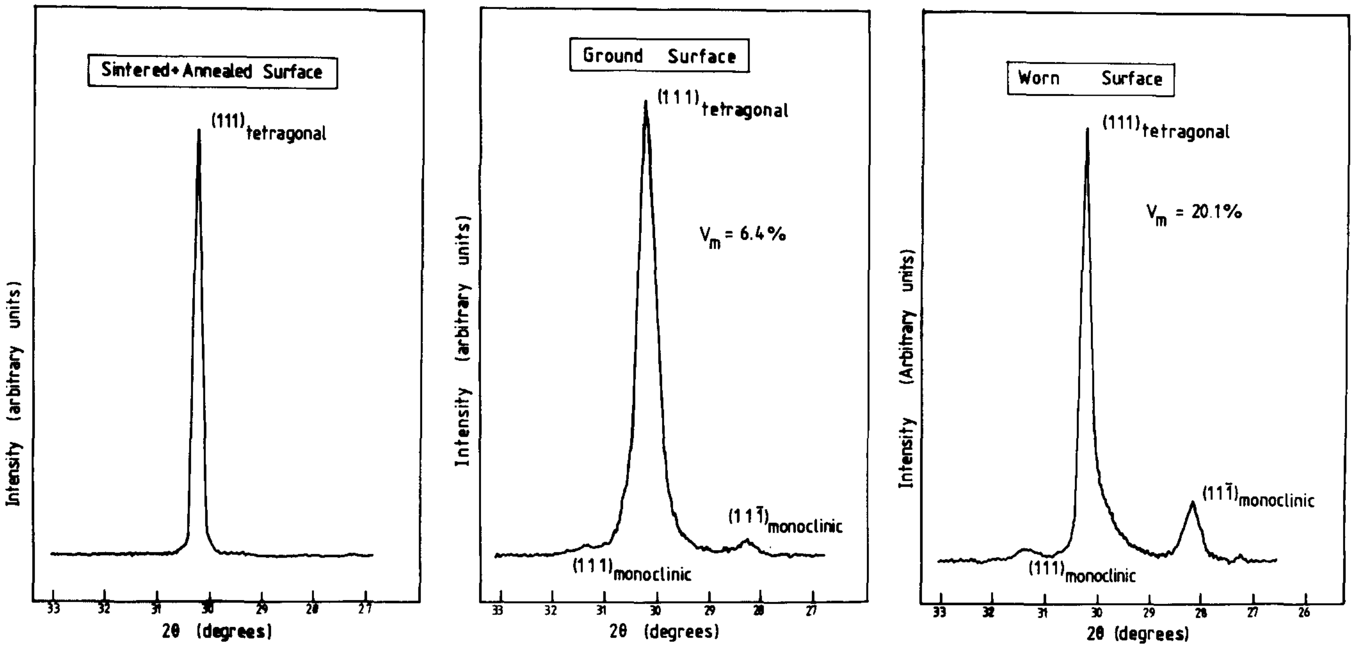


Fig. 10. 2Y-TZP cam follower worn surface.



(a) (b) (c)

Fig. 11. XRD traces of (a) sintered and annealed surface; (b) ground surface; (c) worn surface (2Y-TZP).

evidence of the inter-granular fracture seen with the 2Y-TZP specimens. These results are in agreement with the work of Becker *et al.*[13] who studied the wear of zirconia ceramics with different toughness values against an SAE 4620 steel ring.

The results of the X-ray diffraction work indicate that, during the wear of the 2Y-TZP cam followers, a relatively high degree of surface transformation occurred. It is reasonable to assume that the stresses generated during sliding were responsible for the transformation of both the surface and sub-surface grains. When the subsequent transformation strains can no longer be accommodated by elastic deformation, a grain boundary micro-crack is generated, leading to the subsequent removal of the surface grains, as shown in Fig. 13. It may also be postulated that the wear was initiated in areas corresponding to the boundaries of the original spray-dried spheres of the as-received powders. Impurities concentrate at the surface of these spheres and outline a three-dimensional 'ghost skeleton' of the unsintered body, leading to a network of impurity rich regions. These regions are slightly weaker than other areas due to the increased glass concentration at the interface boundaries. They are, therefore, more prone to subsequent grain removal following the transformation of the tetragonal grains during the wear process.

With regard to the X-ray diffraction traces for the 2Y-TZP material, the preferential orientation of the

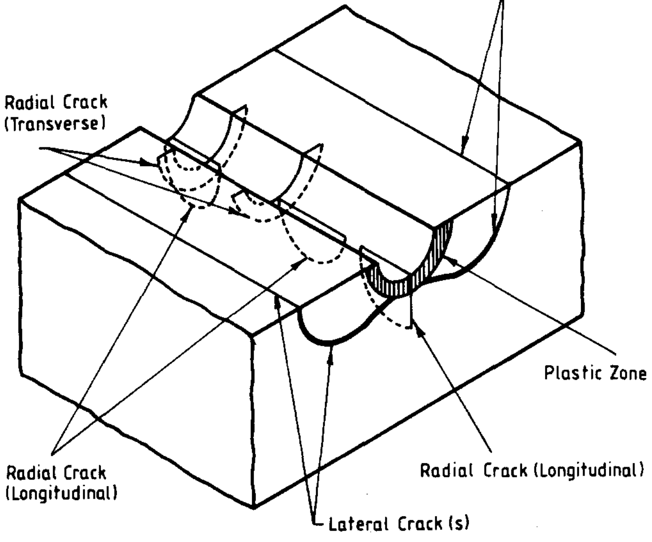


Fig. 12. Schematic of cracking modes in polycrystalline ceramics. (After Rice.[11])

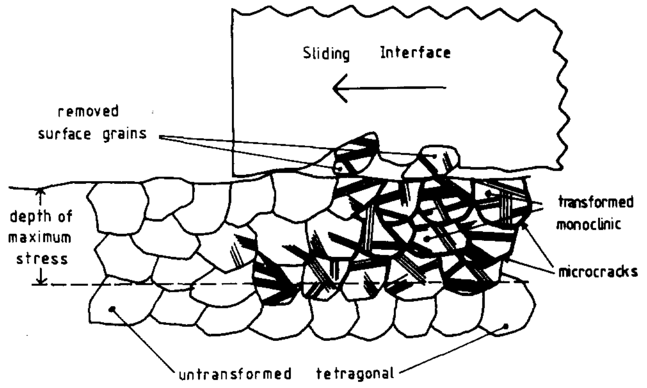


Fig. 13. Schematic of sliding wear process for highly transformable TZP ceramics.

$(11\bar{1})$ monoclinic plane has recently been reported for the fracture surfaces of similar materials sintered under similar conditions to those above.[10] From this work it is suggested that the preferred orientation on the $(11\bar{1})$ plane occurs because of the directional nature of the tetragonal to monoclinic transformation. The directionality of the transformation attempts to minimise the increase in volume in the plane of a crack, and more importantly to maximise it in the direction of the applied tensile stress field. In the case of a worn surface, monoclinic $(11\bar{1})$ reflections are detected more frequently for similar reasons. However, in this case it is the removal of surface grains which produces a pseudo-crack and favours the further transformations of suitably oriented grains, giving rise to the network of wear damage.

The visible differences in the wear mechanisms for TZP ceramics at opposite ends of the transformability scale indicates that the parameters which affect transformation have to be closely controlled in order to achieve the optimum wear resistance. In view of this, the amount and distribution of stabilising oxide needs to be closely monitored, as indeed does the sintered grain size.

Although no indication of the die or cam follower loading conditions have been given in this paper, due to the difficulty in obtaining reliable data from field trials, the effect of surface loading conditions is of great importance. This is due to the direct relationship between the degree of transformation and the contact stress situation which has been shown to occur with other transformation-toughened zirconias.[14,15]

One final point to note is that these components were substituted directly for a metal component. Consequently, it may be expected that the current tribological conditions, in terms of die or cam profile and lubricants, are unlikely to be those which will enhance the useful properties of these ceramics. Further work would be required in order to evaluate the optimum conditions.

5 Conclusions

(1) Highly transformable Y-TZP ceramics display high wear under conditions of heavily loaded lubricated sliding, by a grain removal mechanism.
(2) Control of the stabilising oxide and grain size is essential for optimum wear resistance.
(3) Knowledge of the contact stress situation and critical transformation stress of the ceramic is necessary if wear behaviour is to be predicted.
(4) A high degree of preferred orientation is developed in monoclinic grains present in the worn surface.

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