Abstract

The main goal of the project is to understand the mechanisms of chemical etching to obtain superficial roughness for biomedical applications. The material studied in this project is Yttria Tetragonal Zirconia Polycrystal (3Y-TZP). The project is divided in four different parts in order to better understand the microstructure and the damage of different etching conditions.

The first one is related to evaluate the different levels of roughness of zirconia, mainly by advanced techniques such as profilometer and atomic force microscopy (AFM). In the second part, the mechanical responses by nanoindentation generated under sharp indentation will be detailed by: laser confocal microscopy and AFM for superficial damage, and focused ion beam (FIB) for sub-superficial damage. A third part involves the statistical study of fracture by Weibull analysis. Finally, the tribological properties of the different specimens will be studied by nanoscratch and wear resistance.

These tests permit to understand whether the chemical attacks leave the material's mechanical properties unchanged, with different levels of roughness.
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1. Glossary

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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</thead>
<tbody>
<tr>
<td>AFM</td>
<td>Atomic Force Microscopy</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>Alumina</td>
</tr>
<tr>
<td>CaO</td>
<td>Calcium Oxide</td>
</tr>
<tr>
<td>CeO₂</td>
<td>Cerium Oxide</td>
</tr>
<tr>
<td>CIP</td>
<td>Cold Isostatic Pression</td>
</tr>
<tr>
<td>CLSM</td>
<td>Confocal Laser Scanning Microscopy</td>
</tr>
<tr>
<td>CNT</td>
<td>Carbon Nanotubes</td>
</tr>
<tr>
<td>CSM</td>
<td>Continuous Stiffness Measurements</td>
</tr>
<tr>
<td>E</td>
<td>Elastic modulus or Young's modulus</td>
</tr>
<tr>
<td>ESCA</td>
<td>Electron Spectroscopy for Chemical Analysis</td>
</tr>
<tr>
<td>FDA</td>
<td>Food and Drugs Administration</td>
</tr>
<tr>
<td>FE-SEM</td>
<td>Field Emission Scanning Electron Microscopy</td>
</tr>
<tr>
<td>FIB</td>
<td>Focused Ion Beam</td>
</tr>
<tr>
<td>FSZ</td>
<td>Fully Stabilized Zirconia</td>
</tr>
<tr>
<td>H</td>
<td>Hardness</td>
</tr>
<tr>
<td>h</td>
<td>Hours</td>
</tr>
<tr>
<td>HF</td>
<td>Hydrofluoric Acid</td>
</tr>
<tr>
<td>Kᵥc</td>
<td>Fracture Toughness</td>
</tr>
<tr>
<td>LTD</td>
<td>Low Temperature Degradation</td>
</tr>
<tr>
<td>Mg-PSZ</td>
<td>Magnesium Partially Stabilized Zirconia</td>
</tr>
<tr>
<td>MgO</td>
<td>Magnesium Oxide</td>
</tr>
<tr>
<td>mol %</td>
<td>percent in moles</td>
</tr>
<tr>
<td>NANOZR</td>
<td>Carbon Nanotubes reinforced Zirconia</td>
</tr>
<tr>
<td>nY-TZP</td>
<td>Tetragonal Zirconia Polycristal stabilized with n mol % Yttria</td>
</tr>
<tr>
<td>ºC</td>
<td>Degrees Celsius</td>
</tr>
<tr>
<td>PSZ</td>
<td>Partially Stabilized Zirconia</td>
</tr>
<tr>
<td>PVC</td>
<td>Polyvinilchloride</td>
</tr>
<tr>
<td>Rₘₐₐ</td>
<td>Roughness Average</td>
</tr>
<tr>
<td>RMS</td>
<td>Root Mean Square Roughness (AFM measurements)</td>
</tr>
<tr>
<td>Rₐ</td>
<td>Root Mean Square Roughness</td>
</tr>
<tr>
<td>σᵥm</td>
<td>Flexural Strength</td>
</tr>
<tr>
<td>SiC</td>
<td>Silicon Carbide</td>
</tr>
<tr>
<td>SiO₂</td>
<td>Silica</td>
</tr>
<tr>
<td>SOFC</td>
<td>Solid Oxide Fuel Cell</td>
</tr>
<tr>
<td>t</td>
<td>Time</td>
</tr>
<tr>
<td>T-M</td>
<td>Tetragonal-to-monoclinic</td>
</tr>
<tr>
<td>TZP</td>
<td>Tetragonal Zirconia Polycristal</td>
</tr>
<tr>
<td>UHMWPE</td>
<td>Ultra High Molecular Weight Polyethylene</td>
</tr>
<tr>
<td>wt %</td>
<td>Percent in weight</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>-------------</td>
</tr>
<tr>
<td>XPS</td>
<td>X-Ray Photoelectron Spectroscopy</td>
</tr>
<tr>
<td>XRD</td>
<td>X-Ray Diffraction</td>
</tr>
<tr>
<td>Y$_2$O$_3$</td>
<td>Yttria</td>
</tr>
<tr>
<td>YF$_3$</td>
<td>Yttrium Fluoride</td>
</tr>
<tr>
<td>YSZ</td>
<td>Yttria Stabilized Zirconia</td>
</tr>
<tr>
<td>ZrO$_2$</td>
<td>Zirconia</td>
</tr>
<tr>
<td>ZTA</td>
<td>Zirconia Toughened Alumina</td>
</tr>
<tr>
<td>$\mu$</td>
<td>Friction Coefficient</td>
</tr>
</tbody>
</table>
2. Preface

Ceramics are currently being investigated as candidates for a wide variety of engineering applications such as disc brakes, high voltage insulators, valves and liners. This is due to their desirable properties such as high hardness, good wear resistance, chemical stability, and others.

Yttria stabilized zirconia (YSZ) ceramics display high fracture toughness that makes them suitable for a wide range of structural applications like cutting tools, valve guides, extrusion dies, abrasive tools, implants etc.

Since the end of the 1990s dental and biomedic applications have been under study and quickly became implemented, replacing previously used materials, such as alumina and titania, substantially higher fracture toughness and strength as well as esthetics. An important parameter to take into account is the roughness, which favors the osteointegration.

This work is the continuation of a Final Project of Londiche Bénédicte from last semester (Fall 2013) and focuses on studying different times and concentrations to generate superficial roughness in the ceramic materials, in particular by chemical etching of zirconia.
3. Introduction

3.1. History

Zirconia has been known as a gem from ancient times, but its studies have begun only recently. The Zirconia ($\text{ZrO}_2$) mineral, discovered in 1892 by Joseph Baddeley in Sri Lanka, on average contains 96% to 98% zirconia in mass. The crystals found in the mineral are usually 30-50 µm in size and belong to the monoclinic structure, with a Vickers hardness ($\text{VHN}_{100}$) of 1000-1300 and density of 5.6 - 6.0 g·cm$^{-3}$ [1]. Zirconium production has steadily risen from 10k metric tons to over 1,600,000 metric tons in the last 70 years, see Figure 1 [2].

![Zirconium world gross production](image)

**Figure 1 - Zirconium world gross production [2]**

$\text{ZrO}_2$ presents different characteristics, mainly high melting point ($3100^\circ\text{C}$) [3], high inertness at high temperatures ($2100$-$2200^\circ\text{C}$) and significant refractoriness [4]. The mechanical properties of monoclinic zirconia are shown in Table 1.
### Table 1 - Mechanical Properties of monoclinic Zirconia (1105ºC/5h) [5]

<table>
<thead>
<tr>
<th>Property</th>
<th>Density</th>
<th>Grain size</th>
<th>Young’s modulus</th>
<th>Fracture strength</th>
<th>Fracture toughness</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unit</td>
<td>%</td>
<td>nm</td>
<td>GPa</td>
<td>MPa</td>
<td>MPa m$^{1/2}$</td>
</tr>
<tr>
<td>Value</td>
<td>91.1±0.4</td>
<td>163±22</td>
<td>190±2</td>
<td>220±35</td>
<td>2.00±0.13</td>
</tr>
</tbody>
</table>

This material is widely in production of technological ceramics (Figure 2a), like prostheses and tooth crowns (Figure 2b), as well as protective coatings, high-temperature electrodes, cutting tools (Figure 2c), insulation, abrasive and in fuel cells, employed as electrolytes [6] [7]. Zirconia doped with Yttria and Erbium Oxide was also used as the glowing filament in Nernst lamps (Figure 2d) in the beginning of the 20th century [8].

In 1929 Ruff et al. [13] showed the stability of the cubic phase was possible through the addition of CaO dopants. Stabilising oxides like CaO, MgO, CeO$_2$, Y$_2$O$_3$ to pure zirconia allows to generate multiphase materials known as Partially Stabilized Zirconia (PSZ) [14].

The research on zirconia as a biomaterial was started in the late 1960s, with the first paper concerning biomedical application published in 1969 by Helmer and Driskell, who observed the inertness of zirconia in the femur of a monkey [15].

![Figure 2 - Zirconia applications: a) Technological engineering parts [9], b) Dental implants [10], c) IKEA Ceramic Knife set [11], and d) Nernst lamp [12]](image-url)
In 1972 the mechanical strength of PSZ was improved by an homogeneous and fine distribution of precipitates within the cubic matrix, which led to the development of zirconia as an engineering material [16]. It was shown that to further increase mechanical strength and toughness of zirconia ceramics the tetragonal-to-monoclinic (T-M) phase transformation played an important role. Tetragonal metastable precipitates finely dispersed within the cubic matrix were transformed into monoclinic when the constraint exerted on them by the matrix was relieved, i.e. a crack advancing in the material [17].

In a 1988 study, Christel et al. [18] demonstrated the possibility to manufacture ball heads for total hip replacements with this ceramic biomaterial. It is currently high grade zirconia’s main application, along with blades to cut Kevlar, magnetic tapes, and cigarette filters due to it’s hardness [19]. Since then, interest in zirconia has grown exponentially in the academic community, see Figure 3.

Rieth et al. [21] followed by Gupta et al. [22] managed to obtain ceramics formed at room temperature with a tetragonal phase only, called Tetragonal Zirconia Polycristal (TZP), at the end of the 1970s. These studies were continued for the following decade with various dopants, with Y-TZP being preferred to other zirconia ceramics because of its unique balance of toughness and strength.

Since the late 1980s, Y-TZP has been very popular in the manufacturing of femoral heads for hip prosthesis applications. In 2001, the Food and Drugs Administration (FDA) estimated that of the 200,000 hip replacement surgeries undergone every year, 6% of those use the zirconia femoral head [23], with an 8% in 2003 [24]. Today, more than 600,000 zirconia femoral heads have been implanted worldwide. Zirconia is also increasingly used in dental applications such as endodontic posts and brackets and more recently inlays, crowns, and bridges for restorative dentistry [25].
Due to its slow process, a rather important flaw of Y-TZP became clear only after already being employed: a degradation from T-M phase. First the flaw was discovered for temperatures of 250°C, in a humid atmosphere. Later it became clear that, while much slower, the same process underwent even at 37°C [26].

A series of papers followed the investigation of the process for the following 20 years, referred to as “aging” or Low Temperature Degradation (LTD). The process was thought irrelevant for in vivo prostheses until 2001, when hundreds of hip prosthesis failures were reported [27].

In parallel, some researchers are instead focusing on alternatives to 3Y-TZP where LTD is not present, such as Mg-PSZ, which have slightly lower mechanical properties and higher roughness, which gives higher wear rates [28].

In recent years, there has been an increasing interest in the development of carbon nanotubes (CNTs) reinforced ceramics (NANOZR, in the case of Zirconia ceramics), the aim being to transfer the exceptional mechanical properties of CNTs to the bulk engineering materials [29] [30]. It has been demonstrated [31] [32] [33] that adding an appropriate amount of nanotubes (0.5-1 wt %) to ceramic-base materials can improve the mechanical properties (up to 20% higher fracture toughness and 8% higher flexural strength), making them uniquely attractive.

3.2. Zirconia Properties

Zirconia is a polymorph with three forms: monoclinic, cubic and tetragonal (Figure 4). At room temperature and ambient pressure the most stable form of Zirconia is monoclinic (Figure 4a), which has weak mechanical properties. However it has one of the lowest thermal conductivities in a ceramic and is used as a thermal insulator at elevated temperatures, for example in jet engines [34]. The structure is tetragonal (Figure 4b) between 1170 and 2370°C and cubic (Figure 4c) above 2370°C and up to the melting point (2715°C) [14].
Lattice parameters for pure zirconia in mononoclinic phase are $a = 5.147 \text{ Å}$, $b = 5.206 \text{ Å}$, $c = 5.135 \text{ Å}$ and $\beta = 99.23^\circ$ [36].

### 3.3. Stabilization of Zirconia

Different oxides, such as yttrium oxide ($Y_2O_3$), calcium oxide (CaO), cerium oxide (CeO$_2$) or magnesium oxide (MgO), can be added to zirconia to stabilize it, allowing the tetragonal form to exist at room temperature after sintering. The addition of varying amounts of stabilizers allows the formation of PSZ or Fully Stabilized Zirconia (FSZ) which, when combined with changes in processes, may result in ceramics with exceptional properties such as high flexural strength ($\sigma_m$) and fracture toughness ($K_{IC}$), high hardness (H), excellent chemical resistance and good conductivity ions. A FSZ is obtained by adding sufficient amounts of stabilizing oxides, such as 16 mol % MgO, 16 mol % of CaO or 8 mol % $Y_2O_3$ (8Y-TZP). Since the PSZ is obtained with the same oxides, but in smaller amounts (e.g. 2 to 3 mol % yttria, 2Y-TZP and 3Y-TZP, respectively), a multiphase structure is created, which usually consists of tetragonal and cubic zirconia majority with a mononoclinic phase precipitated minority [19].

#### 3.3.1. Classification

Generally, addition of more than 16 mol % of CaO, 16 mol % MgO, or 8 mol % of $Y_2O_3$, forms Fully Stabilized Zirconia (FSZ). Its structure becomes a cubic solid solution, which has no phase transformation from room temperature up to 2500°C. As a good ceramic ion conducting material, yttria fully stabilized Zirconia (YSZ) has been used in oxygen sensor and solid oxide fuel cell (SOFC) applications. The SOFC applications have recently been attracting more worldwide attention, due to their efficient energy transfer and environment concerns [37].
The microstructure of **Partially Stabilized Zirconia** (PSZ, the most common being Mg-PSZ) consists of an array of cubic zirconia partially stabilized by 8–10 mol % of MgO. Due to difficulty in obtaining free silica Mg-PSZ precursors (SiO₂), magnesium silicates can form a low content of magnesia, favoring the transformation T-M and resulting in lower mechanical properties and stability of the material. Fully sintered blocks have been manufactured with this material, and require rigid and strong machining systems [38]. This material has not been successful due mainly to the presence of porosity, associated with a large grain size (30–60 µm) that can induce wear [19].

**Tetragonal Polycrystalline Zirconia** (TZP) materials, containing approximately 2-3 mol % Y₂O₃, are completely constituted by tetragonal grains with sizes of the order of 300 nm. The fraction of T-phase retained at room temperature is the grade of constraint exerted on them by the matrix. Mechanical properties of TZP ceramics depend on such parameters [19]. The properties of some ceramic biomaterials can be seen in Table 2.

**Zirconia Toughened Alumina** (ZTA) is a ceramic based on zirconia combined with a matrix of alumina (Al₂O₃). The stability of the tetragonal phase at room temperature is controlled by the size, morphology and particle localization (intra or intergranular). In ZTA, particles above a critical size will attain monoclinic symmetry after cooling. However, the amount of porosities has reduced the resistance of prosthetics made with this material. On the other hand, the industrial processing of pre-sintered blocks of the same material results in parts with higher mechanical properties, creating tougher prostheses, but with contractions around 25% [39].

Zirconia that has been stabilized in its tetragonal phase is called **Tetragonal Zirconia Polycristal** (TZP). Among the stabilizants we can find CeO₂ and Y₂O₃ as the most common, completely constituted by tetragonal grains with sizes in the order of hundreds of nanometers has high resistance to fracture [19].

In this project 3 mol % Y₂O₃ stabilized **TZP** (3Y-TZP) has been studied for dental applications, because of the previously stated properties and the possible medical applications. In Table 2 are shown the properties of some ceramic materials previously listed.
Table 2 - Characteristics of some ceramics for biomedical applications [19]

<table>
<thead>
<tr>
<th>Property</th>
<th>Alumina</th>
<th>Mg-PSZ</th>
<th>3Y-TZP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition (wt. %)</td>
<td>99.9% Al₂O₃ + MgO</td>
<td>ZrO₂ + 8-10 mol % MgO</td>
<td>ZrO₂ + 3 mol % Y₂O₃</td>
</tr>
<tr>
<td>Density (g·cm⁻³)</td>
<td>≥3.97</td>
<td>5.74-6</td>
<td>&gt;6</td>
</tr>
<tr>
<td>Porosity (%)</td>
<td>&lt;0.1</td>
<td>-</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Bending strength (MPa)</td>
<td>&gt;500</td>
<td>450-700</td>
<td>900-1200</td>
</tr>
<tr>
<td>Compression strength (MPa)</td>
<td>4100</td>
<td>2000</td>
<td>2000</td>
</tr>
<tr>
<td>Young’s modulus (GPa)</td>
<td>380</td>
<td>200</td>
<td>210</td>
</tr>
<tr>
<td>Fracture toughness (MPa·m¹/₂)</td>
<td>4</td>
<td>7-15</td>
<td>7-10</td>
</tr>
<tr>
<td>Thermal expansion coeff. (K⁻¹)</td>
<td>8x10⁻⁶</td>
<td>7-10x10⁻⁶</td>
<td>11x10⁻⁶</td>
</tr>
<tr>
<td>Thermal conductivity (W·m⁻¹·K⁻¹)</td>
<td>30</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Vickers Hardness (HV₀·₁)</td>
<td>2200</td>
<td>1200</td>
<td>1200</td>
</tr>
</tbody>
</table>

3.4. 3Y-TZP State of the Art

Lattice parameters of 3Y-TZP found by Scott [36] are: \(a = 5.159\ \text{Å}, b = 5.211\ \text{Å}, c = 5.321\ \text{Å},\ \beta = 99.16^\circ\). Compared to pure zirconia, the volume increase is about 0.5%, see section 3.2.

In Figure 5 we can see the phase diagram for the Zirconia-Yttria system relating YO₁.₅ molar % to temperature.
The mechanical properties of 3Y-TZP samples have been studied during the years. The most important properties studied are the Young's modulus (E), hardness (H) (at macro-, micro-, and nanometric scale), fracture toughness ($K_{IC}$), and flexural strength ($\sigma_m$). Different techniques could be used to determine the values of these parameters, such as Nanoindentation, Four-point-bending and Vickers indentation. Also to consider is the fact that not always the same composition and sintering methods were used, the exact preparation methods can be found in the respective references. The reported values of E, H, $K_{IC}$, and $\sigma_m$ of 3Y-TZP are summarized in Table 3, Table 4, Table 5, and Table 6 respectively.

### Table 3 - Literature values of Young’s modulus (E) for 3Y-TZP

<table>
<thead>
<tr>
<th>Year</th>
<th>E (GPa)</th>
<th>Method</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1986</td>
<td>220</td>
<td>-</td>
<td>Swain et al. [41]</td>
</tr>
<tr>
<td>2006</td>
<td>254</td>
<td>Nanoindentation</td>
<td>Chowdhury et al. [42]</td>
</tr>
<tr>
<td>2008</td>
<td>240</td>
<td>Nanoindentation</td>
<td>Chintapalli et al. [43]</td>
</tr>
<tr>
<td>2008</td>
<td>250</td>
<td>Nanoindentation</td>
<td>Gaillard et al. [44]</td>
</tr>
</tbody>
</table>
Table 4 - Literature values of hardness (H) for 3Y-TZP

<table>
<thead>
<tr>
<th>Year</th>
<th>H (GPa)</th>
<th>Method</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>2006</td>
<td>16.6</td>
<td>Nanoindentation</td>
<td>Chowdhury et al. [42]</td>
</tr>
<tr>
<td>2007</td>
<td>12.2±0.1</td>
<td>Vickers Hardness 1 Kg</td>
<td>Roy et al. [28]</td>
</tr>
<tr>
<td>2008</td>
<td>13.14</td>
<td>Vickers Hardness 1 Kg</td>
<td>Chintapalli et al. [43]</td>
</tr>
<tr>
<td>2008</td>
<td>12±2</td>
<td>Vickers Hardness 1 Kg</td>
<td>Trunec [45]</td>
</tr>
<tr>
<td>2008</td>
<td>17.5</td>
<td>Nanoindentation</td>
<td>Gaillard et al. [44]</td>
</tr>
<tr>
<td>2010</td>
<td>16</td>
<td>Nanoindentacion</td>
<td>De Armas et al. [46]</td>
</tr>
</tbody>
</table>

Table 5 - Literature values of fracture toughness \((K_{lc})\) for 3Y-TZP

<table>
<thead>
<tr>
<th>Year</th>
<th>(K_{lc}) (MPa·m(^{1/2}))</th>
<th>Method</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1969</td>
<td>5</td>
<td>-</td>
<td>Helmer et al. [47]</td>
</tr>
<tr>
<td>2008</td>
<td>5-5.7</td>
<td>Vickers 200 N</td>
<td>Chintapalli et al. [43]</td>
</tr>
<tr>
<td>2008</td>
<td>5.2±0.1</td>
<td>Vickers 10, 20, 30 Kg</td>
<td>Trunec [45]</td>
</tr>
</tbody>
</table>

Table 6 - Literature values of flexural strength \((\sigma_m)\) for 3Y-TZP

<table>
<thead>
<tr>
<th>Year</th>
<th>(\sigma_m) (MPa)</th>
<th>Method</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1969</td>
<td>1000</td>
<td>-</td>
<td>Helmer et al. [47]</td>
</tr>
<tr>
<td>2008</td>
<td>1020</td>
<td>Four point bending</td>
<td>Trunec [45]</td>
</tr>
<tr>
<td>2010</td>
<td>1213±93</td>
<td>Piston on three balls</td>
<td>Borchers et al. [48]</td>
</tr>
</tbody>
</table>
3.5. Tetragonal-Monoclinic Transformation

The T-M transformation is martensitic in nature, which is a change in crystal structure that is athermal, diffusionless and involves the simultaneous, cooperative movement of atoms over distances less than an atomic diameter, so as to result in a macroscopic change of shape of transformed regions. The volume increase ranges between 0.04 and 0.06 times, which augments fragility of the material [49].

Lange [50] described the thermodynamics of the T-M transformation in zirconia, considering the simple ideal case of a spherical tetragonal particle in a matrix. The change of total free energy ($\Delta G_{t-m}$) due to the transformation is given by:

$$\Delta G_{t-m} = \Delta G_c + \Delta U_{SE} + \Delta U_S$$  \hspace{1cm} (Eq. 3.1)

where $\Delta G_c$ ($< 0$ when $T < M_s$) is the chemical free energy, $\Delta U_{SE}$ ($>0$) is the strain energy associated with the transformed particles, and $\Delta U_S$ ($>0$) is the change in energy associated with the surface of the particle.

3.6. The mechanism of increased fracture toughness

An increase in fracture toughness was observed in TZP which worked on the basis of the above written phase transformation. This mechanism increases the toughness of the material, because the energy associated with crack propagation is dissipated both in the T-M transformation and in overcoming the compression stresses caused by the volume expansion [17]. A better understanding may be given by a schematic representation (Figure 6), where the crack propagates through the material and the phase around it transforms to monoclinic from tetragonal. To obtain such an fracture toughening mechanism a material needs the following [51]:

1) a metastable phase must exist that can transform into a stable structure by the effect of tensions inducted by the crack,
2) the transformation must take place instantly and not require other processes such as diffusion, and
3) the transformation must be associated with a change in shape and/or volume.

Furthermore, the toughness of the transformed phase must not be considerably lower than that of the original phase, to ensure the increase of toughness. All of these requirements are met in the case of TZP.
3.7. Limits – Low Temperature Degradation

The aging kinetics has been actively debated in the last 20 years, first observed by Kobayashi et al. [26]. The most favored explanation being that of Chevalier et al. [53] and thus described here. In addition, during the last years Muñoz-Tabares et al. [54] modified the degradation method reported by Chevalier et al. [53], in particular describing how grain boundary cracks are parallel to the surface.

Aging occurs experimentally in zirconia samples, mostly in humid atmosphere or in water, thanks to which surface T-M transformation is activated. The fundamental role of internal stresses associated with water diffusion in the zirconia lattice has been demonstrated, rejecting previous hypotheses [55].

Yoshimura [56] summarized the experimental observations as follows:

- The degradation proceeds faster at temperatures of 200-300°C and depends on time.
- The degradation is caused by the T-M transformation and is accompanied by micro- and macrocracking.
- The transformation progresses from the surface to the interior of the specimen.
- Water or water vapor enhances the transformation.
- A decrease in grain size and an increase in stabilizer content delay the transformation.
3.7.1. Aging Mechanism

Water radicals penetrate inside the zirconia lattice during exposure to humidity. Most likely, the oxygen from the water is located on vacancy sites, and the hydrogen is placed on an adjacent interstitial site [57]. In Y-TZP, the presence of numerous vacancies due to the trivalent character of \( \text{Y}_2\text{O}_3 \) makes the diffusion rate of species from the water higher than in other zirconia ceramics (i.e., CeO\(_2\)-doped ZrO\(_2\)). The penetration of water radicals leads to a lattice contraction, which results in the formation of tensile stresses in the surface grains that destabilize the T-phase by reducing \( \Delta U_{SE} \) in the previously mentioned equation. Martensitic transformation of grains (or part of grains) at the surface can then proceed [53].

The transformation begins mostly at grain corners, where residual tensile stresses are the largest, and that one given grain does not transform all at once but rather progressively as the stress state due to water attack and earlier transformation increases [58].

The surface transformation of Y-TZP takes place by an apparent nucleation-growth mechanism; i.e., once a grain is transformed, the extension of the transformation occurs not only at random on the surface but preferentially on the neighboring grains (nucleation is here considered as the transformation of one grain, whereas growth is the extension to its near neighbors) (Figure 7). Nucleation occurs on the most unstable grains subjected to the highest tensile stresses [53].

![Figure 7 - a) Water adsorption on surface, b) Shear strain produced by formation of the martensite plates, c) and grain pullout [54].](image)

Because it is a crystallographic change, aging can be easily characterized by techniques sensitive to crystallography or chemical environment. Among them, X-Ray Diffraction (XRD) is most extensively used. It is a fast and non-destructive technique allowing the monitoring of LTD on one piece [59].
The consequences of aging include volume increase (around 4%), micro cracking and loss of strength in the material. This leads to increased wear, aseptic loosening and decreased mechanical stability. The biological interaction of small particles with the immune system cells then becomes critical. It is indeed currently believed that particles generated at the contact surfaces enter the periprosthetic tissues, which leads to osteolysis, and the need to replace the prosthesis [53].

### 3.8. Applications

Amongst the many applications of zirconia, outstanding is the use as an abrasive material. More exigent applications make use of the toughness, resistance to wear and refractory properties to develop components that are used in aggressive environments, such as: extrusion dice, valves, cutting tools (knives and scissors), guides for sheet metal forming, oxygen sensors, fuel cells, thermal barriers, and finally orthopedic and dental implants, for what it is currently known for [19].

#### 3.8.1. Cutters

The number of applications in the textile industry ranges from splicers, suction tube and residual thread cutters for winding machines, to end thread and diagonal cutters for looms. The properties of 3Y-TZP allow for faster cutting rates with consistent quality, smooth running and allows universal cleaning possibilities [60].

#### 3.8.2. Solid Oxide Fuel Cells (SOFCs)

A solid oxide fuel cell is a device (Figure 8) that generates electricity by a oxidizing fuel, where the electrolyte is a solid ceramic. With an efficiency around 60% and operating temperatures of 1000ºC, SOFCs require high resistance materials to ensure long-term stability [61].
3.8.3. Orthopedic implants

Out of all zirconia-containing ceramic systems, in implants only three are used for implants: yttrium cation-doped tetragonal zirconia polycrystals (3Y-TZP), magnesium cation-doped partially stabilized zirconia (Mg-PSZ) and zirconia-toughened alumina [38].

ZrO₂ was proposed as a new material for hip head replacement instead of titanium or alumina prostheses in the late 1960s. While the first studies were carried out in vivo because in vitro technology was not sufficiently advanced, from the 1990s the biocompatibility was studied in vitro [15].

The most notable uses of 3Y-TZP is in tooth implants and total hip replacements, where it replaces the femoral head. In total hip replacement (called total hip arthroplasty), the damaged bone and cartilage is removed and replaced with prosthetic components, see Figure 9. The plastic liner is made of Ultra High Molecolar Weight Polyethylene (UHMWPE), due to the low wear rate it has with 3Y-TZP femoral heads [62].
3.8.4. Dental Implants

In case of chipped or missing teeth, dental implants are often a good solution to avoid migration and wear of the other teeth, chewing and digestion problems. The implant is made of an artificial root in metal with a ceramic custom made crown, or as one whole ceramic piece [64].

Figure 10 - Tooth in parallel to dental implant [65]
3.9. Increasing Roughness

3.9.1. Definition and Parameters

Roughness is the characteristic corresponding to the measurement of irregularities of the surface material. It is characterized by the vertical deviations of the surface: if the deviations are big, the material is considered rough; if they are small it is considered smooth, with the order of magnitude depending on the application.

There are various ways to characterize the profile and roughness of a surface. To define a profile it is important to determine the components of roughness, waviness and shape. The waviness characterizes the deformations of the whole and the ones created by the bad state or use of the machinery and the machining process.

3.9.1.1. Roughness Average (Ra)

The Roughness Average (Ra), is the arithmetical mean deviation of all points roughness profile from a mean line over the evaluation length. It is the most common parameter used to measure roughness and defined by the following standards: ISO 4287-1997 and ISO 4287/1-1997. The Ra parameter is calculated as follows:

\[
R_a = \frac{1}{N} \sum_{j=1}^{N} |r_j|
\]

(Eq. 3.2)

where \( N \) is the total number of samples and \( r_j \) is the distance from the average height.

3.9.1.2. Root Mean Square Roughness (Rq)

The Root Mean Square, Rq, is the average of the measured height deviations taken within the evaluation length and measured from the mean line, see paragraph 3.9.1.1. This parameter is defined by standards ISO 4287-1997 and ISO 4287/1-1997 [66] [67], and calculated as follows:

\[
R_q = \sqrt{\frac{1}{N} \sum_{j=1}^{N} r_j^2}
\]

(Eq. 3.3)
3.9.2. Effects of Roughness

Surface roughness directly impacts the bioactivity of the material. Yamashita et al. [69] proved that a higher roughness ($R_a \approx 1\mu m$) positively influences the initial attachment of osteoblasts compared to a lower roughness ($R_a \approx 0.2\mu m$) of the same material.

Another consequence of roughness is on the wear rate with different materials. Studies have shown that different roughness levels have different influence on wear rates. However, there is no agreement on the effects on wear of sample characteristics like roughness, lubricant fluid, speed and load, and more research needs to be done [19].

Wear rates are also influenced by lubricants, the presence of which decreases the friction between the two materials. A study comparing the wear of zirconia-on-zirconia showed weight loss about 10,000 times greater when the lubricant was water as opposed to serum [70]. Surface roughness also increases lubricant retention.

3.10. Biocompatibility and Osseointegration

When biomaterials are introduced into human tissue, the biocompatibility of the materials depends not only on their physical and chemical surface properties but also on the initial response of the cells on the material surface. Furthermore, the interaction of the cells with the material surface is fundamentally relevant and contributes to osseointegration. The initial attachment and adhesion on a material surface are followed by cell spreading and migration.
Correlation between chemical treatment and the superficial and mechanical properties of zirconia

The quality of this first phase of cell-material interaction will influence the cell capacity to proliferate and differentiate [72].

Multiple researches have been done to investigate the biocompatibility of zirconia as a dental implant. It has since been defined as bioinert [73]. Biocompatibility of Y-TZP and NANOZR has been found to be similar to commercially pure Ti [74].

The functional activity of cells in contact with the biomaterial is determined by the characteristics of the surface [75]. Furthermore, the surface roughness has been established to play an important role in osseointegration. A few studies have reported on the effect of surface roughness on zirconia [74] [69] [76].

### 3.11. Objectives of the Project

The general scope of the project is to obtain and characterize surface roughness in the zirconia through chemical etching using acid fluoride and compare time versus concentration effects.

#### 3.11.1. Specific Objectives

In order to achieve this objective advanced characterization techniques such as Profilometry, Laser Confocal Microscopy, Atomic Force Microscopy (AFM), Nanoindentation, Focused Ion Beam (FIB) and Field Emission Scanning Electron Microscopy (FE-SEM) have been used.

The specific objectives can be classified in three sub-categories:

- Increase roughness by Hydrofloridric Acid etching in function of:
  - Concentration
  - Time

- Analyze results:
  - Roughness: Profilometery, AFM
  - Sub-supeficial Porosity: FIB
  - Mechanical behavior: Hardness and Elastic modulus using nanoindentation and Fracture analysis using Weibull statistics
o Tribological Behavior: Wear tests, and friction coefficient using a tribometer and nanoindentation technique

• Become familiar with equipments and techniques such as:

  o Sintering and polishing methods of ceramics
  
  o Characterization techniques:
    - Superficial: Atomic Force Microscopy, Scanning Electron Microscopy and Profilometry
    - Sub-superficial: Focused Ion Beam

  o Mechanical tests: Nanoindentation, Wear and Ball-on-three-balls

It is worth mentioning that these novel techniques are extreme powerful tools to understand the mechanical behaviour of the material. Nanoindentation is a key tool to characterize volumes of material as small as few nanometres, such as a degraded layer. FIB allows milling a cross section of several microns in any site of the sample, opening this area for inspection, to obtain a picture of the etched profile. AFM allows to measure topographic changes with subnanometer resolution, and to relate these changes to deformation and fracture mechanisms.
4. Materials and Methods

4.1. Sample Preparation

4.1.1. Sintering

The material used for the creation of the green bodies is pulverized 3Y-TZP from the company TOSOH, Tokyo. To obtain non-porous samples approximately 40 g of the powder were put into a tube-shaped silicon mold. To homogenize the sample and avoid air bubbles it was manually compacted during the filling process. The powder was thus compacted using cold isostatic pression (CIP) up to 200 MPa for a dwell time of 5 minutes, having 2 minute pauses every 50 M Pa to avoid fast pressure changes.

After compactation, the bars were heated in a tubular air oven to 700°C at a speed of 3°C/min with air ventilation and stayed at said temperature for 1 hour in order to burn off the organic binder. Following this it reached 1450°C, where it sinterized for 2 hours, to then cool until room temperature at a speed of 3°C/min. Thus were obtained sintered 3Y-TZP bars long 91±5 mm with a diameter of 9.5±0.5 mm and 38.5±0.5 g in weight.

Figure 12 – Temperature vs. time of the tubular air oven. [77]
4.1.2. Cutting and Polishing

Once the bars have been sintered it is necessary to cut them to obtain disc-like samples with a diameter of 9.5 ± 0.5 mm and a thickness of 1.9 ± 0.3 mm. The cutting was done using the Struers Accutom 2 with a Struers diamond cut-off wheel 127x0.4 mm for HV>800. Because of the machine limitations, the lubricant furnished with the machine was used (Buehler Cool™ 3 mol % in distilled water). The cutting speed was variable between 20 and 30 µm/s, while the disc was rotating at 800 rpm.

The polishing method was experimental and thus done with frequent analyses. To eliminate the burr left from the cutting a wear disc was used solely on the borders of the samples. The samples were then glued using LocTite SuperGlue™ to a metallic disc in an equally distributed manner. Using the automated polishing machine Buehler Automet 2, the suggested mechanical polishing sequence used in the different 3Y-TZP samples employed in this project are:

i) Grinding until planarity using 120, 220 and 500 grit SiC paper 1 hour each, with pressure of 133 N and 100 rpm.
ii) Polishing with 30, 6 and 3 microns diamond suspension for 1 hour each, with pressure of 44 N and 100 rpm.

The metallic disc was then placed in acetone until the samples could be easily detached (4-10 hours), cleaned in ultrasound with distilled water.

4.1.3. Samples Data

After the polishing process the samples were measured and weighted, to obtain the following averages:

<table>
<thead>
<tr>
<th>Weight (g)</th>
<th>Height (mm)</th>
<th>Diameter (mm)</th>
<th>(R_\alpha) (nm)</th>
<th>Density (g•cm(^{-3}))</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.9 ± 0.5</td>
<td>1.9 ± 0.3</td>
<td>9.4 ± 0.1</td>
<td>9 ± 1</td>
<td>5.9 ± 0.1</td>
<td>264 discs</td>
</tr>
</tbody>
</table>

The density was measured by means of the Archimedes principle, under ambient conditions with both distilled water and zirconia being let reach the same ambient temperature.

4.1.4. Chemical Attacks

A strong acid, Hydrofluoric Acid (40 mol % HF), was used to attack the zirconia samples as it was seen more effective in previous experiments [77]. The acid solutions were diluted with...
Correlation between chemical treatment and the superficial and mechanical properties of zirconia

distilled water to reach concentrations of 20, 10 and 5 mol % and kept in Polyvinilchloride (PVC) containers for different periods of time: 0.5, 1, 2, 4, 7, 14 and 24 hours under ambient conditions (20°C and 1 atm). Subsequently the samples were cleaned with ultrasound in distilled water for 15-50 minutes, proportionally to etching times.

Table 8 – Number of samples per condition (HF Concentration\time). Conditions with 19 samples were also analyzed for fracture toughness, whereas the ones with 4 were not. Additional 15 samples were made to be used for comparison.

<table>
<thead>
<tr>
<th>[HF]\Time</th>
<th>0.5h</th>
<th>1h</th>
<th>2h</th>
<th>4h</th>
<th>7h</th>
<th>14h</th>
<th>24h</th>
</tr>
</thead>
<tbody>
<tr>
<td>20 mol %</td>
<td>4</td>
<td>19</td>
<td>19</td>
<td>19</td>
<td>4</td>
<td>19</td>
<td>19</td>
</tr>
<tr>
<td>10 mol %</td>
<td>4</td>
<td>19</td>
<td>19</td>
<td>19</td>
<td>4</td>
<td>19</td>
<td>19</td>
</tr>
<tr>
<td>5 mol %</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>19</td>
</tr>
</tbody>
</table>

As safety measures, all the experiments were done in a controlled environment under a polypropilene fume hood, wearing HF-resistant gloves, and avoiding all glass and metal ware.

Figure 13 - Laboratory set-up for chemical HF etching
4.1.5. Profilometer

Profilometry is a technique that characterizes the surface to obtain measurements of roughness. To study the surface roughness of the zirconia samples after the polishing process and after the chemical etching, a profilometer was used. A profilometer functions by dragging horizontally (x) a diamond tip (radius = 12.5 µm) across the surface and measuring the vertical (y) displacement, having a constant load of 3 mg. This way a profile is obtained, thanks to which it is possible to measure statistically meaningful values such as $R_a$ and $R_q$.

![Dektak 150 profilometer](image)

**Figure 14** – The Dektak 150 consists of a measurement tool for characterizing surface topography.

The profilometer Dektak 150 from Veeco is suitable for the determination of changes in height between 6 Å and 100 Å. The scan was done in 90 seconds with a length of 2000µm, with a resolution of 0.074 µm/sample. Considering the slight curvature of the samples, a smoothing filter was applied to all measures. Finally, using the software of this equipment, the following values were obtained: $R_a$ and $R_q$. Two different samples per condition were measured in order to obtain average values.
4.1.6. Confocal Laser Scanning Microscopy (CLSM)

A scanning type laser microscope aims a laser beam at a very small spot through objective lens and scans over the specimen in x-y directions. It then captures light from the specimen with the detector and outputs the image of the specimen onto the monitor, see Figure 15.

In confocal optics, a pinhole is placed at a position that is optically conjugate with the focusing position (confocal plane) to repel light that comes from outside the focus point. As a result, the part where light is repelled is truly darkened in the image making it possible to slice optically the specimen.

Contrary to it, in an ordinary microscope, the light that comes from outside the focus point is overlapped with the light at focusing position and whole image turns blurry. A light microscope has a resolution limit of 0.2 µm and only allows flat images, whereas a confocal laser microscope can go up to 0.12 µm and 0.01 µm on z-direction, allowing 3D reconstructions [78] [79] [80].

In this project the LEXT OLS Confocal microscope was used with 5x, 10x, 20x, 50x and 100x zoom in ambient environment (1atm, 20ºC, 20-45% relative humidity).
4.1.7. Atomic Force Microscopy (AFM)

The AFM uses a cantilever to probe the sample with it’s tip (as small as 10nm wide), with a photodiode measuring it’s deflection.

It can work in either “contact” or “tapping” mode, by being in contact with the surface or oscillating on a determined frequency, respectively. The topographic map is created thanks to the interaction of the surface with the cantilever, which brings a torsion or deflexion of it, measured by a ray. The resolution of the AFM is considerably higher to that of a profilometer, with a vertical resolution of up to 1 nm and horizontal of 5 nm [81].

![AFM-Dimension 3100](image.png)

Figure 16 - AFM-Dimension 3100

The surface before and after the chemical etching and the residual imprints performed after the nanoindentation tests have been observed by AFM Dimension 3100 from Bruker in tapping mode. Images were subsequently analyzed using the software WSxM 5.0 [82].


A scanning electron microscope (SEM) permits the observation and characterization of heterogeneous materials on a nanometer and micrometer scale, also permitting three-dimensional-like images of surfaces. The area to be examined is irradiated with a focused
Correlation between chemical treatment and the superficial and mechanical properties of zirconia

electron beam, swept in a raster to form images or static to obtain an analysis at one position. The various types of signals produced from the interaction of the electron beam with the sample (characteristic x-rays, and more). Secondary electrons, originating within a few nanometers from the surface, are the most often detected to collect images using low energy (<50eV). Backscattered electrons originate in the electron beam to be reflected by the specimen atoms, and are used to detect contrast between areas with different chemical compositions. Other uses include characteristic x-rays, x-ray spectroscopy and are used to examine the surface topography, crystallography, composition etc [83].

Field emission scanning electron microscopy (FE-SEM) in particular uses a field-emission cathode, which provides narrower probing beams at both low and high electron energy, giving a good spatial resolution without damaging the sample [84].

Some of the FE-SEM advantages over conventional SEM are [84]:

- FE-SEM produces clearer, less electrostatically distorted images with spatial resolution down to 1 nm (3 to 6 times better).
- Smaller-area contamination spots can be examined at electron accelerating voltages compatible with Energy Dispersive X-ray Spectroscopy.
- Reduced penetration of low kinetic energy electrons probes closer to the immediate material surface.
- High quality, low voltage images are obtained with negligible electrical charging of samples.
- Need for placing conducting coatings on insulating materials is virtually eliminated.

A schematic representation of the FE-SEM can be seen in Figure 17.
One disadvantage of the FE-SEM is the requirement for the sample to be made of, or coated with, a conductive material. Because of this, the samples were sputtered with carbon to form a coat of a few nanometers. Surface analyses were performed by FE-SEM at 20 kV (JSM-7001F, Jeol).

4.1.9. Focused Ion Beam (FIB)

A FIB instrument looks and operates much like a SEM: both rely on a focused beam to create a specimen image; an ion beam for the FIB opposed to an electron beam for the SEM. For both instruments, the intensity of the secondary electrons produced at each raster position of the beam is displayed to create an image of the sample. In the FIB, secondary ions may also be detected and used to construct an image of the sample.

Images having magnifications up to 100,000 times are available using a FIB with a very good depth of field. The operation of a FIB begins with a liquid metal ion source, typically a
reservoir of gallium (Ga\(^{+}\)) is positioned in contact with a sharp Tungsten (W) needle. The Ga\(^{+}\) wets the needle and flows to the W tip. A high extraction field (108 V/cm) is used to pull the liquid Ga\(^{+}\) into a sharp cone whose radius may be 5–10 nm. Ions are emitted as a result of field ionization and postionization and then accelerated down the FIB column.

The use of Ga\(^{+}\) is advantageous for two reasons: (i) Ga\(^{+}\) has a low melting point and, therefore, exists in the liquid state near room temperature, and (ii) Ga can be focused to a very fine probe size (10 nm in diameter). FIBs typically operate with an accelerating voltage between 5 and 50 keV. By controlling the strength of the electrostatic lenses and adjusting the effective aperture sizes, the probe current density (and therefore beam diameter) may be altered in order to modify the beam diameter [86].

The degraded layer and the residual imprints were characterized using a dual beam Focused Ion Beam/Scanning Electron Microscopy (FIB Zeiss Neon 40). A thin platinium layer was deposited on the sample prioro to FIB machining in order to minimize superficial ion-beam damage. A Ga\(^{+}\) ion source was used to mill the surface at a voltage of 30 kV. The final polishing of the cross section was performed at 10 pA.

### 4.2. Chemical Analysis

#### 4.2.1. X-ray Photoelectron Spectroscopy (XPS)

XPS is a quantitative superficial technique (5-15 nm) that allows the measurement of elemental composition, chemical and electronic state, and thus obtain the chemical formula of the elements present in a material’s surface. It is also known as Electron Spectroscopy for Chemical Analysis (ESCA).

The physical mechanism behind it is the photovoltaic effect, where a monochromatic X-ray irradiates the surface of study, and an electron collection lens focuses the emitted electrons onto an electron energy analyzer and detector. From there the data is processed by a computer and a human readable output is given.

Each photon of the monochromatic X-ray has the same energy \( h \cdot \nu \) (with \( h \) being the constant of Planck and \( \nu \) the wave’s frequency). Part of this energy is absorbed by the eletrons of the surface atoms, according to quantum physic laws. As the atom becomes unstable, it releases the absorbed energy by emitting a photon, whose kinetic energy \( E_{ki} \) will later be measured by the instrumentation. The formula on which this instrument bases itself is:

\[
E_{ki} = h\nu - E_{bi} - \phi_{sp} \tag{4.1}
\]
where $E_i$ is the bonding energy of the electron in the $i$ orbit, measured in respect to Fermi’s level of the sample (the zero energy level of the sample), and $\varphi_{sp}$ being the correction factor of the spectrometer [87] [88].

The instrument however is limited in the ability to measure elements of low atomic number, such as Hydrogen (Z=1) and Helium (Z=2). To minimize error, an Ultra High Vacuum is required for the analysis, as electron counting detectors are often situated up to 1 meter away from the surface of the sample.

The obtained energy measurements present specific peaks, such as those shown in Figure 18, thanks to which it is possible to determine the chemical composition of the surface. The peaks are determined for each type of bond and chemical compound, as different electrons have different bonding energies.

![Figure 18 - Example graph of elements spectra given by XPS [89]](image)

The experimental procedure includes adding carbon dust on the sample in order to be able to standardize curves. Because of the elements used in this project, only Yttria, Zirconia, Fluorine and Carbon were measured.

The machinery used is the PHOIBOS 225 by SPECS, whereas the results were analyzed using CasaXPS software.
4.3. Mechanical Testing

4.3.1. Nanoindentation

The nanoindentation is a functional and fast technique that can give a lot of information about the mechanical properties of different materials at nanometric scale, from soft to brittle materials. The principle of the technique is the evaluation of the response of a material to an applied load.

Depending on the tipped indenter used, different equations should be applied to study the response of the material, and thus calculate stress-strain curves, and parameters such as hardness, elastic modulus, toughness, yield strength and shear stress. These equations are related to the different deformation mechanisms (elastic and elasto-to-plastic) that the material undergoes [90].

A schemantic representation can be seen in Figure 19, the equipment for performing instrumented indentation test consists of three components:

i) an indenter of specific geometry, usually assembled to a rigid column through which the force is transmitted,

ii) an actuator for applying the force, and

iii) a sensor for measuring the indenter displacement.

Nanoindentations were performed using a Nanoindenter XP from MTS (Agilent Technologies). Continuous stiffness measurements (CSM) were performed during each
indentation to measure the hardness (H) and the elastic modulus (E) continuously as a function of the penetration depth for each test.

To avoid experimental error and deviated values, multiple nanoindentations were performed; in particular an homogeneous 3 x 3 matrix was done, with a distance of 50µm between each imprint in order to avoid any overlapping effect. The maximum depth value was set to 2000 nm or until reaching 650 mN as maximum load. In the case of 3Y-TZP Poisson’s value is 0.32 [91].

4.4. Tribology

Tribology is the science and engineering of interacting surfaces in relative motion. Major types of wear include abrasion, friction (adhesion and cohesion), erosion, and corrosion. The wear behaviour of engineering ceramics is relatively complex and is subject to many variables, with mechanisms including cracking, plastic deformation, tribochemical interaction, abrasion and surface fatigue.

Plastic deformation is favored when the load on the abrasive particles is small. This occurs as a result of small abrasive particles or low applied loads, when the abrasive is blunt or blunts during contact, and when the ratio of fracture toughness to hardness is high. The intersection of slip bands or twins with barriers such as grain boundaries, particles or other slip bands, can commonly lead to stresses which often give rise to crack nucleation and growth [92].

---

Figure 20 - Crack modes in polycrystalline ceramic [92]

A Tribometer TRM1000 by Wazau machine has been used, where a 3Y-TZP ball of 10 mm in diameter and a load of 5 N followed a linear path of 5 mm, for a total length of 10 m. The
tested samples were then observed via SEM, where the width of the wear was measured and damage mechanisms searched. A profilometer (see section 4.1.5) was used to obtain a profile perpendicular to the wear, to then measure the volume of abrasion. To simplify calculations, the following formulas were used to obtain the area and thus the volume, using the following equation:

\[ A = \frac{L}{N} \sum_{j=1}^{N} |h_j| \]  

\[ V = L \cdot A \]  

where \( A \) is the area, \( N \) is the number of steps, \( L \) is the total length and \( h \) is the height measured from the surface.

### 4.4.1. Nanoscratch

The same machine used for nanoindentation (see section 4.2.1) can also be used for nanoscratching (see Figure 21 for a representation), a technique which allows us to evaluate mechanical and tribological properties of the material. In particular we are looking for the friction coefficient (\( \mu \)) between the tip and the material.

![Nanoscratch linear test](image)

**Figure 21 - Nanoscratch linear test [93]**

We have used a progressing load, starting with 0 mN and increasing in a linear mode (with a direct correlation between distance and load, as shown in Figure 22) until 500 mN, having thus a total length of 500 \( \mu \)m, with 3 scratches per sample.
4.5. Fracture

4.5.1. Biaxial flexion “Ball-on-three-balls”

The mechanical essay to measure flexion resistance by means of bi-axial flexion was done with a ball-on-three-balls configuration. This technique is used on fragile materials such as ceramics and allows the samples to be of small size, in particular discs of 9 mm diameter and 2 mm in height.

The polished face is placed facing downwards, onto the three hard metal balls, which are equidistant from the center and have a diameter of 5.89 mm (see Figure 23). The top surface is put under pressure by a fourth ball in it’s center, which grows as the mechanism pushes down with constant speed. In particular a higher speed is chosen to avoid stable cracking in the zirconia, which most non-ceramic materials do not suffer.
The maximum tension is in the center of the lower surface, the polished one in this case, and depends on the geometry of the disc, the applied load, material, as well as the shape and position of the balls. This unfortunately gives room for error, and adding to that the random material defects, calls for a statistical analysis of the results.

### 4.5.1.1. Weibull Statistics

To obtain statistically meaningful results up to 15 specimens were fractured and analyzed through Weibull statistics [95]. The maximum stress was obtained through the following equation:

\[ \sigma_{\text{max}} \approx \frac{3F(1 + \nu)}{4\pi t^2} \left\{ 2\ln \left( \frac{R}{\alpha t} \right) + \frac{1 - \nu}{1 + \nu} \left( \frac{R}{R_D} \right)^2 \right\} \]  

(Eq. 4.4)

where \( R_D \) is the diameter of the disc, \( \nu \) is Poisson’s ratio (0.32 for 3Y-TZP), \( \alpha \) is an adimensional parameter (0.2 for ball-on-three-balls), \( F \) is the applied force, \( t \) is the thickness of the disc, and \( R \) is the radius of the virtual ball-bearing ring.

Considering the failure probability resulting in Eq. 4.5, with \( N \) being the total amount of samples and \( n \) the rank of the sample if put in crescent order of \( \sigma_{\text{max}} \).

\[ p_f = \frac{n}{N + 1} \]  

(Eq. 4.5)

To better visualize the results logarithmic scales are to be used, and linear fitting gives us a graph similar to Figure 24.
Figure 24 - Weibull plot with linear fitting
5. Results and Discussion

5.1. HF Etching

5.1.1. pH

In the experiments done in this research project there was no relationship found between the pH and the results. In fact, the pH does not seem to have any effect on the etching of 3Y-TZP. Because of this, further discussions regarding pH will be avoided. In Table 9 is shown the pH of various concentrations of HF.

<table>
<thead>
<tr>
<th>HF concentration (mol %)</th>
<th>5</th>
<th>10</th>
<th>20</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
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<td>4.5</td>
<td>4.1</td>
</tr>
</tbody>
</table>

5.1.2. Weight Loss

The graph in Figure 25 was obtained with averages that were measured with four samples per condition, before and after the chemical etching. This is considering the weight/surface ratio being the same for all samples. We can observe that the initial phase of attack is faster in higher concentration (20 mol %) during the first 4 hours. After that, the chemical attack remains quite linear with time. However, for soft chemical etchings (5 and 10 mol %), this attack is slower, whereas the rate becomes linear after the first 4 hours. Therefore, during the first four hours, no significant weight loss effects have been observed.
5.1.3. Roughness

The results of chemical etching upon the 3Y-TZP samples could be seen by the naked eye in some cases, with the sample being opaque instead of reflective. In some particular cases, the center of the sample was smoother than the side closer to the edges. Microscopic images of 50 by 50 µm² obtained by AFM (3D image mode) can be seen in Figure 26, showing the surface at micrometric scale after chemical etching.

However, the RMS values were slightly offset by random peaks caused by outside debris that were impossible to get rid of through cleaning. Considering their consistency among all the samples, their influence was ignored as seen of little influence, whereas more importance was given to the general comparability of the data.
Figure 26 – AFM image (3D mode) of 50 by 50 µm² scan
The RMS ($R_m$) obtained through the WSxM software [82] was measured for each of the conditions and the results can be seen in Figure 27. We can see that for 20 mol % HF did not show significant roughness under 4 hours, but disregarding errors, we can say that roughness grows linearly after such time. In addition, for low concentrations of HF the etching effect is not considerable for periods of time under 14 hours, but is more significant in longer periods.

![Figure 27 - RMS in function of time](image)

Another observation is the reaching of the same RMS with times that are proportional to the HF concentration, in particular 20 mol % gives approximately the same RMS in half the time of 10 mol % and 1/4th of HF 5 mol %. By doing a linear fit we can obtain the graph in Figure 28, where it is easier to observe the linear growth of roughness increase speed.

The linear equation obtained from data shown in Figure 27 is of the form:

$$RMS = m \cdot t + b$$  \hspace{1cm} \text{Eq. 5.1}

with $m$ being a product of the concentration in molar % and a constant that was determined experimentally to be between 0.5 and 0.6, and $t$ the time in hours. The constant depends on the activation energy of the surface etching mechanism, taking up to 4 hours to enter linear mode. It is to be remembered that this is only observed for concentrations of 5, 10 and 20 mol %, with room temperature (20ºC), and is probably dependent on the temperature itself.
Profiles along the 50µm of study taken from the AFM scans show in greater detail the difference of roughness obtained by chemical etching in function of time. In Figure 29a, with etching times of half an hour, we see similar profiles, with higher molarity having higher peaks and lower valleys, as well as rougher than the 5 mol % HF one. In contrast, Figure 29b, with an etching time of 4 hours, shows a much higher and rougher profile for 20 mol % HF in comparison to the other two etchings.
We can also observe that with longer times and higher concentration, the peaks and valleys are sharper, in comparison to more rounded angles of the less etched samples, as well as the distance between peak and valley being around 20 nm, being of the same order as the roughness. This is possibly the reason why roughness was not observed during the first stages, with etching time under 4 hours. This is more visible in Figure 30, where a 5 µm profile of a smaller area (5 by 5 µm²) was studied.

![AFM profiles of etched samples with t=0.5 h](image)

**Figure 30 - AFM profiles of etched samples with t=0.5 h**

With the longest examined time, 24h (Figure 31), the profiles are again more similar in terms of roughness, with sharp peaks and valleys appearing in all three cases. Also observable is that the distance between peaks and valleys (d=800 nm) is higher to the previously shown Figure 29b (d=400 nm), and approximately 45 times higher than that of half hour etching. The rate of increase of this distance is lower as time progresses.
In all these observations it is important to note that with AFM only the surface could be studied, and not the porosity, which was also obtained, as observed through FE-SEM and FIB analyses. The obtained porosity however is of a very superficial form and can be explained by the attack of different grains, thus creating small pores with low penetration depth.

In Figure 32 we can observe the high roughness and porosity of a 24 h etched sample in 20 mol % HF solution. Pores appear only in the superficial layer, and are scarce but noticeable. The cause for these pores seems to be a preferred attack grain, which once etched becomes the destination of further attacks, making few big pores instead of many small ones.
5.1.4. CLSM

CLSM analysis showed relatively few results, because the resolution did not permit to observe the surface at a nanometric scale, thus only macroscopic observations were made.

Low HF concentrations and etching times gave very similar results, not very distinguishable from the polished sample. However, the etching brought to light polishing rays that were not possible to be seen in polished samples, as shown in Figure 33.
Correlation between chemical treatment and the superficial and mechanical properties of zirconia

Figure 33 - CLSM images with 50x zoom of a) polished 3Y-TZP and b) 10 mol % HF etched with t=0.5h

Through CLSM observation a few peculiarities were found: pitting-like degradation of 3Y-TZP was observed in particular phases (10 mol % at 7 h and 9 h, 20% at 0.5 h) of the etching process, such as those seen in Figure 34.

It is possible that the HF etching process includes this step, to then proceed expanding the affected area and achieve a homogeneously etched surface. This is why in short times the etching is heterogeneous and as time increases, becomes more homogeneous.
5.2. Chemical Properties

5.2.1. XPS

XPS allowed us to study the evolution in time of the chemical composition of the surface layer (up to 5 nm deep) of the samples. There seems to be a build up of fluorine on the surface of the samples up to \( t=1 \) h and \( t=4 \) h in the 20 mol % and 10 mol % solutions, respectively, whereas for the 5 mol % solution a longer time is likely needed (see Figure 35), as it is clearly seen the trend is positive but no peak is seen. Once a peak is reached (circa 35% atomic concentration), the mechanism activates and starts etching the material more rapidly, thus decreasing the amount of F on the surface, which dissolves in the solution.
One of the newly formed compounds is metallic yttrium (Y), according to the XPS binding energy peaks, as well as yttrium fluoride (YF$_3$), the existence of which is confirmed by the Yttrium-Fluoride relationship observable in Figure 36. There is a 1:3 relationship between Y and F in the time period of the first 2 hours, which subsequently decreases to become 1:2. We can thus suppose Y in its metallic form is most present in the samples etched in 20 mol % HF for short periods of time, to be then superseded by Y$_2$O$_3$ and YOOH [96], with traces of YF$_3$. 
With longer times we can observe the formation of metallic yttrium (Y) in small quantities, which possibly has formed with shorter times but suffered oxidation (forming Y$_2$O$_3$) before it was analyzed.

Research was limited due to time constraints and further analysis of the data could give more interesting results regarding the stoechiometry of the compounds found on the surface.

5.3. Mechanical Properties

5.3.1. Nanoindentation

Figure 37 shows the hardness (H, left column), and the elastic modulus (E, right column) against penetration depth. Both hardness and elastic modulus were found to change widely in the specimens because of their different porosity. A correlation between hardness, elastic modulus and roughness can be seen in all the samples: with increased etching time, hardness and elastic modulus decrease. However, the hardness trend for the specimens etched during 14 and 24h are more or less overlapped. This is because the depth of the etched layer remains the same and only moves deeper into the sample, redissolving complete layers of material.
The lowest hardness value is that of the 20 mol % HF etched sample for a period of 24 h, reaching 10 GPa as highest, compared to a 17 GPa of 5 mol % HF at 0.5h. The source of this hardness difference could be from three reasons: (i) machine limit, where maximum force was limited to 650 mN, (ii) geometrical difference, that is to say, porosity, (iii) phase transformation, and/or (iv) chemical modification, where the Y-ZrO₂ equilibrium was changed by the etching. The latter was checked using XPS, see section 5.2.1.

A closer inspection of the curves of etched specimens reveals that, after a certain penetration depth, the elastic modulus and hardness tend to recover their values for non-etched specimens because of the effect of the healthy non degraded material beneath the affected surface layer.

Comparing the obtained values of E to literature [42] [43], we may notice that the topmost values, obtained from analysis of 0.5 h etched samples with 5 mol % HF, are matching. However, the values for and H are slightly higher than the literature ones [42] [46], but similar to more recent results obtained by Gaillard et al. [44].
Figure 37 - Hardness and Elastic modulus values of etched 3Y-TZP in function of penetration depth a) 5 mol % HF, b) 10 mol % HF, and c) 20 mol % HF
During the analysis of the nanoindentations, pitting-like shapes were again observed (Figure 38), as previously discussed (see section 5.1.4). The height difference is under 5 nm, as observed by AFM.

![Figure 38 - FE-SEM image of a Nanoindentation array 7 h HF 10 mol % etched sample.](image)

After the superficial surface observation of the nanoindentation array, a sub-superficial study has been performed using FIB in order to observe the etched layer and the grain reaccomodation under the imprint. In Figure 39 the thickness of the etched layer is variable and areas with higher porosity can be observed, ranging from 300 nm to 400 nm. Grain size also appears to be constant throughout all the observed samples, although no thorough study was done.
An increase in porosity can be observed at the sides of the sample etched for 7 h, in Figure 40. The central area is lacking porosity because it has been compressed through nanoindentation. In the same area (just under the imprint) we can observe an apparently smaller grain size distribution, an effect of compaction from nanoindentation, compared to the normal grain size of 3Y-TZP, which is in the order of 300 nm. Furthermore, this image exhibits the etched layer is lower than 1 μm, in particular a) measures 520 nm and b) measures 640 nm.
5.4. Tribological Properties

5.4.1. Nanoscratch

Through nanoscratch the coefficient of friction $\mu$ was determined for the different samples of study with different rugosities. In Figure 41 the trace (bottom) and retrace (top) profiles can be observed, where higher concentration shows more vertical spread, given by the lower density and higher roughness of the superficial layer. The elastic deformation is the difference between the trace and retrace. However, the plastic deformation is the difference between the retrace and the surface (penetration depth = 0 nm). The plastic deformation appears to be higher for higher concentrations, but this is probably due to the easier abrasion of the topmost layer.

![Figure 41 - Penetration depth vs. scratch resistance](image)

A comparison of the friction coefficient to time is given in Figure 42. To note is the coefficient of friction of non-etched 3Y-TZP being 0.12, which we also see with the lightest etched (30 min and 5 mol $\%$ HF) sample’s 200-300 $\mu$m scratch.

Short periods of etching bring results which are similar to pure zirconia, as not enough damage is done to the superficial layer, or rather: only the very superficial part is actually being attacked in a light way. This means that right underneath the thin layer, the ceramic is left untouched.

Increasing etching strength and time brings fluctuations, caused by the heterogeneous material in which we have obtained superficial porosity. This is especially noticeable in Figure
42c, with longer periods of time. The results are what we expected, considering the increase of roughness and superficial porosity formation. It also means that the distance between peaks is in the same magnitude of the nanoscratching precision, and that macroscopic friction tests should give more homogeneous results.

The tendency of the friction coefficient is decreasing in function of stronger and longer etching, most likely because of the aforementioned heterogeneous structure created by etching. However it is also possible that phase changes have occurred and brought a decrease in friction.

![Friction coefficient vs scratch distance](image)

**Figure 42 – Friction coefficient vs scratch distance in a) 5 mol % HF, b) 10 mol % HF and c) 20 mol % HF etched samples**

Through FE-SEM we have observed the truck of the nanoscratch (see Figure 43), where we can notice small crack-looking elements formed at the top of the scratched layer, but also deeper in the scratch. The cracks closer to the surface are more likely to be actual pores...
formed by HF etching, whereas the ones closer to the center are caused by the fragility of the ceramic, as porosity is absent.

Also observable is the superficial roughness and likely porosity obtained in the untouched areas. This shows that although AFM analysis is of great use (see section 5.1.3), it does not furnish complete data regarding the surface, leaving out porosity as a hidden feature.

5.4.2. Wear tests

The profiles through the wear truck were obtained using the profilometer (see section 4.1.5). The obtained profiles with the area measured highlighted in light blue can be seen in Figure 44, regarding 5, 10 and 20 mol % HF etched samples. We can observe the increase of the area, as the time of etching increases.

Something to notice is the roughness in the worn area, which shows us that adhesive forces are stronger than abrasive forces, accumulating debris in the canal.
In Figure 45 we can observe that the speed of wear of zirconia on etched zirconia. Each graph has a first peak at 1 h, 2 h and 4 h, respectively to 20 mol % HF, 10 mol % HF and 5 mol 5 % HF. After the peak, it is possible that the activation mechanism takes place, leaving a structure that is more resistant to wear. On the other side, we can clearly see that higher etching times and acid concentration lead to faster wear rates, while a constant wear rate is
observed for 5 mol % HF etched samples, with a possible increase of wear rate with t>24 h. Further studies are needed to confirm these hypotheses.

Figure 45 - Wear rate of Zirconia on etched Zirconia

In Figure 46 we see a FE-SEM image of the wear truck left by the zirconia ball with the according measurement of the truck length. Noticeable are the irregularities left in the truck, with an apparent sub-microscopic roughness.

Figure 46 - FE-SEM image of wear truck on t=0.5h 10 mol % HF etched 3Y-TZP

In Figure 47 we can see a close up of the details, with a) depicting the beginning of the truck, where contact was first struck as there are less debris along the borders, b) the central part
with a more homogeneous texture and c) the tail of the truck, where most debris are accumulated on the first scratch.

Figure 47 - FE-SEM detailed images of wear truck on t=7 h 20 mol % HF etched 3Y-TZP
   a) being the beginning of the truck, b) the central part and c) the end

Figure 48 compares the trucks of a 20 mol % HF etched for 7 hours sample, on the left, with one etched for 0.5 h in 10 mol % HF, on the right. The most obvious difference is the width of the two trucks, with the more attacked one being wider, as it was easier to remove mass from it and thus the sphere could go deeper into the sample.

Another difference we can spot is the rougher surface on the image on the left, where adhesive forces are strong enough to hold the generated debris attached to the surface. The same effect can be seen in Figure 44.
Correlation between chemical treatment and the superficial and mechanical properties of zirconia

Figure 48 - Detail of a) 7 h etched sample in 20 mol % HF and b) 0.5 h etched sample in 10 mol % HF

5.5. Fracture

5.5.1. Ball-on-three-balls

Figure 49 gives us a graphic overview of the Weibull statistics interpretation of the ball-on-three-balls fracture tests. A vertical line was drawn to depict the failure stress of non-etched 3Y-TZP to be able to compare other results. It is slightly lower to that of Borchers et al. [48].

For 4 and 14 hour etchings we can see the tension decrease, due to the homogeneous degradation, giving us a thinner virgin zirconia sample underneath the etched layer, compared to other samples. This allows the fracture to occur with a lower tension value.

The same effect is not seen with the 10 mol % HF etched samples, as we have already seen in AFM analysis (see section 5.1.3) where roughness was still low in comparison to higher molarity HF and/or attack time. Here we see that the degradation begins to be of importance
with etching times longer than 7 h. On the other hand, the roughness we have introduced is not so important, keeping the fracture constant, within margin of error, with etching times under 7 hours.

The ball-on-three-balls fracture essay gave expected results, where degradation of the upper layer changed only slightly the mechanical properties of the sample. It is important to consider the standard deviation in this case, which makes the graph more reasonable, in the fact that while the failure stress does indeed decrease, it does so in a not very significant way.

The higher than expected difference of failure stress comes from the fact that Weibull measures the failure stress of a surface, not of the whole element, and we also have to keep in mind that the results are statistical and not absolute.

![Graph](image)

*Figure 49 - \( \sigma \), of Weibull statistical fittings*
Conclusions

The main conclusions are summarized as follows:

a) An efficient way to increase surface roughness is HF etching, with the roughness value controllable by the concentration of HF and the time samples are exposed to it. RMS increases in a linear way, with double concentration meaning double speed (with HF concentrations between 5 and 20 mol %).

b) The pH does not appear to have an effect on roughness, nor on other mechanical properties, it is instead the concentration of HF and time of etching that determines roughness, at room temperature.

c) Weight loss % is constant in time, showing a linear relationship in function of the initial concentration of HF. Mass however is not directly proportional to the concentration, with higher concentrations consuming mass faster in the beginning, and linearly after the first 4 hours.

d) No superficial microcracks were observed following HF etching through AFM and FE-SEM, nor were internal microcracks found through FIB and FE-SEM. However, microcracks were found in nanoscratched trucks through FE-SEM observation.

e) 3Y-TZP shows good structural and mechanical stability in the corrosive solution, having little to no change in fracture toughness, despite having rugose structure, as this is only a very superficial layer.

f) Chemical analysis shows an evolution of the compounds present on the surface, as well as presence of YF₃ and Y in small quantities.

g) The surface hardness and the elastic modulus is significantly decreased on the surface, especially with longer times and higher concentration HF. For weak etchings, depths after 600nm show little to no change, whereas for stronger etchings the effects can be seen for depths of up to 2 µm.

h) Short periods of etching bring friction coefficients that are similar to pure zirconia, underneath the thin layer the ceramic is left untouched.

i) Wear tests show adhesive forces being stronger than abrasive forces when roughness is low.
Costs and Environmental Impact

Costs

The main expense of the project has been that of laboratory personnel, sinterization oven and advanced technique (FIB, Nanoindentation) analysis machines. An estimation of the total cost follows:

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<thead>
<tr>
<th>Personnel</th>
<th>Cost</th>
<th>Nº of hours</th>
<th>Total (€)</th>
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<tr>
<td>Junior Engineer</td>
<td>15 €/h</td>
<td>400</td>
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<tr>
<td>Laboratory Technician</td>
<td>50 €/h</td>
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<tr>
<td>Tutor (Ph.D.)</td>
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Subtotal: 11,000 €

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<td>Lubricant Buehler Cool</td>
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Subtotal: 367.95 €
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**Subtotal:** 9,305 €

**Total Spending:** 20,672.95 €

**Environmental Impact**

The main environmental impact are the chemical wastes produced from manufacturing the samples, including lubricants, diamond slurries and HF, as well as energy used for the tubular oven, among other things. To try to reduce the environmental impact, HF waste and lubricantes were collected for disposal according to local laws. The same was not possible for diamond slurries, as the machinery drainage was directly connected to the hydraulic system.

A big quantity of water was used during the polishing and cleaning process, also paper for general purpose and gloves for safety.
Future Works

There appears to exist a relationship connecting acid concentration, time and obtained surface roughness, similar to that of plastic deformation over time vs temperature (creep). Further investigation with smaller time intervals could bring to light the relationship between time, concentration and etching effects.

Research also needs to be done in the biocompatibility of the different rugosities, in order to determine what is considered to be the optimal roughness for each element of the implant, allowing precise studies to be made with a clear aim, as well as further analysis of XPS data.

The composition of different techniques should also be considered, such as sandblasting previous to HF etching, in order to obtain both micro- and nanometric roughness.

While fracture tests have been done, there was not enough time to analyse through FE-SEM the obtained fractured samples, in order to better understand how the fracturing process works.
Aknowledgements

I would like to thank:

• The Erasmus LLP for making this exchange a reality.
• Prof. Marc Anglada for giving me the opportunity to work on this project.
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Bibliography


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