FOCUSED ION BEAM TOMOGRAPHY OF THE DAMAGE PRODUCED IN ZIRCONIA TOUGHENED ALUMINA

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ABSTRACT

Two different three-dimensional reconstructions of the crack propagation induced by mechanical testing in zirconia-toughened alumina (ZTA) were made. The first tomography is of the damage caused by an indentation, with the objective to visualize how the crack propagates inside of the material and how it interacts with the different phases that compose the material. The second reconstruction is based on the damage caused by a scratch test on the surface of the material and the fissures generated. By doing a Focused Ion Beam (FIB) tomography it is possible to understand what happens inside of the material when a mechanical test is performed, instead of just the surface. From the fissures obtained by both the indentation and the scratch tests, it can be calculated if the crack has a phase propagation tendency, the tortuosity of the crack, the crack opening displacement and a complete characterization of the material. Also, the precise reconstruction of the microstructure and geometry of the different phase grains is possible. A comparison between the two samples is done regarding all the previously mentioned aspects to study.
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1. Preface

1.1. Origin of the Project

This project is part of an ongoing research directed by the Prof. Emilio Jiménez Piqué from the Department of Material Science and Metallurgy that concerns tomography reconstructions executed with focused ion beam of advanced ceramic materials. The study pertains the deep understanding of materials in three dimensions, by being able to characterize its internal structure and composition while having an adequate visualization of the material. For the better comprehension of damage inside the material, three-dimensional reconstructions prove to be a highly capable resource.

1.2. Motivation

Great improvements have been made over the last thirty years in advanced ceramics for applications in orthopedics. High performance ceramic composites seem to have the qualities necessary for a successful total hip arthroplasty. Alumina-based composites are one of the most common and successful advanced materials used for femoral heads of hip replacements. This composite has been well studied over time and there are multiple reports on its properties and characterization, but there is lack of information in three dimensions of damage produced to the material. Focused ion beam tomography aids in characterizing in three dimensions the composite and being able to calculate precise volume information and phase interaction.

1.3. Project Aspects

This investigation is held within the Structural Integrity and Reliability of Materials Center (CIEFMA) research group of the Department of Material Science and Metallurgy. The laboratory equipment used for the experiments is located in the Universitat Politècnica de Catalunya research center named
the Centre de Recerca en Nanoenginyeria (CRnE). Most of the information
gathered for this investigation came from the Focused Ion Beam system of
the CRnE laboratory. The three-dimensional tomography reconstructions were
done in the well-equipped computer station of this same research center with
all the necessary accessories to aid in the reconstruction. The software used
for the reconstructions and volume analysis is the Avizo Fire 8.0. Avizo is a
three dimensional data processing, modeling and analysis software.
2. Glossary

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
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<tbody>
<tr>
<td>ZTA</td>
<td>Zirconia Toughened Alumina</td>
</tr>
<tr>
<td>FIB</td>
<td>Focused Ion Beam</td>
</tr>
<tr>
<td>APT</td>
<td>Atom Probe Tomography</td>
</tr>
<tr>
<td>LMIS</td>
<td>Liquid Metal Ion Source</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
</tr>
<tr>
<td>HV</td>
<td>Vickers Hardness</td>
</tr>
<tr>
<td>$K_{ic}$</td>
<td>Fracture Toughness</td>
</tr>
<tr>
<td>HIP</td>
<td>Hot Isostatic Press</td>
</tr>
<tr>
<td>$E$</td>
<td>Elastic Modulus</td>
</tr>
<tr>
<td>$\tau$</td>
<td>Crack Tortuosity</td>
</tr>
<tr>
<td>COD</td>
<td>Crack Opening Displacement</td>
</tr>
</tbody>
</table>
3. Introduction

Over the last thirty years there has been an increase in the interest of technical ceramics for orthopedic implants. The development of hip arthroplasty components has raised concerns regarding the implant design and the material selection. The bearing materials used for the implantation, play a decisive role on the size, volume and resistance to abrasion. It has become important to use materials that do not trigger hypersensitivity and allergic reactions, therefore it is needed an implantation material that exhibits a biologically compatible behavior in the body [1, 2]. Nowadays, there is a high demand for better, more resistant materials for the younger and more active patients [3]. High performance ceramic composites seem to have many of the qualities necessary for the success of total hip arthroplasty.

Advances in manufacturing technology have resulted in a greater density, lower porosity and an increase in the fracture toughness, making these ceramics a more feasible option [4]. Alumina-based materials are currently used for total hip replacements as the femoral head, since they offer significant reductions in bearing wear rates that make them suitable for prosthesis.

It is important to characterize the damage produced in these materials by fissuration and wear in order to assure the structural integrity and reliability of the product. Due to the complexity of the microstructure with two main phases, a 3D characterization should provide a deeper insight on the interaction between microstructure and cracking. Focused ion beam tomography has been performed (FIB) in order to have an optimal material visualization and understanding. A three dimensional reconstruction of the alumina matrix composite is made from the different inflicted damage showing the fissures generated and its behavior. By reconstructing the material, precise characterization is possible.
3.2. Tomography

Tomography is the technique to reconstruct an object in 3D after the acquisition of sequential images in 2D. There are many kinds of tomography methods ranging from x-ray tomography, sequential mechanically polished sections, atom probe tomography and FIB tomography. The main difference between these techniques is the physical phenomenon used for sectioning and therefore, its resolution and applications. In Table 1, it can be seen some of the different types of tomography and the resolutions that can be obtained. The FIB tomography was used in this investigation for material slicing, in the next section it will be discussed it’s principle and functioning.

<table>
<thead>
<tr>
<th>Type of Tomography</th>
<th>Spatial Resolution</th>
<th>Use</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atom Probe Tomography (APT)</td>
<td>$10^{-10}$ m [5]</td>
<td>Material Science</td>
</tr>
<tr>
<td>Focused Ion Beam Tomography (FIB)</td>
<td>$10^{-8}$-$10^{-6}$ m [9]</td>
<td>Semiconductor Industry, Material Science, etc.</td>
</tr>
<tr>
<td>Neutron Tomography</td>
<td>$10^{-6}$ m [6]</td>
<td>Mineralogy and Geochemistry</td>
</tr>
<tr>
<td>X-Ray Tomography</td>
<td>$10^{-6}$-$10^{-4}$ m [7]</td>
<td>Geoscience, Medicine, etc.</td>
</tr>
</tbody>
</table>

3.3. The Focused Ion Beam System (FIB)

The Focused Ion Beam System (FIB) is an important tool for understanding and manipulating the structure of materials at the nanoscale. The FIB’s principle consists of directing a beam of high energy ionized atoms of a relatively massive element, in this case Ga⁺, produced by a liquid-metal ion source (LMIS) at the top of the column [8]. In the Figure 1, it is shown the schematic of the FIB system, including the liquid metal ion source.
Figure 1. The Focused Ion Beam System

Gallium is the most commonly used as a LMIS in FIB systems for a number of reasons:

i. It has a low melting point
ii. It’s mass is heavy enough to allow milling of heavier elements, but not excessively heavy that destroys the sample
iii. It has low volatility at the melting point
iv. Low vapor pressure
v. Can be easily distinguished from other elements

The Ga\(^+\) ions are then accelerated and focused into a beam by an electric field [8]. This system allows working on specific sample regions while preserving the integrity of the sample.

By focusing the beam of ions into a sample, four basic outcomes may be possible dependent on time and current intensity:

- Milling
- Deposition
- Implantation
• Imaging

As a result of using ions with relatively high mass, milling is achieved in the sample surface [9]. Deposition is also possible if an organometallic molecule is adsorbed at the surface inserted by a gas injection system. When combined with milling the FIB deposition can create almost any microstructure, such as the gold nanoboxes shown in Figure 2 [10]. Ion implantation is as well, an important tool commonly used in the semiconductor industry [11].

![Figure 2. Au Nanoboxes (Osaka University) [10]. This nanoboxes were created with the FIB by a combination of deposition and milling.](image)

The focused ion beam may also be used for imaging but can cause damage to the sample. This is where the cross-beam FIB/SEM system, both the electron beam and ion beam in a single microscope, work as a single system that can function as an imaging, analytical, and sample modification tool [9]. Both systems are placed in fixed position with an angle of 45-52° degrees between the two beams for best performance, allowing sample imaging and modification without having to move the sample, as can be seen on Figure 3.
3.4. Zirconia Toughened Alumina Composites

The material used for the tomography is an alumina matrix composite known as zirconia toughened alumina (ZTA), in specific the commercial brand Biolox® delta. This material is used for hip arthroplasty, for the phemoral heads of the hip replacements as the ones shown on Figure 5. These phemoral heads are shaped using hot isostatic pressing (HIP) technology for its near-net shape. The ZTA is used because of its many characteristics that are optimal for hip prosthesis, such as its hardness, surface smoothness, excellent wettability, resistance to wear, stability and biocompatibility [2]. Table 2 presents the mechanical properties of ZTA, obtained from the manufacturer.

The material is comprised of an alumina rich continuous matrix (81%) with evenly distributed zirconia particles as the secondary phase (roughly 17%), the composition can be seen on Table 3. Yttria (Y₂O₃) is added as a phase stabilizer of the metastable tetragonal zirconia. On the SEM image shown on Figure 4, the white grains are the zirconia phase and the grey phase is the alumina matrix. It can also be seen the needle-like platelets. The
needle-like platelets are composed of alumina and SrO and are homogenously distributed in the alumina matrix. Zirconia phase transformation mechanism and the platelets act as a crack stopping mechanism in the ZTA (see Figures 6 and 7). The zirconia acts as a crack stopping mechanism by the stress induced volume expansion caused by the propagation of the crack, which leads to the tetragonal to monoclinic phase change. The needle-like platelets tend to deflect the crack when it reaches the platelets, thus impeding the continuation of the propagation and consequently increasing the overall material strength. The $\text{Cr}_2\text{O}_3$ (<1% of total volume fraction) is in a solid state solution with the alumina matrix compensating for the drop in hardness caused by the addition of the zirconia. The monolithic alumina phase when combined with the tetragonal zirconia brings advantageous properties resulting in a higher strength and fracture toughness, while maintaining its elastic modulus and hardness, as can be seen on the properties shown on Table 2 [4].

Table 2. Mechanical Properties of Zirconia Toughened Alumina (Biolox® delta) (adapted from [2])

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>4.37 ± 0.01 g/cm³</td>
</tr>
<tr>
<td>Grain Size $\text{Al}_2\text{O}_3$</td>
<td>0.56 ± 0.036 μm</td>
</tr>
<tr>
<td>4 point bending strength</td>
<td>1384 ± 67 MPa</td>
</tr>
<tr>
<td>E-module</td>
<td>358 ± 1 GPa</td>
</tr>
<tr>
<td>Fracture Toughness</td>
<td>6.5 MPa·m$^{1/2}$</td>
</tr>
<tr>
<td>Hardness HV1</td>
<td>19 GPa</td>
</tr>
</tbody>
</table>
Figure 4. SEM image of the ZTA surface. The white grains are the zirconia phase and the grey grains are the alumina. The needle-like platelets composed of alumina and SrO can be observed in this image.

Figure 5. Zirconia Toughened Alumina (ZTA) composite phemoral heads Biolox® delta. These phemoral heads are shaped by hot isostatic press [2].
Table 3. Chemical Composition of Zirconia [2].

<table>
<thead>
<tr>
<th>Component</th>
<th>Volume Fraction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZrO₂</td>
<td>17</td>
</tr>
<tr>
<td>Y₂O₃*</td>
<td>0.55</td>
</tr>
<tr>
<td>Cr₂O₃**</td>
<td>0.3</td>
</tr>
<tr>
<td>SrO*</td>
<td>0.6</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>81.55</td>
</tr>
</tbody>
</table>

*Stabilizers, **Additives

3.4.1. Phase Transformation and Physical Properties

The stress induced phase transformation in zirconia from the metastable tetragonal phase (t) to the monoclinic phase (m) at ambient temperature results in a volume expansion of 4% and an approximate 7% increase in shear strain (see Figure 8) [12]. Inelastic deformation is induced in the polycrystalline ceramic in consequence of the change in volume. The monoclinic phase zirconia has a lower hardness and lower fracture toughness in comparison to the tetragonal phase. In ZTA materials enhanced crack propagation resistance is achieved via the transformation of t→m, also known as the crack stopping mechanism.
as the martensitic transformation, that occurs around the crack tip (see Figure 9) and requires additional energy to propagate through the new compressive layer of monoclinic zirconia [4].

Martensitic transformation is affected by many factors such as yttria content, thermal history, grain size, and water environment, among others. The increase in the zirconia phase volume opposes crack propagation enhancing fracture toughness.

The martensitic transformation leads to a material that is more susceptible to damage and surface roughening because of the volume expansion, thus increasing the wear rate, which is undesirable for applications of hip bearing [14]. Zirconia possesses a stable monoclinic structure at room temperature and by introducing a dopant such as yttrium oxide (yttria) it can retain the metastable tetragonal phase, which is stable only at high temperature. Yttria is used as a phase transformation decelerator, hence, stabilizing the monolithic zirconia at room temperature. By controlling the composition and processing conditions it can be manufactured a ZTA material that retains a metastable phase that transforms to a stable phase at room temperature when it is exposed to stress [15].
By controlling the martensitic transformation it can be improved the mechanical properties of these ceramics [16-19]. Alumina aids in the increase of the bending strength and hardness of the ZTA [21, 22]. Alumina is a very stable matrix that encases the phase transformation of the zirconia and prevents the transformation from propagating to neighboring grains.

It has been found that the smaller the grain size of the metastable tetragonal phase the more difficult is the transformation [20]. The amount of transformation increases with an increase in isothermal aging time. The driving force for the $t \rightarrow m$ transformation at a given temperature becomes greater as the yttria content decreases [20]. A water environment acts as a trigger to initiate the transformation and results in a degradation of the mechanical properties [18, 19]. The performances of these ceramics depend on the control of the behavior of the transformation by adjusting composition and the manufacturing process [14].
4. Objectives

The present study aims to access the different mechanisms that occur inside of the zirconia toughened alumina when damage is inflicted in the surface by doing a FIB tomography three-dimensional reconstruction. Two mechanical tests were performed on the surface: the indentation and the scratch test. It is of these two samples that the study is based upon. The following points are the main objectives of this project.

i. Produce damage to the surface of the samples. The first sample consists of a Vickers indentation test, it is from the print left behind and the subsequent fissures that the area for the FIB tomography is chosen. The second sample consists of a scratch test with increasing force that left behind a series of microfissures in its trail, an area with microfissures was chosen for the tomography.

ii. To obtain a series of ZTA slices from the FIB tomography. These images will be joined and worked on, which give the tomography reconstruction.

iii. Characterize the behavior of the fractures produced by the surface damage.

iv. Determine if the crack has a tendency to propagate towards any specific phase in the ZTA.

v. Characterize the microstructure of the 3D reconstructions.

vi. Determine the reconstruction information such as: volume, surface area, grain size, phase contiguity, crack opening displacement, percentage of material densification, among others.
5. Experimental Methods

5.1. Material Characterization

Vickers hardness microindentation tests were performed on the surface of the zirconia toughened alumina in order to produce fissures on the material and study its behavior and characteristics. In addition, scratch tests were made to observe the micro-fissures typical to this kind of damage on the material surface. The following sections will provide more detail on the mechanical tests performed.

5.5.1. Hardness and Fracture Toughness by Vickers Indentation

Measuring the hardness and fracture toughness of the ZTA was made with a Vickers Hardness Test. The Vickers hardness uses a square based pyramid diamond indenter with an angle of 136 degrees between the opposite faces at the vertex. The tip is pressed into the surface of the material leaving an area imprint. The ratio between the maximum applied load and the area of the imprint is the Vickers Hardness ($H_v$), and it is defined by the equation:

$$H_v = 1.86 \frac{P}{d^2}$$  \hspace{1cm} (1)

where $P$ is the maximum load applied and $d$ is the average length of the diagonals of the imprint [23].

The measured $H_v$ by using a maximum load of 30kg was of $18\pm1$ GPa. The hardness value given by the commercial producer is of $H_v=19$GPa, being this value in the same range as the measured value.
The radial cracks generated in this kind of brittle materials are Palmqvist cracks (see Figure 10) and can be evaluated using a fracture-mechanical and dimensional analysis technique [24]. From the image shown in Figure 10, it can be seen the resulting crack and its tortuosity. Fracture toughness ($K_{lc}$) was measured with the Vickers hardness microfracture indentation method by calculating the $K_{lc}$ as a function of the lengths of the cracks that emanate from the indentation with the Niihara method equation:

$$K_{lc} = 9.052 \times 10^{-3} \frac{H^2}{E} \frac{d}{l}^{1/2}$$  \hspace{1cm} (2)$$

where $E$ is the elastic modulus and $l$ the crack length. In order for the model to be consistent it should meet the requirement of imprint mean diagonal to crack length of $0.4 < \frac{d}{2l} < 1$. The calculated value for the fracture toughness was of $6.9\pm0.2$ MPa-m$^{1/2}$ and the commercial given value is of $6.5\pm0.3$ MPa-m$^{1/2}$.

Figure 10. SEM image of the 30 kg indentation print and its resulting fissure. It can be seen the tortuosity in the crack resulting from the high-energy indentation.
5.5.2. Scratch Test

To simulate the damage that can occur in the femoral head of a hip prosthesis, a scratch test was made on the surface of the zirconia toughened alumina. The test was made with an increasing force from 0.9N until a maximum of 100N over a length of 2mm, at a rate of 5N/s. A Rockwell diamond tip with a radius of 200μm was used causing a maximum penetration depth of 100μm. On the Figure 11, is the trail left from the scratch test, resulting in a material breakage at the end. At the end of the trace of the scratch test it was observed with scanning electron microscopy, parallel microfissures at the surface of the material, this area was chosen for the FIB tomography, as can be seen in the Figure 12.

Figure 11. Trail mark left from the scratch test at increasing force until 100N.
Traces of plastically deformed grooves with intact edges along the length path are observed. The closely spaced parallel lines and microcracks, indicative of plastic deformation during the scratch process, were observed within the scratch path [25]. The FIB tomography slices show that the type of fracture observed in this mechanical test are transgranular and grain boundary fracture.

5.6. Crack Tortuosity

Macroscopic cracks in many polycrystalline ceramics advance along the grain boundaries since the grain boundary acts as the path of least resistance to crack propagation [32]. Crack deflection acts as a toughening mechanism in the zirconia toughened alumina. In this scenario crack tortuosity (τ) can be defined as the path length of the crack in relation to a straight line in the same area. In the image shown below the blue line is the
crack path length and the red line is the straight-line measurement. The equation used to describe this relation is:

\[ \tau = \frac{L_{\text{real}}}{L_{\text{line}}} \]  

(3)

From the equation 3, \( L_{\text{real}} \) is the crack path length and \( L_{\text{line}} \) is the reference line length. The ratio between both lengths gives the crack tortuosity [26, 27]. The path lengths were measured directly with image analysis for both damage samples.

Figure 13. Crack tortuosity measurement. The red line is the crack path and the blue line the straight reference line.
5.7. Phase Agglomeration

From the stack of images obtained it can be clearly seen that some of the zirconia phase tends to form agglomerates with itself mostly consisting between two and eleven grains. In order to find out how much of the zirconia phase has this tendency a grain agglomeration calculation must be made. The following equation gives the percentage on which zirconia forms agglomerates on each sample by taking into consideration the measured zirconia average size:

\[
\%\text{Agglomeration} = \frac{S_{Zr} - S^*_{Zr}}{S_{Zr}} \quad (4)
\]

From the equation (4) \( S_{Zr} \) is the superficial area of all of the zirconia present in the sample calculated using the measured zirconia grain size and the number of grains present per sample and \( S^*_{Zr} \) is the superficial area of all of the zirconia present in the sample, calculated by the Avizo Fire software.

5.8. Samples

Two FIB tomography were made in the zirconia toughened alumina sample for the purpose of the three dimensional reconstruction. Each tomography sample has a different damage inflicted on its surface, summarized on Table 5. The first tomography sample was indented with 30kg and it was observed the common radiating cracks from the Vickers indentation print. The second tomography sample was scratched with an increasing force from 0.9 to 100N, and it was observed microcracks all along the trail left by the scratch.
Table 4. ZTA Tomography Sample Summary.

<table>
<thead>
<tr>
<th>Test</th>
<th>Indentation</th>
<th>Scratch</th>
</tr>
</thead>
<tbody>
<tr>
<td>Force</td>
<td>30kg</td>
<td>0.9-100N</td>
</tr>
<tr>
<td>Crack Observations</td>
<td>Radial cracks</td>
<td>Microcracking</td>
</tr>
</tbody>
</table>

The sample of ZTA was polished with diamond paste with decreasing particle size until 3μm, with a finish of colloidal silica.

5.9. Tomography

The equipment used for the tomography is the Cross Beam Zeiss Neon-40 FIB-SEM as the one shown in Figure 14. As mentioned before, the ion column does the milling while the electron column permits viewing of the material in real time.

Figure 14. Zeiss Neon-40 FIB-SEM Cross Beam System.
Before performing a tomography, it is suitable that the FIB/SEM system is turned on at least 24hrs before with the sample inside, to avoid thermal drift.

The sample is mounted in a sample holder and it is attached with a conductive silver adhesive 503 (62%wt solid), that same adhesive was spread in the entire sample as a coating so that the sample could be conductive. It takes around 30 minutes for the adhesive to harden. Since zirconia toughened alumina has a low electrical conductivity at room temperature, hence it is coated with a 20nm coating of evaporated gold palladium on the top of the sample.

Once inside the focused ion beam vacuum chamber the stage is tilted until it is perpendicular to the electron beam and the sample is centered. A platinum coating is deposited onto the surface of the sample to flatten the surface, ensure proper milling and prevent the curtain effect (see Figure 15(a)) within tomography slices.
A squared trench around the platinum deposited area is milled like the one shown of Figure 15(b), so that we could be able to see the cross section and not have shadow effects on the tomography images. Next, the milling region is selected with the milling current and intensity, which determines the milling depth and speed.

The FIB tomography image recollection is a time consuming process that for obtaining high-resolution images takes long hours. Each tomography took from 12 to 16 hours to complete. It takes around 45 seconds of milling, 1 minute for SEM imaging and another minute for the software to make a drift correction per image.

### 5.10. Three Dimensional Reconstruction

The FIB sections the material in thin parallel slices like the one shown in Figure 16, obtaining a stack of images that can later be assembled together to reconstruct the volume. After the FIB tomography is completed a trench is left (see Figure 17) of the sectioning trail on the material. For the
reconstruction and material analysis process the Avizo 8.0 software was used. Avizo is a three dimensional data processing, modeling and analysis software that uses modules to visualize data objects. The components are attached by lines indicating processing dependencies between modules and data objects.

Figure 16. Example of a ZTA slice obtained from the FIB.

Figure 17. Trench made by the FIB.
For the completion of the three dimensional reconstruction of the volume and further analysis, the steps on Figure 18 were followed, which in the continuing sections will be discussed in depth.

Figure 18. Steps followed for the 3D reconstruction and volume analysis [28].

5.10.1. Slice Alignment

Once the tomography images are obtained, we can proceed to the alignment of the slices. The alignment of the slices permits to correct the drift
and to reposition the images. In order to do so, it is of convenience to have a reference line in all of the sectioned volume to facilitate alignment. The reference line is milled on the surface of the volume with the FIB.

A stack of images is loaded into the Avizo Fire software and a voxel size is chosen. The voxel size represents a value, in this case the volume of each image, on a grid in a three dimensional space. The chosen voxel size for the volume depends on the pixel size determined by the magnification on the images, with an average slice thickness of 20 nanometers. The slice alignment is done manually in order to obtain a more precise alignment as can be seen on Figure 19. There are other options for slice alignment such as automatic alignment using a least squares fitting, landmark alignment and edge detection.

![Figure 19. Manual Slice Alignment. On the top of the slices it can be seen the reference lines that aid in the manual alignment.](image)

### 5.10.2. Image Correction

After aligning the slices, an interest area is chosen and cropped. The area chosen for both reconstructions is where the fissures propagated. For the later differentiation of phases in the material it is important to correct the
images saturation, contrast, intensity and shading [28]. Five image filters were used to achieve the above-mentioned (see Figure 20):

a. *Match Contrast*: computes a new image referencing another image with the desired intensity histogram. This filter is important in order to apply the same process to all of the images without having very different results.

b. *Noise Reduction Median Filter*: it reduces the brightness variation thus reducing the noise on each image, 10 iterations were made in order to obtained the desired noise reduction. This filter replaces each pixel by its grey value (from 0 to 255) and applying a mask that takes the median value of the matrix.

c. *Edge Preserving Smoothing Filter*: Gaussian like filter that softens the grey level values of each pixel with its neighboring. Also, stops the smoothing in high gradients.

d. *Intensity Remapping*: Sigmoid type filter that enhances contrast.

e. *Shading Correction*: uses a flat field correction that computes an illumination profile to flatten the image, normalizing the background.
Figure 20. Different image filters used: a) original image, b) match contrast, c) noise reduction median filter, d) edge preserving smoothing filter, e) intensity remapping, f) shading correction.

5.10.3. Segmentation

Image segmentation refers to the assignment of labels to an image in order to separate the different elements that compose it creating a map, so that a three-dimensional reconstruction and analysis can be possible. The separated elements involved in this reconstruction are the matrix of aluminum
oxide, the phase of zirconium oxide, the fissures produced by the inflicted damage and the pores generated during manufacture, as can be seen in Figure 21. In this reconstruction, the phases of $Y_2O_3$, $Cr_2O_3$ and $SrO$ (1.45% of total volume fraction), will not be taken into account since they are solid state solutions difficult to distinguish with the imaging software. Every single element must be individually selected by using a color histogram threshold in order to proceed to the surface generation, as shown in Figure 21 and 22.
5.10.4. Surface Reconstruction

Following the image segmentation, the surface reconstruction is fairly easy by simply applying the Surface Generate module. This module generates a triangular mesh of the total volume and it is obtained a very large three-dimensional surface of the whole previous segmented volume.

Both reconstructions ranged around the 40-50 million triangles in magnitude as can be seen on Figure 23(a) in red, and hence it has to be reduced drastically with the Simplification Editor module in order to be a workable volume (see Figure 23(b)). Since all the elements have been previously isolated, it is possible to view the ones you choose or the whole 3D reconstruction with the Surface View command.

![Figure 23. Simplified surfaces with 800,000 faces (a) and 80,000 faces (b) without losing too much definition. In red are the triangle mesh.](image)

5.10.5. Analysis and Exporting Surface

Analyzing elements in Avizo is fairly straightforward since it does not require surface visualization and computation time is quick.
There are many analysis tools in the software such as Material Statistics module that was used for volumetric analysis such as volume per phase and volume per slice. Attaching the Surface Area Volume module on patches is useful for obtaining information on contact area between phases and other elements in the material.

In depth analysis of the three dimensional volume can be done by exporting the surface mesh to a finite element analysis software. The surface can be exported with another format such as .inp for Abaqus, m-file for Matlab, .ans for Ansys, among others [28].
6. Results and Analysis

The three-dimensional reconstructions are shown in the following sections. Two FIB tomography reconstructions were made with the Avizo Fire 8.0 software. The first sample consists of a 30 kg Vickers indentation test with one central crack produced in account of the absorbed energy. In the section 6.1, it will be shown the corresponding images obtained from the indentation test reconstruction.

The second sample consists of a scratch test with increasing force from 0.9N until 100N, this resulted in a scratch trail that had along its path multiple microcracks emanating. In the section 6.2, it will be shown the corresponding images obtained from the scratch reconstruction.

6.1. Indentation Sample

The following figures (Figure 24(a-to-h)) show the indentation test sample FIB tomography reconstruction. It can be seen from the complete volume reconstruction the isolated elements such as the crack, pores, and combinations of elements such as zirconia and the crack, and alumina and the crack, in order to see more in detail how the crack is behaving along is propagation path. From the Figure 24(a), the complete ZTA volume reconstruction it can be seen the homogeneity of the phases in the volume. The generated indentation crack shows that is quite tortuous, which will be accounted for in the following sections. As for the pores in the volume, they only account for 0.04% of the total volume. The zirconia phase (shown in Figure 24(d)) shows that part of the grains are fused with other zirconia grains, an estimate of this zirconia grain agglomerate percentage will be discussed further on. The images of the fissure with zirconia and alumina (see Figure 24 (g and h)), shows the interaction of the indentation crack with each phase.
a) Complete Indentation Sample Surface Reconstruction

b) Generated Indentation Crack

c) Pores
d) Zirconia Phase

e) Alumina Phase
f) Indentation Crack and Pores

g) Zirconia Phase, Indentation Crack and Pores
6.2. Scratch Sample

The figures that follow (Figure 25 (a-to-h)) show the FIB tomography reconstruction of the scratch test sample. It can be observed the complete volume reconstruction, the multiple cracks formed from the mechanical test, the pores and the zirconia and alumina phase. It is also shown, combinations of different volume elements such as the interaction of the crack with the alumina and zirconia phase. From the image shown in Figure 25(a) it can be seen the complete volume reconstruction and the microcracks formed from the scratch test.

In the Figure 25(b) are shown the microcracks, and it can be seen that they do not have a continuous path, they behave more as if a cluster of
microcracks. The pores as well as in the indentation sample account for a negligible volume. As for the zirconia phase shown in the Figure 25(d), it can be seen that part of the phase tends to form agglomerates, and it can be said that part of the phase is contiguous. On the Figures 25 (g and h), it can be seen the interaction of the crack with the phases of zirconia and alumina, respectively.

![Complete Scratch Sample Surface Reconstruction](image)

a) Complete Scratch Sample Surface Reconstruction
b) Multiple Scratch Cracks  
c) Pores  
d) Zirconia Phase
e) Alumina Phase

f) Multiple Scratch Cracks and Pores
Figure 25. Scratch Sample. a) Complete Surface Reconstruction, Isolated Elements: b) Cracks, c) Pores d) Zirconia Phase, e) Alumina Phase, f) Pores and cracks, g) Zirconia phase, pores and cracks, h) Alumina phase and cracks.
6.3. Tomography Analysis

On the table shown below are the reconstruction conditions used for each sample. As mentioned before the chosen voxel size for the volume depends on the pixel size determined by the magnification on the images, with an average slice thickness of 20 nanometers.

In both sample reconstructions the phases of Y$_2$O$_3$, Cr$_2$O$_3$ and SrO (1.45% of total volume fraction), were not taken into account since they are solid state solutions difficult to distinguish with the imaging software.

The Avizo Fire 8.0 software was used to quantify the volume of each sample, the surface area of each element and the fissure propagation tendency. Other software like ImageJ was used for analyzing the average grain size of the zirconia phase, the crack opening displacement and the crack tortuosity measurements. In the following sections it will be discussed the different measurements and calculations executed for the analysis of the indentation and scratch test sample reconstructions.

<table>
<thead>
<tr>
<th>Size</th>
<th>Indentation</th>
<th>Scratch</th>
</tr>
</thead>
<tbody>
<tr>
<td>Voxel Size (nm)</td>
<td>13 x 13 x 20</td>
<td>11.45 x 11.45 x 20</td>
</tr>
<tr>
<td>Cube Size (voxels)</td>
<td>851 x 431 x 558</td>
<td>1005 x 517 x 531</td>
</tr>
<tr>
<td>Cube Size (μm)</td>
<td>11.06 x 5.6 x 11.16</td>
<td>11.51 x 5.92 x 10.62</td>
</tr>
<tr>
<td>Cube Volume (μm$^3$)</td>
<td>691.39</td>
<td>723.42</td>
</tr>
</tbody>
</table>

6.3.1. Volume

The volume was directly measured from the reconstruction surface, and the results are shown in the table below. Volume percentages of the phases in the material go in accordance with the reported values in Table 3.
Table 6. Calculated Volume of the Phases in the ZTA.

<table>
<thead>
<tr>
<th>Material</th>
<th>Volume Fraction [μm³]</th>
<th>% of Material in Volume</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Indentation</td>
<td>Scratch</td>
</tr>
<tr>
<td>Zirconia</td>
<td>133.26</td>
<td>152.48</td>
</tr>
<tr>
<td>Fissure</td>
<td>3.96</td>
<td>2.18</td>
</tr>
<tr>
<td>Pores</td>
<td>0.36</td>
<td>0.21</td>
</tr>
<tr>
<td>Alumina</td>
<td>554.18</td>
<td>568.56</td>
</tr>
<tr>
<td>Total Volume</td>
<td>691.76</td>
<td>723.42</td>
</tr>
</tbody>
</table>

From this data we can calculate the percentage of densification of the material by taking into account the pores in the volume, which gives a 99.96±0.01% of material densification, implying a complete material sinterization.

6.3.2. Densities and Masses

By taking into account the Table 7, it can be calculated the mass of each component present in the volume. The calculated mass and density show that the reconstructed volumes are accurate.

Table 7. Mass of each component present in the ZTA volume.

<table>
<thead>
<tr>
<th>Material</th>
<th>Theoretical Density (g/cm³)</th>
<th>Mass (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alumina</td>
<td>3.75-3.95 [31]</td>
<td>21.34</td>
</tr>
<tr>
<td>Total</td>
<td>4.37</td>
<td>29.43</td>
</tr>
</tbody>
</table>

The calculated total density was of 4.25 ± 0.05 g/cm³, giving an error percentage between 1.46-2.75%. The difference in densities is attributed to the fact that Y₂O₃, Cr₂O₃ and SrO, which contribute to a 1.45% of volume
fraction (see Table 3), were not considered in this analysis, due to difficulty on imaging segmentation.

6.3.3. Grain Size

For the further characterization of the zirconia toughened alumina, it was necessary to know the average zirconia grain size. A direct linear measurement was made on a large range of grains with quantitative imaging and the zirconia grain size distribution is shown in the Figure 26, giving a zirconia average grain size of $0.39 \pm 0.13 \mu m$. The measured grain sizes vary from $0.12 \mu m$ to a maximum of $0.79 \mu m$, showing that the ZTA has a non-homogenous zirconia particle size. In the Figure 27 it can be seen the zirconia grain size ranges and the frequency of these grain size measurements. Most of the zirconia grains sizes fall in between the ranges of $0.3 \mu m$ to $0.5 \mu m$.

![Figure 26. Average zirconia grain size distribution. Obtaining an average grain size of $0.39 \pm 0.13 \mu m$.](image-url)
From the phase volumes obtained in Table 6, and the measured average zirconia grain size, it can be calculated the approximate number of zirconia grains per volume. By considering the zirconia grains as spheres and using the equation:

\[ N = \frac{f}{\frac{4}{3} \pi r^3} \]  \hspace{1cm} (5)

where \( f \) is the zirconia volume fraction and \( r \) is the radius of the sphere, it can be obtained the number of grains of zirconia in the volume, the results are shown in the Table 8, obtaining 5025 grains of zirconia for the indentation test sample and 5750 for the larger scratch test sample.

<table>
<thead>
<tr>
<th>Table 8. Number of zirconia grains in each volume sample.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
</tr>
<tr>
<td><strong>Indentation</strong></td>
</tr>
<tr>
<td>Number of grains of ZrO(_2)</td>
</tr>
<tr>
<td>ZrO(_2) Volume Fraction ((\mu\text{m}^3))</td>
</tr>
</tbody>
</table>
In the same way it was calculated the number of zirconia grains in the volume, it can be calculated the number of pores in the volume by considering the pores spherical. The percentage of pores in the volume accounts for less than 0.04% of the total material volume. The average pore size measured for the zirconia toughened alumina is of 0.16 μm, with an average of 130 pores per sample volume.

### 6.3.4. Agglomeration

It is seen from the reconstruction that there is some zirconia phase contiguity, meaning that the grains tend to form agglomerates. By using equation (4), we can obtain the percentage of zirconia phase that is joined to each other. In order to calculate the agglomeration percentage of the zirconia phase in ZTA, it is necessary to know the surface area of the phases.

The surface area was directly measured from the reconstructed volume, with the software analyzing tools, on the Table 9 are shown the results. A total surface area of 5364 μm$^2$ was calculated for the indentation test sample and 5352 μm$^2$ for the scratch test sample.

<table>
<thead>
<tr>
<th>Material</th>
<th>Area [μm$^2$]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Indentation</td>
</tr>
<tr>
<td>Zirconia</td>
<td>2364</td>
</tr>
<tr>
<td>Fissure</td>
<td>192</td>
</tr>
<tr>
<td>Pores</td>
<td>17</td>
</tr>
<tr>
<td>Alumina</td>
<td>2791</td>
</tr>
<tr>
<td><strong>Total Area</strong></td>
<td><strong>5364</strong></td>
</tr>
</tbody>
</table>
Calculations show that the zirconia phase in both samples has an agglomeration percentage of roughly 8%. Further on, it will be discussed more in detail and segmented these grain agglomerates to show how many grains of zirconia compose these agglomerates.

6.4. Single Grain Segmentation

Zirconia grains from each sample were segmented individually. Below are shown only two grains of each sample. From the Figure 28, it can be seen that the grains are fairly spherical for all samples. Since both tests were made in the same sample, it is expected to obtain the same volumetric information.

![Segmented grains](image)

Figure 28. Segmented grains. (a) and (b) zirconia grains from indentation sample, (c) and (d) zirconia grains from scratch sample.

Volume and surface area was measured in each zirconia grain, below is the average of the results. The results obtained in the Table 10, coincide
with the quantitatively measured zirconia grain size and all values obtained do not differ much from each other.

<table>
<thead>
<tr>
<th></th>
<th>Volume (μm³)</th>
<th>Surface Area (μm²)</th>
<th>Mean Size (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zirconia Grains</td>
<td>0.026±0.01</td>
<td>0.47±0.13</td>
<td>0.39</td>
</tr>
</tbody>
</table>

**Table 10. Mean values for the segmented zirconia individual grains.**

6.5. **Agglomerate Segmentation**

As mentioned before in the agglomeration section, the zirconia grains tend to form agglomerates, in this section it is shown their segmentation in order to see how many zirconia grains are joined in the agglomerates. On the Figure 29, it can be seen an example of the zirconia agglomerates; each different color represents an individual zirconia grain. The segmentation was made with the Avizo Fire 8.0 software, by manually isolating each zirconia grain.

![Image](image_url)  
**Figure 29. Agglomerates found in the ZTA slices. Each different color is an individual zirconia grain.**
On the next figure (Figure 30) it is shown two different agglomerate systems consisting of six grains (a) and seven grains (b). The agglomerates tend to consist between two to eleven grains. Both volume reconstructions show that the zirconia grains in the volume tend to form agglomerates and hence show zirconia phase contiguity. Individual zirconia grain volumes in the agglomerates fall between the average measured values of 0.39 μm. A mechanism that explains why the zirconia grains tend to agglomerate is not understood, but the non-homogenous zirconia particle size might have an influence.

Figure 30. Zirconia grain agglomerates. (a) Six grain agglomerate, (b) Seven grain agglomerate. Each different color is an individual zirconia grain.

6.6. Fissure Propagation Tendency

The damage caused by the surface 30 kg indentation consists of a single central crack that passes through the volume. Whereas, the damage caused by the scratch test on the surface of the sample consists of a series of parallel main micro-cracks and a cloud of microcracks around them. This behavior raised questions regarding the fissure propagation tendency towards the alumina or zirconia phase. On the Figure 31, it is shown a single slice of
the indentation sample of the ZTA volume, it can be seen the path of the crack (red).

![Figure 31. Single slice of the volume of the ZTA indentation sample. In red is the path of the indentation crack.](image)

The tendency of these fissures can be studied with the complete reconstruction of the volume. In specific it can be measured the times the crack passes through the alumina and zirconia phase, and this is shown on the Table 11.

<table>
<thead>
<tr>
<th></th>
<th>Indentation</th>
<th>Scratch</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alumina</td>
<td>82.72</td>
<td>89.04</td>
</tr>
<tr>
<td>Zirconia</td>
<td>17.19</td>
<td>10.87</td>
</tr>
<tr>
<td>Pores</td>
<td>0.08</td>
<td>0.09</td>
</tr>
</tbody>
</table>

From the Table 11, we can see that for the indentation sample, the fissure passes an approximate of 83% through the alumina phase and roughly a 17% through the zirconia phase, but since the volume fractions for alumina and zirconia in the ZTA are of approximately 82% and 17% respectively, it appears that there is no fissure propagation tendency. Whereas, for the scratch sample, 89% of the cloud of microcracks passes though the alumina phase and an approximate 11% passes through the zirconia phase. It can be observed from the scratch sample reconstruction that a series of microcracks
formed in the alumina phase (see Figure 32), most probably before the main cracks formed. This hypothesis is based on the lower fracture toughness of alumina when compared to zirconia, in the Table 12, it is shown the different values of hardness and fracture toughness for ZTA and its components.

Table 12. Hardness and fracture toughness of ZTA components.

<table>
<thead>
<tr>
<th>Material</th>
<th>Hardness (GPa)</th>
<th>Fracture Toughness $K_{IC}$ (MPa$\cdot$m$^{1/2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alumina</td>
<td>19 [29]</td>
<td>4 [1]</td>
</tr>
<tr>
<td>ZTA</td>
<td>18±1</td>
<td>6.9±0.2</td>
</tr>
</tbody>
</table>

Figure 32. Scratch sample slice. In red the main cracks and in blue the microcracks.

6.7. Crack Opening Displacement

Crack opening displacement (COD) varies from the alumina phase to the zirconia phase. The COD measurements were done using quantitative imaging. Images from the reconstruction show that when the crack passes through some of the zirconia grains the thickness of the crack is considerably smaller in comparison to when the crack passes through the alumina,
implying that the zirconia martensitic transformation is taking action. Crack opening displacement measurements show that when the crack passes through the alumina phase the average displacement is of 0.06 μm, whereas, when it passes through zirconia the average COD is of 0.03 μm, indeed showing that there is martensitic transformation. On the Figure 33, it is shown the different COD’s measured for the alumina and zirconia phase. The maximum crack opening displacement measured was of 0.11 μm for the alumina and a minimum of 0.02 μm. Whereas, for the zirconia the maximum COD measured was of 0.07 μm and a minimum of 0.002 μm.

![Crack Opening Displacement](image)

**Figure 33. Crack Opening Displacement.** The average crack opening displacement for the alumina phase is of 0.06 μm and 0.03 μm for the zirconia phase.

### 6.8. Crack Tortuosity

Crack tortuosity can be quantified by measuring the real crack length and taking the ratio with respect to a reference straight line of the length of the crack area. The crack real lengths were measured manually with quantitative imaging and the ratio between the real length and a reference line is shown on the Figure 34 below. Macroscopic cracks seen in this polycrystalline
ceramic advances along the grain boundaries since the grain boundary acts as the path of least resistance to crack propagation, thus acting as an toughening mechanism in the zirconia toughened alumina.

![Graph showing tortuosity values for indentation and scratch samples.](image)

**Figure 34.** Crack tortuosity values for the indentation and scratch samples. Both samples show that they have approximately the same tortuosity.

The values of tortuosity obtained for the ZTA indentation and scratch tests samples are shown on the Table 13. It can be seen that there is no significant difference between the tortuosity values of each sample, thus implying that one sample is no more tortuous than the other and even though the mechanical imposed stresses are different, the fracture is similar.

**Table 13. Tortuosity values for ZTA’s indentation and scratch tests samples.**

<table>
<thead>
<tr>
<th>Tortuosity</th>
<th>Indentation</th>
<th>Scratch</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\tau = \frac{L_{\text{real}}}{L_{\text{line}}}$</td>
<td>1.3±0.1</td>
<td>1.2±0.1</td>
</tr>
</tbody>
</table>
7. Concluding Remarks

Indentation and scratch test three-dimensional reconstructions show that the percentages of phases present in the volume is in accordance with the data provided by the manufacturer, thus proving that the reconstructions are well made. Volume analysis permits to calculate the masses and densities of each component in the reconstruction, obtaining results that support that indeed the reconstructions are satisfactory. Furthermore, it was calculated that the densification percentage of each reconstructed volume and it resulted on a 99.96% of complete material densification, proving that the sinterization process used by the manufacturer is adequate.

By measuring the average zirconia grain size it was possible to calculate in the reconstructed volume the number of zirconia grains present. Also, in a similar manner by knowing the average pore size on the volume, the number of pores was calculated, information that without the aid of a tomography would be difficult to measure.

Surface area data aided in the agglomeration percentage calculations made for the zirconia agglomerates, resulting in a 8% of zirconia phase agglomeration for ZTA samples. Zirconia agglomerates consisted between two and eleven grains.

Focused ion beam tomography gives a unique advantage to material characterization by being able to explore inside of the material instead of only the surface, like most characterization methods. It has permitted the segmentation of single grains and agglomerates of zirconia, and to know the volumetric information for each element.

The cracks generated during the indentation and scratch tests were explored in detail, finding out information like crack opening displacement and tortuosity. Resulting in an average crack opening displacement for the phase
of alumina of 0.06 μm and for the zirconia phase of 0.03 μm, indicating that the zirconia martensitic transformation may have taken place. Also, it was found that there is no notable difference between samples regarding crack tortuosity, thus even tough the mechanical solicitations were different the fractures were similar.

Nonetheless, it was possible to calculate if the crack generated by the inflicted damage on the sample surface had a tendency to propagate to the alumina or the zirconia phase. For the indentation test sample it was observed there is no preference for the propagation of the fissure and for the scratch test sample it was seen that there is a slight tendency for the fissure to propagate before, on the alumina phase, but this finding might be explained by the lower fracture toughness of alumina in comparison to the zirconia’s.

This study has proved that by making a focused ion beam tomography reconstruction it is possible to visualize the entire volume of the sample in three dimensions, thus making this an indispensable tool for the better understanding of material anatomy. Likewise, zirconia toughened alumina’s microstructural components prove to have effective crack stopping mechanisms making this material a good choice for hip prosthesis.
8. Economic Valuation of the Study

For the completion of this project it was necessary the focused ion beam cross beam work station, a well-equipped computer station with the indispensable hardware to process the large data of the tomography, and accessories such as a digital drawing pad and the three dimensional reconstruction software. For each FIB tomography preparation it took 6 hours for the sample preparation and 16 hours for each tomography. The computer time requirements for each reconstruction was on average 80 hours. The project started on January 15th 2014 and was completed by July 25th 2014. Total dedication time was 40 hours per week. The estimated project costs are shown in the table below.

Table 14. Estimated Project Costs.

<table>
<thead>
<tr>
<th></th>
<th>Unit Cost</th>
<th>Quantity</th>
<th>Subtotal</th>
</tr>
</thead>
<tbody>
<tr>
<td>FIB/SEM System</td>
<td>250€/h</td>
<td>44 h</td>
<td>11 000€</td>
</tr>
<tr>
<td>Avizo Fire 8.0 License</td>
<td>8 400€</td>
<td>1</td>
<td>8 400€</td>
</tr>
<tr>
<td>Computer Equipment</td>
<td>1 200€</td>
<td>1</td>
<td>1 200€</td>
</tr>
<tr>
<td>Computer Consumption</td>
<td>0,11€/KWh</td>
<td>250 h</td>
<td>27,5€</td>
</tr>
<tr>
<td>Junior Researcher</td>
<td>30€/h</td>
<td>1120 h</td>
<td>33 600€</td>
</tr>
<tr>
<td>Project Director</td>
<td>60€/h</td>
<td>60 h</td>
<td>3 600</td>
</tr>
<tr>
<td>FIB Technician</td>
<td>30€/h</td>
<td>40 h</td>
<td>1 200</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
<td>59 028€</td>
</tr>
</tbody>
</table>
9. Environmental Impact

The present environmental impact section will only consider the energy consumption of all of the electronic equipment that was in use during this investigation. Other impacts of the human footprint such as transportation emissions, generated waste and other human activities were not taken into account. Taking into consideration that the price of the electricity at present in Barcelona is around 0,11€/KWh (according to the electric company), all calculations were made. According to the PER 2011-2020 (Plan de Energías Renovables), the emissions of carbon dioxide are of 0,233 kilograms of CO₂ per kilowatt-hour. Considering the time usage of the FIB/SEM Cross-Beam system (see Table 17) and the power consumption of this equipment is of 3,3KWh, then is calculated that the carbon footprint is of 33,8 kg of CO₂. For the computer working station, the energy consumption is of 260Wh, generating a total of 15,1 kg of CO₂. Thus it can be said that the project had a total carbon footprint of 48,9 kg of CO₂ for its entire length.
Agradecimientos

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References


