# Tribological Characteristics of Partially Stabilized Zirconia Ceramics

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# 論文内容要旨

**Chapter 1 Introduction**

In the 1980s considerable scientific interest was devoted to the newly developed partially stabilized zirconia ceramics (PSZ and TZP). The main attractions of these materials were very high fracture toughness (compared to other ceramics), high bending strength, and good oxidation and corrosion resistance. This unique combination of material properties opened a possibility for partially stabilized zirconia ceramics to be used in tribological contacts where these properties of zirconia ceramics could be beneficial.

For most of the tribological applications materials must possess low friction and low wear rates under specific operating conditions. Therefore this project was undertaken to assess the suitability of zirconia ceramics for tribological contacts. The two main aims of the project were: (i) to investigate the tribological characteristics of two partially stabilized zirconia ceramics, i.e. Mg-PSZ and Y-TZP, under various operating conditions, and (ii) based on the experimental results to select operating conditions suitable for tribological applications of these materials.

**Chapter 2 Characteristics of Zirconia Ceramics - Literature Review**

High fracture toughness of PSZ and TZP ceramics depends on the transformation toughening mechanism, unique for partially stabilized zirconia ceramics. Since microfracture is often observed as a main wear mechanism in tribological contacts of ceramics, high hopes were put in PSZ and TZP ceramics abilities to resist crack propagation in sliding or rolling contacts. To fully describe the tribological characteristics of any material the tests are necessary under a wide range of conditions such as contact load, stroke/distance, type of motion, temperature, environment (dry or lubricated) and the counterpart.

The literature available on the tribological characteristics of zirconia ceramics was limited and the published results were often conflicting. Wide ranges of unlubricated friction and wear coefficients were reported with most attention being devoted to the more popular PSZ ceramics. The majority of tests were conducted under unidirectional sliding conditions and only single reports were available on the fretting behaviour of these materials. The effect of relative humidity on the unlubricated friction and wear was not clear. It appeared, however, that some form of lubrication or surface modification would be necessary for most of the practical tribological applications of zirconia ceramics. When water was tried as a lubricant, both the detrimental and beneficial effects on friction and wear of zirconia ceramics were reported. Traditional lubricants such as mineral or synthetic oils usually reduced friction and wear of zirconia ceramics.

In view of the published literature a research program was devised to investigate the tribological characteristics of zirconia ceramics using operating conditions not investigated by other researchers.

**Chapter 3 Experimental Procedures and Materials**

The experimental tests were conducted on a friction and wear test apparatus specifically designed to assess both unlubricated and lubricated friction and wear characteristics of various material combinations at different temperatures (25-400°C). The heart of the apparatus is an electrodynamic vibration exciter, which provides a reciprocating motion with variable stroke (25 μm-6 mm) and frequency (2-50 Hz) to cover both fretting and reciprocating sliding conditions. Two test configurations were used: crossed cylinders in fretting tests and pin-on-plate in reciprocating tests.

Two toughened zirconia ceramics, magnesia-partially stabilized zirconia (Mg-PSZ) and yttria-tetragonal zirconia polycrystals (Y-TZP), obtained from ICI Advanced Ceramics (formerly Nilcra Ceramics), Australia, were used in the tribological experiments. Metallic counterparts included two types of steels, grey cast iron, leaded brass and leaded bronze. In fretting tests alumina ceramic was used for comparison purposes. Ion-implantation with C or a combination of Ti+C was used to modify near surface layers of PSZ and TZP ceramics in an attempt to reduce unlubricated friction and wear levels.

Optical microscopy and scanning electron microscopy (SE and BSE imaging) were used to measure the wear scars and examine the wear morphology and wear debris. X-ray energy dispersive spectroscopy was used to investigate the composition of film transfer forming on the wear scars. Talysurf profilometry was employed to measure changes to surface roughness and depths of the wear scars.

**Chapter 4 Fretting Friction and Wear Behaviour of Zirconia Ceramics**

Fretting of self-mated PSZ and alumina ceramics in air with medium humidity resulted in a much lower wear than was observed during fretting of self-mated steel under the same conditions. During fretting of self-mated alumina polishing and surface cracking occurred, and the apparent wear damage on alumina was lower than that on zirconia. Zirconia ceramics were found to be good substitutes for steel materials under unlubricated fretting conditions.

During fretting of self-mated PSZ and TZP ceramics the resulting wear damage was due to microfracture, tribolayer formation and its subsequent delamination. Lower fretting wear damage was observed on the self-mated PSZ ceramics compared to the self-mated TZP ceramics, and the reason was a more stable tribolayer on the PSZ samples.

During fretting of PSZ and alumina against steel, metal transfer onto the ceramic surfaces was found. For zirconia ceramics this transfer was small, while for alumina ceramics the film transfer was quite heavy and the wear of steel was high due to higher reactivity between alumina and iron/iron oxide. The combination of steel-PSZ materials was found to exhibit moderate friction and low fretting wear in air with medium humidity and should be a good material choice for such applications.

**Chapter 5 Unlubricated Friction and Wear Behaviour of Zirconia Ceramics at Room Temperature**

In unlubricated reciprocating sliding with moderate speed and loads the coefficients of friction for zirconia-zirconia pairs were high, in the range of 0.6-0.7. Coefficients of friction for metal-zirconia sliding pairs were moderate to high, in the range of 0.3-0.6. Softer metals such as brass generated lower friction of 0.3. The results obtained indicated the necessity of providing additional means for friction reduction such as lubricants or surface modification.

Microfracture, tribolayer formation and its subsequent delamination were the dominating wear mechanisms for self-mated PSZ and TZP zirconia ceramics under the test conditions used. The wear coefficients in the range of $10^{-14}$ $m^3N^{-1}m^{-1}$ indicated a moderate wear regime. Such wear coefficients are usually too high for practical tribological applications.

Metal-zirconia sliding process was always associated with metallic film transfer on to the ceramic surface. For the metal-zirconia sliding pair the damage to the ceramic was minimal and mainly involved surface polishing while the amount of metal wear varied from low to high depending on the type of material. For the test conditions applied in this study (moderate loads and speeds) grey cast iron-zirconia ceramic sliding pairs exhibited moderate coefficients of friction (0.4) and the best wear performance of all tested materials (mild wear). It seems that this material combination is a good candidate for tribological applications under similar conditions.

**Chapter 6 Unlubricated Friction and Wear Behaviour of Zirconia Ceramics at Elevated Temperature**

In unlubricated sliding at temperatures up to 400°C the coefficients of friction of self-mated zirconia ceramics were high, in the range of 0.5-0.7, and were slightly increasing with the temperature. Under the same conditions the coefficients of friction of metal-zirconia pairs were in the range of 0.3-0.6 and were mostly increasing with the temperature. Softer brass and bronze pins generated a slightly lower friction than the harder grey cast iron pins but none of the metals tested acted as a good solid lubricant at elevated temperatures.

Wear coefficients of the metallic pins after unlubricated sliding contact with zirconia plates increased with the temperature and were in the high wear regime at elevated temperatures. At temperatures higher than 200°C the wear of metallic pins was higher than that of the zirconia pins. The metal-ceramic sliding contacts were always associated with metallic film transfer onto ceramic surfaces. The thickness of the metallic layer increased with the temperature. The mechanism of oxidative wear was dominating at elevated temperatures.

Wear coefficients of the zirconia pins slid against zirconia plates initially increased for PSZ ceramics, reaching its maximum at about 200°C, and then decreased again at 400°C to its lowest value. The wear coefficients of TZP ceramics initially decreased obtaining its minimum at about 200°C and then slightly increased. Self-mated PSZ ceramics exhibited higher wear resistance than TZP ceramics at 25°C and 400°C and lower wear resistance than TZP ceramics at 200°C. The variation of wear with temperature is usually explained by the phase transformation taking place in zirconia ceramics at elevated temperatures which alters their wear characteristics. The critical temperature at which the wear rates change appears to depend on sliding speed. The trend is: the higher the sliding speed is the lower the critical temperature. It seems possible to select load and speed conditions such as to reduce wear of PSZ ceramics to the levels of $10^{-15}$ $m^3N^{-1}m^{-1}$.

**Chapter 7 Friction and Wear Characteristics of Ion-implanted Zirconia Ceramics**

The friction coefficients of the Ti+C and C ion implanted PSZ and TZP ceramics were not significantly affected by ion implantation compared to those of the unimplanted ceramics tested under the same conditions. The duration of lower friction was rather short.

The Ti+C ion implantation did not reduce the wear of PSZ ceramics and slightly reduced the wear of TZP ceramics due to a short lifetime of the ion implanted layer. The C ion implantation reduced the wear of both PSZ and TZP ceramics. The most wear reduction was obtained for the C ion implanted PSZ ceramics at a load of 1.2 N where wear coefficients slightly below $10^{-15}$ $m^3N^{-1}m^{-1}$ were recorded.

The main disadvantage of ion-implantation is a very low thickness (usually below 0.5 μm) of the modified surface layer. Therefore any beneficial effects in terms of friction and wear reduction are short lived.

**Chapter 8 Lubricated Friction and Wear Zirconia Ceramics**

Coefficients of friction of PSZ and TZP zirconia ceramics in self-mated reciprocating sliding are reduced in liquid environments (water, ethanol, silicone oil) compared to those in humid air under moderate load/speed conditions. Under liquid environments conditions the lubricated wear coefficients of PSZ and TZP ceramics are two orders of magnitude lower than those in air of medium humidity. The following factors may contribute to this phenomenon: (i) liquid film lubrication, (ii) frictional heat dissipation by the liquid, (iii) lower contact stresses due to surface smoothing, and (iv) presence of the protective surface layers.

General smoothing of the as-ground ceramic surfaces is observed in all the liquid environments tested. Also TZP ceramics display a higher susceptibility to wear in water compared to PSZ ceramics.

**Chapter 9 Conclusions**

The tribological characteristics of PSZ and TZP ceramics in various environments should always be assessed with respect to the specific operating conditions of load, speed and temperature. Depending on these conditions the tribological performance of zirconia ceramic may vary exhibiting low to high coefficients of friction and mild to severe wear regimes.

Self-mated unlubricated PSZ and TZP tribological contacts at moderate load and/or speed conditions usually exhibit high coefficients of friction and moderate to high coefficients of wear. However, a combination of load, speed and temperature can be selected to obtain mild wear of PSZ ceramics with wear coefficients around $10^{-15}$ $m^3N^{-1}m^{-1}$.

Under fretting conditions, despite high levels of friction, self-mated PSZ ceramics exhibit much lower wear than self-mated high carbon steel. These findings, supported by the review of published literature, suggest that zirconia ceramics could be suitable for tribological applications under operating conditions generating low frictional heating, i.e. low contact loads and low sliding speeds.

Most practical unlubricated self-mated applications of PSZ and TZP ceramics, however, would need some form of surface modification to obtain low levels of friction and wear. For long lasting effects the modified surface layers should be thicker than those provided by ion-implantation.

Simple liquid lubricants such as water or ethyl alcohol can reduce friction and wear of self-mated PSZ and TZP ceramics to levels acceptable for low temperature tribological applications under moderate load and speed conditions.

Zirconia ceramics exhibit lower chemical reactivity with ferrous-based materials than that of alumina or

Sialon ceramics. Therefore at room temperature grey cast iron-zirconia (reciprocating sliding) and steel-zirconia (fretting) are good material combinations with moderate friction and low wear under specific load and speed conditions. Under those conditions zirconia ceramics are a better choice as a counterpart for ferrous-based materials than alumina or Sialon ceramics.

## 論文審査結果の要旨

部分安定化ジルコニアセラミックスは高硬度と高靭性及び耐食性に基づく優れたトライボロジー特性のゆえに、過酷な使用条件の工具や軸受等に用いられてきており、今後の一層の用途拡大が期待されている。このようなニーズの背景のもとに、本研究は Mg-PSZ と Y-TZP の２種類の部分安定化ジルコニアセラミックスについて、それらの摩擦と摩耗の基本特性を室温と高温の空気中、及び純水、エタノールとシリコンオイル中において、広範囲な荷重と速度及び材料の組み合わせのもとに明らかにし、これらを摩擦部材として使いこなすための基礎知識を体系化している。本論文はその研究成果をまとめたものであり、全編１０章よりなる。

第１章は緒論であり、本研究の背景と目的及び構成を述べている。

第２章では、上記 PSZ と TZP の２種類のセラミックスの基本特性を説明している。

第３章では、摩擦摩耗の試験方法を説明している。

第４章では、空気中の PSZ 同士のフレッティング摩耗が鉄鋼同士の場合に比べ小さいことを明らかにしている。さらに，PSZ と鉄鋼の組み合わせにおけるフレッティング摩耗はアルミナと鉄鋼の組み合わせに比べ３分の１以下であることを明らかにしている。これは PSZ の耐フレッティング材としての有用性を示すものであり重要な知見である。

第５章では、PSZ、TZP、鉄鋼、鋳鉄及び黄銅間の種々の組み合わせにおける空気中の滑り摩擦における摩擦係数と摩耗率の測定を行い、PSZ と黄銅の組み合わせが 0.33 の最小の摩擦係数を示し、TZP と鋳鉄の組み合わせにおいて TZP が $10^{-5}mm^3/Nm$ の桁の最小の摩耗率を示すこと、及びそれらの結果が摩擦面における移着膜の形成形態で説明されることを明らかにしている。これらは実用的にも学問的にも重要な知見である。

第６章では、PSZ、TZP、鉄鋼、黄銅及び青銅間の種々の組み合わせにおける室温から 400℃までの空気中の滑り摩擦における摩擦係数と摩耗率を求め、材料組み合わせと温度によって摩擦係数が 0.25～0.67 の範囲で変化し、ピンの摩耗率が $9.2\times10^{-7}$～$1.3\times10^{-3}$ $mm^3/Nm$ の範囲で変化することを明らかにしている。さらに摩擦面の微視的な観察と分析により、観察された多くの部分が、セラミック摩耗面に形成される金属の移着膜によって説明されることを明らかにしている。これらは実用的にも、学問的にも重要な知見である。

第７章では、PSZ と TZP に対する(C)並びに(Ti+C)のイオン注入が摩擦と摩耗に及ぼす影響を調べ、PSZ/PSZ－C 及び TZP/TZP －C の組み合わせにおいて相手材の摩耗は半分以下に減少することを明らかにしている。これは重要な知見である。

第８章では、純水、エタノール及びシリコンオイル中の PSZ/PSZ および TZP/TZP の組み合わせにおける摩擦係数と摩耗率を広範囲の条件下で求め、純水とエタノールがシリコンオイルに劣らない潤滑効果を発揮することを明らかにしている。これは有効かつ重要な知見である。

第９章では、室温と高温の空気中、及び純水、エタノールとシリコンオイル中での PSZ/PSZ, TZP/TZP, Metal/PSZ, Metal/TZP の組み合わせにおける摩擦摩耗特性を総合的に評価し、部分安定化ジルコニアセラミックスを摩擦部材として使いこなすための指針を与えている。これらは実用的に重要な知見である。

第１０章は結論である。

以上要するに本論文は、PSZ と TZP の部分安定化ジルコニアセラミックスの基本的なトライボロジー特性を種々の広範な実験により明らかにし、得られた特性の科学的理解を深めると共に、応用に有効な指針を与えたものであり、機械システムデザイン工学及びトライボロジーの発展に寄与するところが少なくない。

よって、本論文は博士（工学）の学位論文として合格と認める。