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Processing and sintering of complex ceramics obtained by additive manufacturing

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MATERIAL ENGINEERING MASTER THESIS

Processing and sintering of complex ceramics obtained by additive manufacturing

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Abstract

Additive manufacturing of ceramics has expanded significantly in recent decades due to its exceptional advantages in flexibility and lower cost over the traditional manufacturing process. Currently, additive manufacturing of ceramics is of great interest due to the growing demand for lightweight and complex shaped components, such as ZrO2, which is mainly used in biomedicine and space.

In this work, two ceramics of technological-industrial interest have been investigated: zirconia (ZrO2) and zircon (ZrSiO4). The aim of this research is to design and manufacture complex ceramics by 3D printing and then use different types of sintering (conventional and non-conventional) to obtain a dense material with exceptional final properties.

The first step consists of designing the final part to be printed using Solidworks software. Afterwards, the printed part will be conditioned and then sintered at high temperature, where the appropriate time/temperature ratio will be studied in order to obtain the best final properties. Microwave sintering, which is a fast and environmentally sustainable method, will allow us to control the microstructure which will have a high impact on the final properties of the material. Finally, mechanical properties such as hardness (Vickers), porosity and shrinkage percentage were investigated. Furthermore, the microstructure was analyzed by high resolution scanning electron microscopy (FESEM). In addition to all these tests, a thermogravimetric analysis (TGA) was also carried out on the starting material to study its behavior at high temperature.

Key word*: complex ceramics, 3D printer, microwaves sintering, conventional sintering, mechanical properties, Zirconia*

Resumen

La fabricación aditiva de las cerámicas se ha expandido significativamente en las últimas décadas debido a sus excepcionales ventajas en flexibilidad y menor coste sobre el proceso tradicional de fabricación. En la actualidad, la fabricación aditiva de las cerámicas despierta un gran interés debido a la creciente demanda de componentes ligeros y de formas complejas; como el ZrO_2, que se utiliza principalmente en biomedicina o en el ámbito espacial.

En este trabajo se han investigado dos cerámicas de interés tecnológico-industrial como es la circona (ZrO_2) y el circón ($ZrSiO_4$). El objetivo de esta investigación es diseñar i fabricar cerámicas complejas mediante impresión 3D y, a continuación, utilizar distintos tipos de sinterización (convencional y no-convencional) para obtener un material denso con unas propiedades finales excepcionales.

El primer paso consiste en diseñar la pieza final a imprimir mediante el programa Solidworks. Después, se acondicionará la pieza impresa para posteriormente sinterizarla a alta temperatura, donde se estudiará la relación adecuada tiempo/temperatura para obtener las mejores propiedades finales. La sinterización por microondas, que es un método rápido y medioambientalmente sostenible, nos va a permitir controlar la microestructura la cual tendrá una alta repercusión en las propiedades finales del material. Por último, se investigaron las propiedades mecánicas como la dureza (Vickers), la porosidad y el porcentaje de contracción. Además, se analizó la microestructura mediante microscopía electrónica de barrido de alta resolución (FESEM). Además de todas estas pruebas, también se ha realizado un análisis termogravimétrico (TGA) al material de partida para estudiar su comportamiento a alta temperatura.

Palabras clave: Cerámicas complejas; Impresora 3D; Sinterización por microondas; Sinterización convencional; Propiedades mecánicas, Circona

Resum

La fabricació additiva de les ceràmiques s'ha expandit significativament en les últimes dècades a causa dels seus excepcionals avantatges en flexibilitat i menor cost sobre el procés tradicional de fabricació. En l'actualitat, la fabricació additiva de les ceràmiques desperta un gran interès degut a la creixent demanda de components lleugers i de formes complexes; com el ZrO_2, que s'utilitza principalment en biomedicina o en l'àmbit espacial.

En aquest treball s'han investigat dues ceràmiques d'interès tecnològic-industrial com es la circona (ZrO_2) i el circon ($ZrSiO_4$). L'objectiu d'aquesta investigació és dissenyar i fabricar ceràmiques complexes mitjançant impressió 3D i, a continuació, utilitzar diferents tipus de sinterització (convencional i no-convencional) per a obtindre un material dens amb unes propietats finals excepcionals.

El primer pas consisteix en dissenyar la peça final a imprimir mitjançant el programa Solidworks. Després, es condicionarà la peça impresa per a posteriorment sinteritzar-la a alta temperatura on s'estudiarà la relació adequada temps/temperatura per a obtindre les millors propietats finals. La sinterització per microones, que és un mètode ràpid i mediambientalment sostenible, ens permet controlar la microestructura la qual tindrà una alta repercussió en les propietats finals del material. Finalment, s´han investigat les propietats mecàniques com la duresa (Vickers), la porositat i el percentatge de contracció. A més, s´ha analitzat la microestructura amb la microscòpia electrònica d'escombratge d'alta resolució (FESEM). A més de totes aquestes proves, també s`ha fet un anàlisis de termogravimetria (TGA) al material de partida per a estudiar el seu comportament front a la temperatura.

Paraules clau: Ceràmiques complexes; Impressora 3D; Sinterització per microones; Sinterització convencional; Propietats mecàniques; Circona

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1. Introduction

1.1. Objectives of the project

Nowadays, ceramics are especially known for their high biocompatibility, their hardness, their high temperature resistance but also for their high mechanical strength, complex ceramics are constantly used in cutting-edge areas of technology as biomedical or space. However, research is made to improve these qualities and overcome their brittleness. To do so, zirconia (ZrO_2) and zircon ($ZrSiO_4$) are studied as raw material to create complex samples with a honeycomb structure.

For the creation of the green body, the conventional methods (dry and wet processes) are not possible because they require too much energy and complex shapes are difficult to achieve, so additive manufacturing is chosen in this study. At the beginning, samples will be composed of PLA and zircon powder and then when the process will be mastered, a binding agent (polymers) will be mixt to zirconia powder. Mixture with polymer (PLA) is used to reduce the manufacturing temperature. Indeed, zircon or zirconia do not have the same melting point, it allows to save energy. Then, for the sintering part, conventional and non-conventional techniques as microwaves sintering will be investigated. At the end, characterization tests will be carried out on their density and hardness. Fracture and the size of the grain will be observed with the electronic microscope.

The aim of this project is to find optimal parameters during the processing and the sintering of complex ceramics to get the best properties of the ceramics. The contraction of the sample before and after the sintering will also be studied, in order to obtain all the information concerning different complex structure of the zircon and zirconia.

1.2. Workplan

This project is divided in 3 parts: the green body creation, the sintering and finally the characterization of the samples. To be more specific:

The green body part:

- Creation of the design of the sample on *solidworks* or thanks to the database.
- Comparing different parameters of the 3D print (flow, speed, size of the powder)

The sintering part:

- Testing several temperatures and times of sintering with conventional method (oven)
- Testing new type of sintering with unconventional method (microwaves) and compare

The characterization part:

- Test the density thanks to the Archimedes equation
- Measure the contraction of the sample due to the sintering
- Vickers test for the hardness
- Field Emission Scanning Electron Microscopy (FESEM) for the size of the grain and to analyze the fracture

2. State of the art

2.1. Additive manufacturing

Since the apparition of the 3D print in 1995, research on additive manufacturing continues to grow. Indeed, it is a tool that has not finished improving and facilitating the manufacture of complex objects. It has been a major turning point in the industry, and it has opened doors to the creation of custom-made biomaterials (teeth, femur heads) that would have been impossible before. This way of printing an object at once allows to improve all its mechanical characteristics because there is no weak point in this assembly as welding as it can be seen in figure 1. It is a whole and even the internal structure can be made to improve the mechanical properties which is very difficult to achieve with other processes.

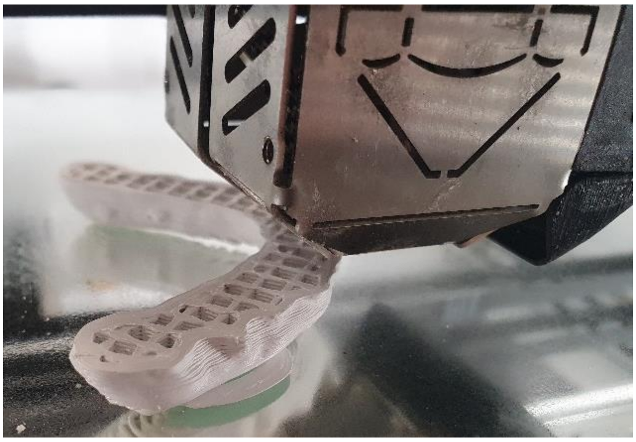


Figure 1: 3D printer making a denture

During the last 20 years, research on AM has been carried out and a great degree of knowledge has been acquired notably on alumina, zirconia, and their alloys. In addition, factors that determine the final properties of ceramics such as particle size and distribution, particle homogeneity, temperature and sintering time have also been studied during these years of research. Recently, zirconia has been studied even more than alumina due to the increasing demands of the biomedical market. Nevertheless, despite the increasing use of AM techniques for low volume and complex shapes, conventional methods will always be favored for mass production. (Olhero, 2022)

The fact of creating an object that is not completely full has been considered in particular to overcome the low toughness (their resistance to impact and crack propagation). Indeed, the internal structure is printed to initially maintain the external structure but also to prevent the propagation of cracks. If the printed object falls and part of the internal structure breaks, the crack cannot spread throughout the sample, unlike a completely filled sample. This is due to the internal structure of the bones, which are made up of many small cells to increase their resistance, especially during shocks. (Mirkhalaf, 2022)

Moreover, in a society where it is now essential to produce sustainably, it is important to consume less, and this is what is done because less material is used, and it is done in a very short time which allows to save energy. In 1995, only metal powders could be used, now polymers and ceramics can be used as well, which makes this technique indispensable for the future.

Figure 2: Distribution of the AM market by category (Olhero, 2022)

This technique is quite recent for ceramics as shown in figure 2. According to the report of the Additive Manufacturing Landscapes 2020, it can be seen that the main market is hardware (with 3D machines as main segment) and that ceramic represents only 7 % of the market, which is really low compared to metal or polymers. (Olhero, 2022)

While nowadays the demand for complex ceramic parts is increasing in very specific fields (such as medical, aerospace) and conventional processes do not work to manufacture these parts. The market for ceramic additive manufacturing (AM) continues to grow and will continue to grow exponentially in the coming years as shown in figure 3. According to Smart Tech ceramics report, alumina and zirconia will together produce half of the gains in the AM ceramics market in 2029. The report was done before covid-19 so the numbers have of course been impacted but the growth trend will remain the same. This trend is supported by the numerous current research projects that will eventually lead to new reliable AM technologies. (Olhero, 2022)

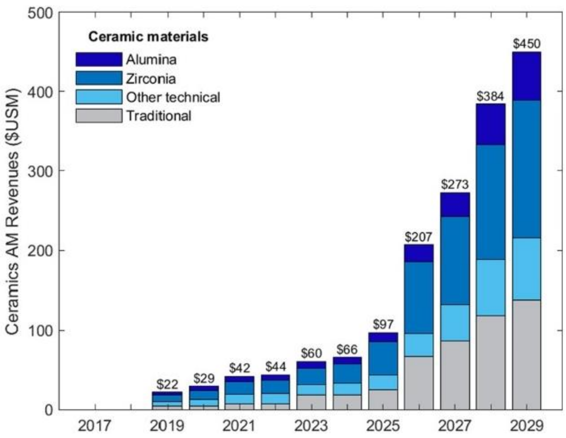


Figure 3: Future AM revenues by ceramic materials: alumina, zirconia, other technical (biomedical, oxide and nitride) and traditional (sand, cement, and glass). (Olhero, 2022)

In the coming years, new AM technologies will be studied as well as am variants that are already used on other materials such as metals or polymers. Furthermore, Al_2O_3-ZrO_2 composites are still in their infancy so this will be a topic for R&D in the AM. (Olhero, 2022)

2.2. Materials

2.2.1. Zircon

Zircon ($ZrSiO_4$) is a mineral that belong to the silicates group, it is a natural zirconium silicate. The figure 4 shows it structure.

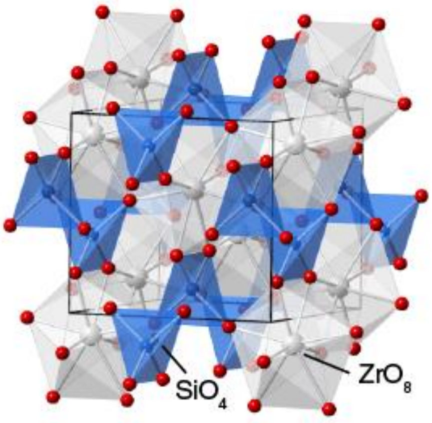


Figure 4: Structure of the zircon (Remy,2021/2022)

Electrostatic and electromagnetic techniques can be used to obtain zircon. Besides there are various other techniques such as be synthetized by melting SiO_2 and ZrO_2 into an arc furnace or by creating a reaction between a sodium silicate and a zirconium salt in an aqueous solution.

Zircon is widely used in the ceramics industry (construction, sanitary, artisanal…) or as a refractory material due to its excellent mechanical, thermal and chemical properties. In addition, it can be used as protective coating for tools thanks to its low thermal conductivity and the good resistance to corrosion. (Remy, 2021/2022)

2.2.2. Zirconia

Zirconia (ZrO_2) is a ceramic used a lot in different areas such as spatial, biomedical, and piezoelectric components. Zirconia has good thermal and mechanical properties, excellent biocompatibility and a great esthetic appearance. It is one of the most use ceramics in the industry with alumina. At the beginning, ZrO_2 is a white powder found which can be found in the natural environment in a form of a mineral. As almost every material, zirconia has various phases according to the different temperatures. As shown in figure 5, ZrO_2 has 3 phases: monoclinic, tetragonal, and cubic. (Moulin, 2008) (Sun, 2023)

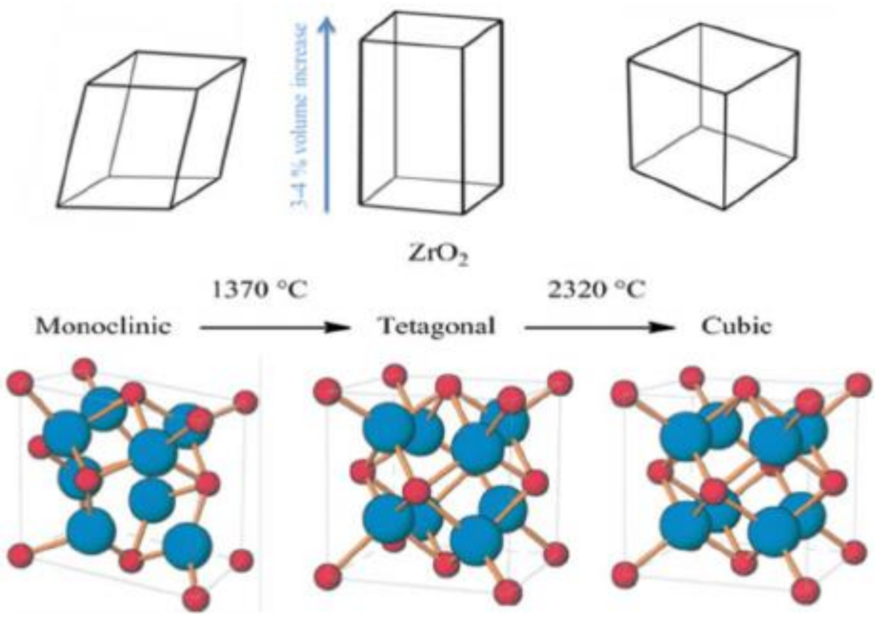


Figure 5: Phases of the zirconia depending on the temperature

The monoclinic phase is present from 0 °C to 1170 °C, then come the tetragonal phase from 1170 °C to 2370 °C, and finally until 2715 °C the phase is cubic. All of these phases, have their specific characteristics. However, the main issue is that during the cooling that led to the transformation from tetragonal to the monoclinic, the volume increases of 4 % and this weakens the structure and makes the material very vulnerable. (Cormery, 2020/2021) (Kelly,2007)

For this reason, tests on tetragonal and cubic phases were made with zirconia stabilized with oxide as Yttrium (Y_2O_3), magnesium (MgO), cerium (CeO_2) to determine their properties. Finally, tetragonal, and cubic phases obtain the best properties. (Borrell, 2018)

2.2.3. Yttrium-doped tetragonal zirconia

The purpose is to obtain the tetragonal phase at room temperature without going through the transformation tetragonal to monoclinic. Indeed, the figure 6 shows that during the cooling this transformation would lead to tensions created by a volume increase. At the end, cracks would appear, and the ceramics may be broken. To avoid that, zirconia is stabilized with oxide. In this study, 4 % (mol%) of Yttrium (Y_2O_3) is add to zirconia. (Kelly, 2007)

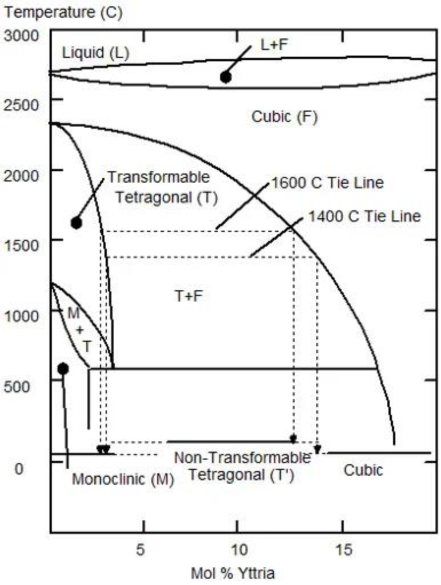


Figure 6: Phase diagram of zirconia

Several tetragonal phases can be obtained however the TZP is chosen because of its properties. Indeed, this phase is known to improve the resistance against the crack propagation. In the next figure, the mechanism is shown. First, there is a stress field that acts on the material and after the cracks appear. If the structure was monoclinic, the cracks would grow and eventually break the ceramic. In this case, at the beginning of the crack, the stress field give enough energy to transform the tetragonal phase into a monoclinic phase. During the transformation, the part that had enough energy to transform itself will see its volume increase. This increasement of volume around the crack implies a compressive tension which is oppose to the stress field, and to the crack propagation. This is a material that can be call self-repairing. (Horwat, 2020) (Butler, 1985)

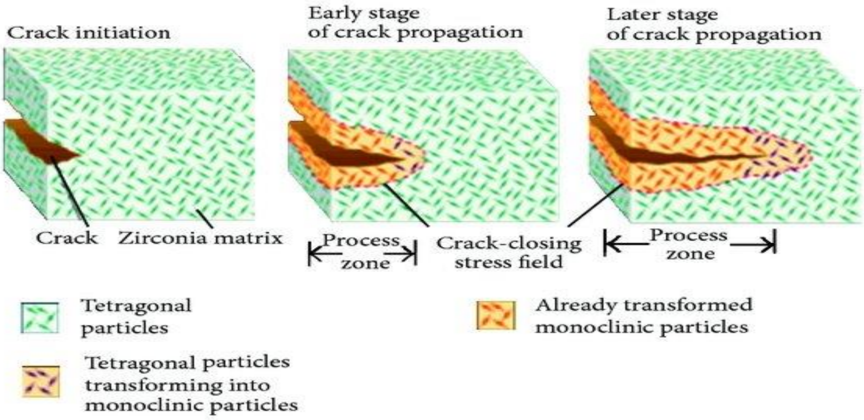


Figure 7: Phase transformation in Zirconia

In the table 1, the properties of the zirconia doped with 4 % of yttrium are summarized:

Table 1: Properties of the Zirconia (Borrell, 2020)

Properties	**Y-TZP**
Density (g/cm^3)	6.05
Grain size (nm)	70
Porosity (%)	<0.10
Hardness Vickers (H_V)	1200-1250
Melting point (°C)	2380
Elasticity modulus (GPa)	210
Critical toughness, K_{IC} (MPa m$^{1/2}$)	1-2
Thermal expansion coefficient (10^{-6} K^{-1})	11.50

2.3. Sintering

Sintering is a process that allows to form the materials. Indeed, this process is used to go from the green state to a ceramic body. This transformation consists in heating compacted powder without reaching the melting point of the material. The main goal of the sintering mechanism is the reduction of the system’s energy. However, the mechanisms that lead to this reduction can be numerous depending on the case.

2.3.1. Solid-state sintering

Solid state sintering is the union and densification of particles when thermally applied at a temperature below the melting point. The driving force is to decrease the total energy of the system.

In this state of sintering, it is mainly the diffusion process that comes into play and leads to the cohesion of the green body. Figure 8 shows the possibilities that can occur during solid state sintering. The aim is always to have a density very close to the theoretical one, which is why it is important to favor the diffusion mechanisms that will lead to a densification and then a coarsening of the grains while avoiding their thickening. This is even more important because once the pores are stabilized it is kinetically impossible to remove them. (Borrell, 2018) (Salernitano,2022)

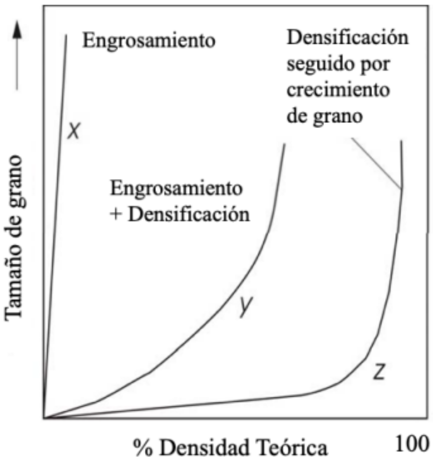


Figure 8: Grain size as a function of density (Borrell, 2018)

The first step of the solid-state sintering is the transport of the matter from area with high potential chemical to area with low potential chemical. This happens due to the potential chemical which exist between the surface area of the particle and the neck region. It is these transport mechanisms that lead to a high or low density depending on the phenomenon they facilitate. The table 2 sum up every mechanism and their effect. However, to differentiate them it is sufficient to look at the path that the matter follows: When the matter comes from the surface to the neck area it allows to make them grow and not to bring them closer (path 1,2 and 3 from figure 9). Whereas, when the matter comes from the border of the grain to the neck area (path 4 and 5 from the figure 9), particles become closer and lead to a densification. (Borrell, 2018) (Gilbert, 2021/2022)

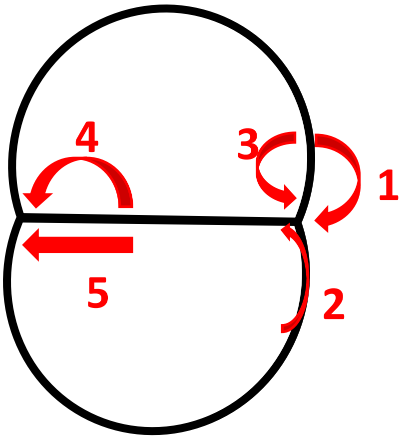


Figure 9: Different transport mechanisms between two grains during sintering (Gilbert, 2021/2022)

Table 2: Mechanisms of matter transport and their effect on the system (Gilbert, 2021/2022)

Mechanism	**Displacement nature**	**Source**	**Phenomenon**
1	Gaz transport	Grains surface	Grain growth
2	Superficial diffusion	Grains surface	Grain growth
3	Volume diffusion	Grains surface	Grain growth
4	Volume diffusion	Grain boundary	Densification
5	Grain boundary diffusion	Grain boundary	Densification

After that, the structure change, the grains become closer, bigger and start to create grain boundaries between pores. At the end of this step, the densification has created a continuous network and pores become isolated.

The last step is one of the most important because it remain only isolated porous. Often, they are located at the borders of the grains or trapped inside the grains and this step of the solid-state sintering aims to remove them in order to get the best material properties. Finally, the three steps are well summarized in the figure 10. (Borrell, 2018)

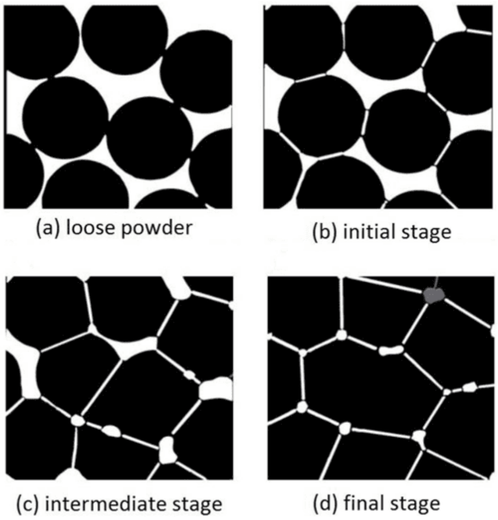


Figure 10: The various stages of sintering

2.3.2. Non-conventional sintering: Microwaves sintering

Nowadays, the microwaves sintering is more widely used because of all of its advantages. As a matter of fact, this technique is faster than conventional technique of sintering and attracts companies. In addition of that, the density is really close to the theorical and the size of the grain stays the same that improve the final mechanical properties. In conclusion, it is faster, consume less energy and a better piece is obtained.

2.3.2.1. Interaction microwave/matter

During the conventional sintering, the main source of heat come by conduction or radiation. In this case, at first the compacted powder absorbs the electromagnetic energy due to the microwaves that hit the green body. Then, once the energy is absorbed it is transformed into heat. It is diffused into all the volume of the green body and helps the diffusion mechanism. On the contrary of conventional sintering the heat come from the inside and it allows a better homogeneity.

There are three main categories into which the interactions between microwaves and matter can be classified (Gilbert, 2021/2022) (Borrell, 2018):

- Transparent materials allow microwaves to pass through without absorbing energy (figure 11a).
- Opaque materials do not let the waves penetrate and reflect them 100%. These are called conductors (figure 11b).
- Transparent/translucent materials absorb some of the microwaves depending on their dielectric loss coefficient (figure 11c)

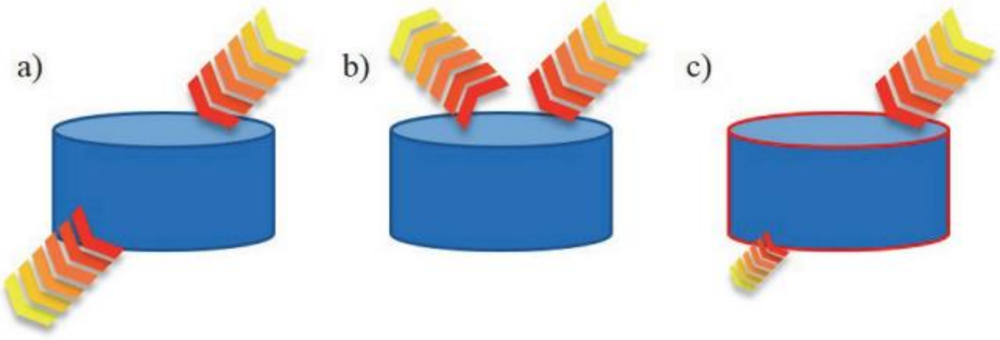


Figure 11: Matter-microwave interaction (Borrell, 2018)

2.3.2.2. Heating mechanisms

Four different mechanisms of heating lead to a large-scale heating: bipolar rotation, resistive heating, electromagnetic heating, and dielectric heating. The mechanism used depends on the response of the material to radiation (Borrell, 2018).

- Bipolar rotation takes place on electrically neutral molecules. The charges start to rotate and create molecular friction under the oscillation of the magnetic field. This friction is then transformed into heat.
- Resistive heating occurs on conductors or semi-conductors with high electrical resistance. The electrons or ions must have enough freedom to generate a current that will turn into heat.
- Electromagnetic heating happens on materials that have a high magnetic susceptibility. As for bipolar rotation, heat comes from the rotation of the magnetics poles under the effect of magnetic waves.
- Dielectric heating is a mixture of bipolar rotation and resistive heating. It is the mechanism that occurs most often during the sintering of ceramics.

As dielectric heating occurs the most in ceramics, the theoretical aspects will be introduced. In the case of absorbent materials, there are two important parameters to describe. The first is P (equation 1) the absorbed power, the energy that the material will absorb. The second is D (equation 3) the depth of penetration of the microwaves which determines the penetration at which the power is reduced to half.

P is calculated by the following equation. In this expression, the radiation frequency is represented with f, the electric field intensity with E, then the vacuum permittivity and the dielectric constant of the material with ε_0 and ε' respectively. (Borrell, 2018) (Gilbert, 2021/2022)

$$P = \sigma |E|^2 = 2\pi f \varepsilon_0 \varepsilon' \tan\delta \, |E|^2$$

Equation 1: Power absorbed by the materials

$$\tan\delta = \frac{\varepsilon''}{\varepsilon'}$$

Equation 2: Loss tangent

The tangent loss allows to calculate the capacity to convert the incident energy into heat. In equation 2, ε'' loss factor is used to measure the ability of the material to transfer microwave energy into heat. When we divide this quantity by ε' which allows to know the polarization of the material the tangent loss is obtained.

These two quantities depend on the temperature and the frequency. At low frequency all the energy is absorbed by the rotational movement of the dipoles and the dielectric constant is at its maximum. At higher frequencies, ε' is minimal because it cannot follow the electric field. The goal is to find the right frequency for each material and make sure that ε' and ε'' are high.

In summary, the goal is to force the molecules to change their position quickly so that they create heat. And this operation is possible thanks to the change of polarities of the field.

The second reason why low frequencies are preferred is that there is a direct link with the depth of penetration of microwaves. in fact, the lower the frequencies are with small dielectric values, the more the heating will be done in the whole volume.

$$D = \frac{3\pi_0}{8{,}686\pi \, tan\,\delta \left(\frac{\varepsilon'}{\varepsilon_0}\right)^{1/2}} = \frac{C}{2\pi f\sqrt{2\varepsilon'}\left(\sqrt{1+\tan^2\delta - 1}\right)^{1/2}}$$

Equation 3: Penetration depth of microwaves into the material

2.3.2.3. Hybrid heating system

The biggest problem with microwave sintering is temperature control. The fact is that thermal instability can lead to excessive heating which can cause non-homogeneous properties in all material. This happens especially with alumina or zirconia because they follow a gauss curve when heated. The coefficient of this curve is the most important around 400 °C.

A hybrid heating system is therefore set up which consists in heating by microwave and by transmission. If the basic component has a low dielectric loss at low temperature as zirconia, it is necessary to place it with a component that has a high dielectric loss at low temperature as silicium carbide, which is called a susceptor. The microwaves will be absorbed by the susceptor, which will rise in temperature and transmit it to the sample by transmission. Once the temperature reaches the temperature where dielectric properties are better, the sample itself can absorb the microwaves.

2.3.2.4. Components of microwave oven

In this study, a single mode microwave oven manufactured by ITACA-UPV (Instituto de Tecnología de la Información y de las Comunicaciones Avanzadas) is used. Below, the components will be described, and a schematic sketch (figure 12) will be provided to visualize. (Borrell, 2018)

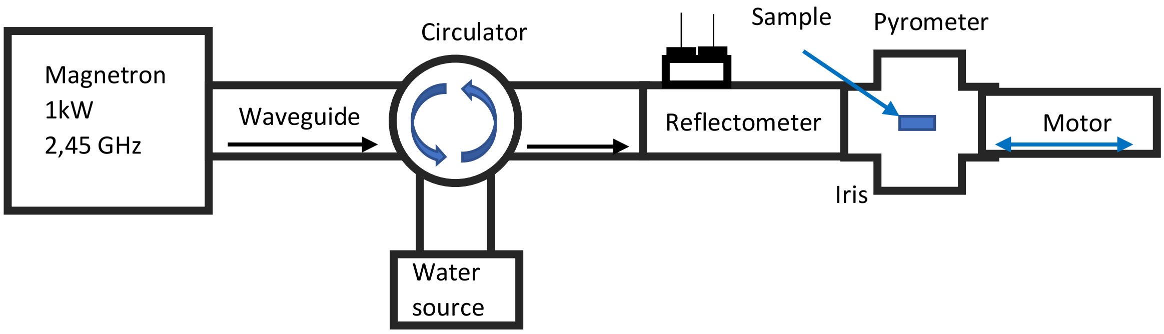


Figure 12: Schematic of a monomodal microwaves oven (Borrell, 2018)

- Magnetron is the power source of the microwaves: it transforms electric energy into electromagnetic energy. Usually, the frequency used is 2.45 GHz.
- The circulator is used to protect the Magnetron. Indeed, there is some microwaves that can be reflected and damaged the magnetron. To avoid that, the circulator redirects unconsumed waves to a water source.
- The reflectometer measured the incidental and reflected power to have a reliable indication of the absorption value and the real power used.
- Iris couples the power of the microwaves into the cavity.
- The rectangular cavity of section 86.36 mm x 43.18 mm can be modified during the sintering to make the waves resonant and thus control the temperature.
- The pyrometer is added in the part superior of the cavity to always have a control of the temperature.
- The motor which controls the dimensions of the cavity.

3. Equipment techniques and method

3.1. Pellets

Pellets always play a big part in the creation of the sample. Indeed, quality of the pellets has a direct relationship with the mechanical properties of the final part. In this study, the first zircon-PLA pellets (figure 14) were used with a 63 %wt zircon content. These had a non-homogeneous size that made printing part a little difficult. After some testing, the pellets were crushed in a grinder (figure 13) to reduce their size. The same issue occurred with 86 %wt (50 vol%) zirconia and the binding agent (figure 13). For this material, a spool of wire was received and had to be cut once and then run through the grinder as well.

Figure 15: Zirconia (ZrO_2) + binding agent

Figure 14: Grinder

Figure 13: Zircon ($ZrSiO_4$) + PLA

3.2.Powders characterization

3.2.1. Thermogravimetric analyzer (TGA)

The purpose of this characterization is to confirm the quantity of each component in the powder. Indeed, once the green state of the sample is obtained, the thermogravimetric analyzer (figure 16) is used to measure the weight change as a function of the temperature. The sample is heated with hydrogen until 700 °C at constant rate (5 or 10 °C/h) to eliminate every trace of binding agent, and the weight is constantly measured. At the end, we get a graphic the percentage of weight in function of the temperature and the weight loss is the percentage of binding agent in the powder. This characterization technique allows to verify the composition of the powder, in this study only two components are used (ZrO_2/$ZrSiO_4$ and the binding agent) but lots more can be identified if you know the melting point of the different compounds.

Figure 16: Thermogravimetric analyzer (TGA)

This test has been carried out five times. The two first times were on green body state of zircon and zirconia to verify that the powder was in accordance with the material's data sheet. After two tests (for zircon and zirconia) were made after the sintering to check if there is some binding agent/PLA remaining. This allows to control the quality of the sample with a high percent of ceramic. And finally, the last test has been done for the zirconia just after the acetone bath to know how effective this step was. the last test if it is satisfactory, allows to change a little the conventional sintering by removing a stage at 200 °C, which can make save time and energy.

3.3. Processing 3D printing

3.3.1. Design of the piece

The sketch of the piece is drawn on the software *solidworks.* This is a 3D design assistance software that allows to design all desired shape at the desired dimension. Once the STL file is created, another software *simplify3D* change the original file to g-code file that allows the printer to read it. *Simplify 3D* is not only a converter of file, but some parameters are also adjustable before the conversion such as the percent of infill which allows the creation of grid pattern on the piece. The height of one layer, the overlap between two filaments, the size of the piece and even more can be control via this software. Then, the computer is connected to the 3D printer and the g-file is upload on it.

At the beginning of the study, only disks were made. It was the easiest shape to obtain, and this has allowed for the adjustment of printer parameters such as temperature, percentage of infill, the height between two layers, the size of the sample, the speed, and the flow. Moreover, it was on disks that all tests have been carried out. Then, come the square and the cross the designs were a bit more complicated. As some problems have emerged at the beginning, it was an occasion to see if the 3D print could make more complex shapes. And at the end, when it was sure that the parameters were well adjusted, some large complex samples have been shaped as teeth, high cone, high tube, bolts, and dentures.

3.3.2. Parameters of the 3D printing

Before launching the printing, it is necessary to have created a file for the special material that is used to indicate to the printer what is the appropriate temperature, speed, and flow. Two were required, one for the zircon and the other for the zirconia. However, after several try to shape a disk, the number of failed attempts was much greater than the number of successful attempts. Someday, ten attempts were tried to obtain one good green state body.

The problem was an amount of material half melted which blocked the hole where the pellets pass. There are two temperature captors in the 3D print: one is on the nozzle of the tool and the temperature need to be sufficient to have a continuous filament during all the process and the other one is into the hole where the pellet are coming. The temperature of these two was way too hot (220 °C-180 °C instead of 180 °C-110 °C), so it melted the pellets too early which clogged the hole, and nothing flowed. Another problem was the height between two layers. at the beginning 0,4 mm was chosen and sometimes some layers were missed because the filament did not lie on the last layer. Finally, 0,25 mm was more accurate. In the same range of issue, when the percentage of infill was too high, there was a surplus of material, and the green state body was not as expected. For small disk or piece, the best infill was 10 % because the nozzle was not enough precis and too many materials ruin the sample. For large piece, 20 % or 30 % was used because from 40 % there was a surplus of material and at the end the shape could have been different and the properties too.

3.4. Sintering

3.4.1. Conventional sintering

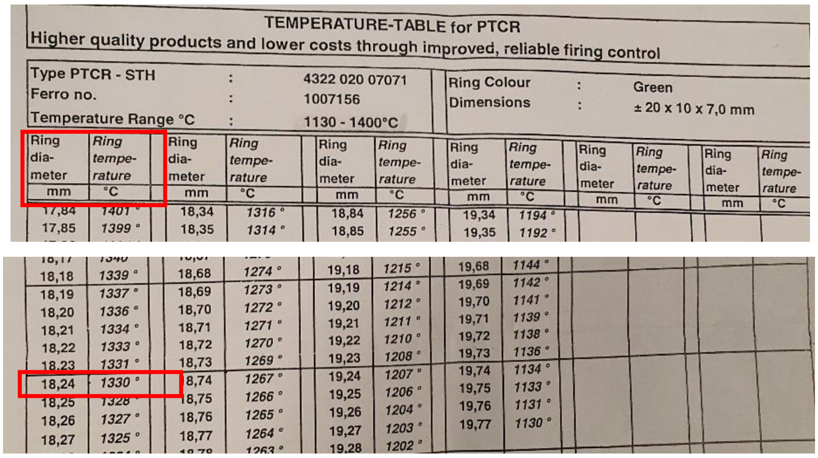
In this project, a solid-state sintering is made, that’s why a special oven for ceramics (carbolite gero shown in figure 17) is used. This oven can be programmed and reach the temperature of 3000 °C.

During the experiments, some parameters as the heating rate or the stage duration has been changed to obtain a better quality of the sample.

Figure 17: Carbolite Gero high temperature oven used for conventional sintering

The green body part is composed by two materials zircon (or zirconia) and binding agent, so at least two stages are required during the sintering. The first stage needs to be around 400 °C to remove the binder. The other one is around 1500 °C (1400 °C for zirconia) to increase the density of the materials and take away porous. The temperature inside the oven was verified thanks to a PTCR-STH. As the figure 19 shows it, it is a ring that have a contraction during the heating. At the end, the ring is measured and with a table (figure 18) it is possible to know the temperature inside the oven.

Figure 19: Size PTCR-STH after sintering



TEMPERATURE-TABLE for PTCR
Higher quality products and lower costs through improved, reliable firing control

Type PTCR - STH : 4322 020 07071
Ferro no. : 1007156
Temperature Range °C : 1130 - 1400°C
Ring Colour : Green
Dimensions : ± 20 x 10 x 7,0 mm

Ring diameter mm	Ring temperature °C	Ring diameter mm	Ring temperature °C	Ring diameter mm	Ring temperature °C	Ring diameter mm	Ring temperature °C	Ring diameter mm	Ring temperature °C	Ring diameter mm	Ring temperature °C
17,84	1401 °	18,34	1316 °	18,84	1256 °	19,34	1194 °				
17,85	1399 °	18,35	1314 °	18,85	1255 °	19,35	1192 °				
18,17	1340	[illegible]	[illegible]	[illegible]	[illegible]						
18,18	1339 °	18,68	1274 °	19,18	1215 °	19,68	1144 °				
18,19	1337 °	18,69	1273 °	19,19	1214 °	19,69	1142 °				
18,20	1336 °	18,70	1272 °	19,20	1212 °	19,70	1141 °				
18,21	1334 °	18,71	1271 °	19,21	1211 °	19,71	1139 °				
18,22	1333 °	18,72	1270 °	19,22	1210 °	19,72	1138 °				
18,23	1331 °	18,73	1269 °	19,23	1208 °	19,73	1136 °				
18,24	1330 °	8,74	1267 °	19,24	1207 °	19,74	1134 °				
18,25	1328	8,75	1266 °	19,25	1206 °	19,75	1133 °				
18,26	1327 °	18,76	1265 °	19,26	1204 °	19,76	1131 °				
18,27	1325 °	18,77	1264 °	19,27	1203 °	19,77	1130 °				
[illegible]	[illegible]	18,78	1263 °	19,28	1202 °						

Figure 18: Temperature table for PTCR

At the beginning, a first sintering has been decided to get a first impression. After that, the sintering was empirically improved until the moment the samples were good enough to be analyzed. There is in the table 3 the summary of all the sintering tested.

Table 3: Different sintering applied

Attempts	**Material**	**Heating rate (°C/min)**	**Stage (°C)**	**Stage duration (h)**	**Heating rate (°C/min)**	**Stage (°C)**	**Stage duration (h)**	**Heating rate (°C/min)**	**Stage (°C)**	**Stage duration (h)**
1	$ZrSiO_4$	5	400	3	10	1400	2			
2	$ZrSiO_4$	5	200	2	5	400	2	10	1500	2
3	$ZrSiO_4$	0.5	200	2	0.5	400	2	5	1500	2
4	ZrO_2	0.5	200	2	0.5	400	2	5	1400	2
5	ZrO_2	0.5	400	2	5	1400	2			
6	ZrO_2	0.5	400	2	5	1300	2			

Once the best one has been found, the samples were made in zirconia to replace the zircon. This material just reduces the final stage by 100 °C (from 1500 °C to 1400 °C) and adds one step before the sintering because it required to be leave in acetone during six hours at 40 °C and then let the whole night rest. The first time, the acetone step was forgot, and the samples were cracked. That is why, this is an important step which allows to remove a first big part of acetone.

For the fifth sintering, the stage at 200 °C was removed to win some time. Moreover, as the big part of binder is gone thanks to acetone, there is no difference. The last sintering has been made to have a comparison at the same temperature than the Microwave sintering. As it is not possible to exceed 1300 °C with the latter, the sintering in the oven was reduced by 100 °C.

3.4.2. Microwaves sintering

For the Microwaves sintering, a monomodal microwaves device has been used (figure 20). It is a device made by ITACA-UPV (Instituto de Tecnología de la Información y de las Comunicaciones Avanzadas) in collaboration with the ITM-UPV (Instituto de Tecnología de Materiales). The sample is placed into a silicon carbide crucible surrounded by Alumina fiber to control the increase of the temperature and adjust the height. Indeed, if the sample is not places into a crucible, the heating is not linear and there is a huge increasement of temperature around 400 °C.

Figure 20: Monomodal microwave oven designed at ITACA-UPV

Once the sample is put into the resonant cavity and the power is set to 350 W, the test can begin. The first step is to fill some values in the software as the emissivity and the transmissivity of the material. Then, tuning position (motor position) is put on the origin and gradually increases. The person managing the test must increase the tuning position carefully because it has a relation with the temperature. Indeed, the temperature follow a Gauss curve when the tuning position increase. Once the maximum point is reached, there are few adaptations left to keep the maximum heat and the sample is let five minutes to be sintered.

One sample has been sintered at 1200 °C and another at 1300 °C. The first sintering broke the sample in pieces, the heating was too fast, and the sample could not handle the temperature increase. The heating at 1300 °C was slower and the other sintering was a success. Finally, characterization test was carried out on both samples.

3.5. Samples preparation

After sintering, the sample is small enough to enter in the hot mounting press (figure 21). The sample must rest on the flattest surface. Indeed, it is the flattest surface that will be analyzed. Then, the thermoplastic acrylic is filled on top and after five minutes of heating and five of cooling at 15 N, the sample is mounted.

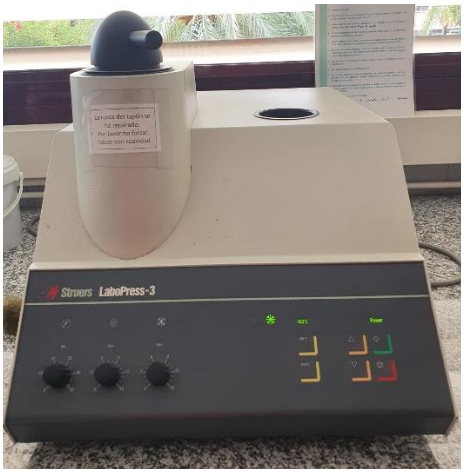


Figure 21:Mounting press

After being mounted, the sample is polished according to a specific protocol which is the same for each sample. The table 4 summarized it. Polishing is useful to get a perfectly flat surface and to decrease the roughness before doing characterization tests. After the last three polishing steps, an ultrasonic cleaning is performed for one minute. Then, the sample is rinsed with distilled water and dried carefully.

Table 4: Polishing steps

Size (µm)	**Time (min)**	**Lubricant**	**RPM**	**Force (N)**
75	5	Water	100	10
40	1	Water	100	10
20	1	Water	100	10
10	1	Water	100	10
6	10	6 µm lubricant	150	20
3	8	3 µm lubricant	150	20
1	8	1 µm lubricant	150	20

Figure 22: Polishing machine

3.6. Samples characterization

After the coating and the polishing, the samples are ready for characterization. For complex ceramics lot of tests are available, but not all are necessary. The most important tests for ceramics sample are at first, density to see if the material is not too porous. If it is not, sample is unusable. Then comes the microhardness test which is performed with the Vickers Test. And finally, the size of the grain and the fracture of the sample is analyzed with the Field Emission Scanning Electron Microscopy (FESEM). Once that all those tests are completed, discussion and hypothesis can begin.

3.6.1. Contraction

During the sintering of ceramics, the sample always undergoes a contraction due to the densification of the piece. The goal here is to measure the size of the samples (width, length, height, thickness, diameter) before and after the sintering to have precise data on the contraction of zircon and zirconia. Thanks to these data, it will be possible in the future to make custom-made parts in the bio-medical field. All the sample are measured with a digital millimeter caliper.

3.6.2. Density

Density of the final part is very important because if it is not enough the mechanical properties are low. There is no need to test them, if the porosity is too important, Vickers test and FESEM are useless. That is why, the quality of the powders and the sintering are important.

To calculate the density, the Archimedes equation is use:

$$\rho = \frac{W(a) * \rho(fl)}{W(a) - W(fl)}$$

Equation 4: Formula of Archimedes density

First, the piece is immersed in distilled water. This water is heated for 3 hours and then left in water all night. The wet piece is weighted with a precise scale W(fl). The setup is shown in the picture 23.

Figure 23: High precision scale

Later, the piece is dry in a 100 °C oven for 2 hours and then the mass of the sample is measured W(a). In addition, the tables give us the density of the water at the room temperature. The density of the experimental piece is now calculated with Archimedes equation. From that porosity can be obtained with a rule of three with the theorical density of the material.

3.6.3. Microhardness

To obtain the microhardness of the sample, the Vickers test is done. This test consists of applying a pyramid-shaped diamond indenter with a square base and an angle at the top between the face equal to 136 °C as shown in figure 24. The print let on the material is used to calculate the hardness. (Cormery, 2020/2021)

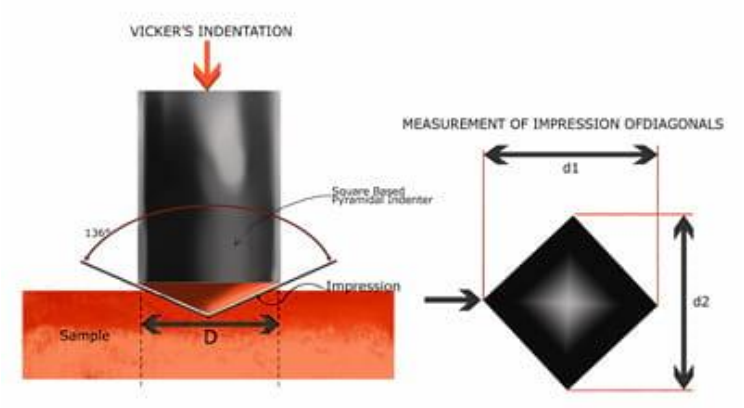


Figure 24: Principle of the Vickers test

The force applied can be change according to the hardness of the material. In order to get accurate result, 10 measurements are made per samples. The diagonals of the print are measured and give an average value that allow to calculate the hardness with the equation 5. At the end, the aberrant values are removed to obtain a reliable value of the hardness.

$$H_v(MPa) = \frac{1{,}85.F(N)}{d^2(mm)}$$

Equation 5: Vickers Hardness

All the hardness tests have been carried out with a force of 4.903 N (H_V 0,5) except the test on the sample sintered in the microwave at 1200 °C. The same force as for the other samples leaving a mark too big to measure so we had to reduce the force to 490.3 mN. The sample was broken during sintering that can explain a lower hardness.

3.6.4. Field Emission Scanning Electron Microscopy (FESEM)

Electronic microscope (figure 23) is a tool that allows to discover the topography of the sample. This is obtained thanks to an interaction electron/matter. Indeed, the principle is to send an electron beam on the surface of the sample. Due to the interaction between the matter on the surface of the sample and the electrons, secondary electrons are emitted. Then, the secondary electrons are captured by a sensor which can transform them into an electrical signal. Finally, a software re-creates the topography of the sample. (Mutalib, 2017)

Figure 25: Electronic microscope

However, in this study there is one step to do before putting the samples into the electronic microscopy. Indeed, due to the yttrium which stabilizes the zirconia, the sample has become electrically. Therefore, a thin layer of Au/Pd is coated on the sample using a vacuum sputtering (figure 26) technique to allow the use of the electronic microscope.

Figure 26: Sputtering machine

In this study, the electronic microscope is used for several reasons. The first one, is for high spatial resolution, to calculate the size of the grain or to see the porosity of the sample. For that, the samples were previously thermally etched. The second one is to observe how the sample fractured. Concerning the grains size, the purpose is to compare the grain size between different materials, different sintering but also to analyze the evolution of the grain size. That's why zircon and zirconia pellets have been thermally etched and observed in the electrical microscope.

Usually, the thermal etching takes place for 30 minutes at 100 °C below the sintering temperature. However, the thermal etching of zircon was done at the same time as the thermal etching of zirconia to analyzed them at the same time in the electronic microscope. The problem is that the temperature of sintering of zircon is 1500 °C and zirconia's is 1400 °C. So, the thermal etching has been done at 1300°C during half an hour. Finally, the thermal etching was not enough for the zircon sample.

4. Result and discussion

4.1.Powder characterization

4.1.1. Zircon

The first TGA test has been made on the Zircon pellets to verify that the data sheet stated the correct value of PLA in the zircon pellets. Above 400 °C, there is no PLA left as the figure 27 shows. The exact percent can be read on the Y-axis. So, at the beginning, there is indeed 38.5 %wt PLA and 62.5 % of $ZrSiO_4$.

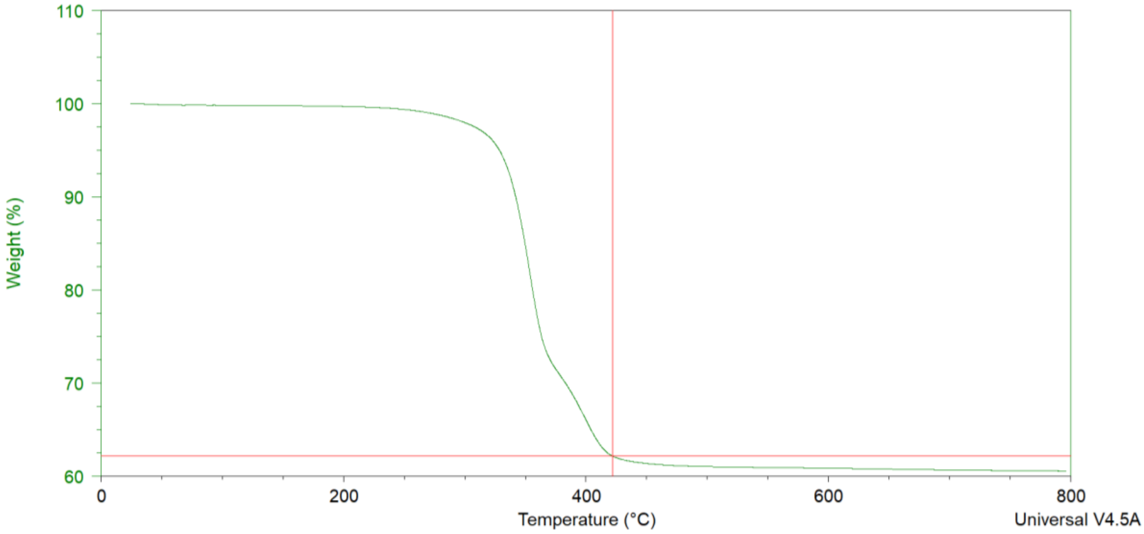


Figure 27: Proportion of PLA into the zircon pellets

Then the second test is on a zircon sample after the sintering 3 to check that there is no PLA remaining into it. The TGA test (figure 28) shows no weight loss in the sample. That means that the sample is composed exclusively of zircon and there is no PLA remaining.

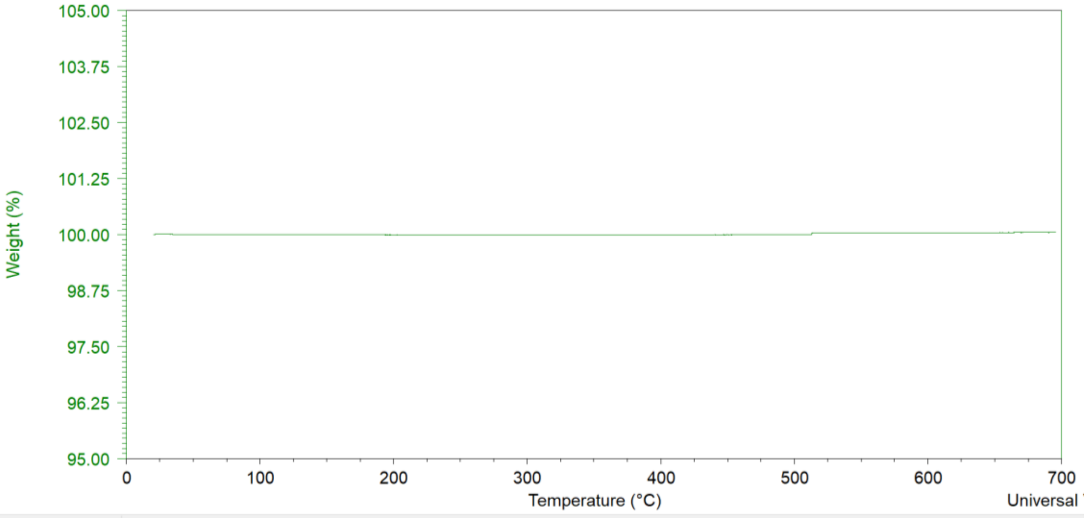


Figure 28: Proportion of PLA into the zircon after sintering

4.1.2. Zirconia

The test on the zirconia pellets is done for the same reasons that for the zircon. The data sheet announced 86 wt% zirconia for 14 wt% of binding agent. The graph below (figure 29) illustrates that with the stage after 500 °C at 86 wt%. The stage is higher than for the zircon because the binding agent has not the same melting point than the PLA. However, it remains a mixture of polymers with a lower melting point than zirconia.

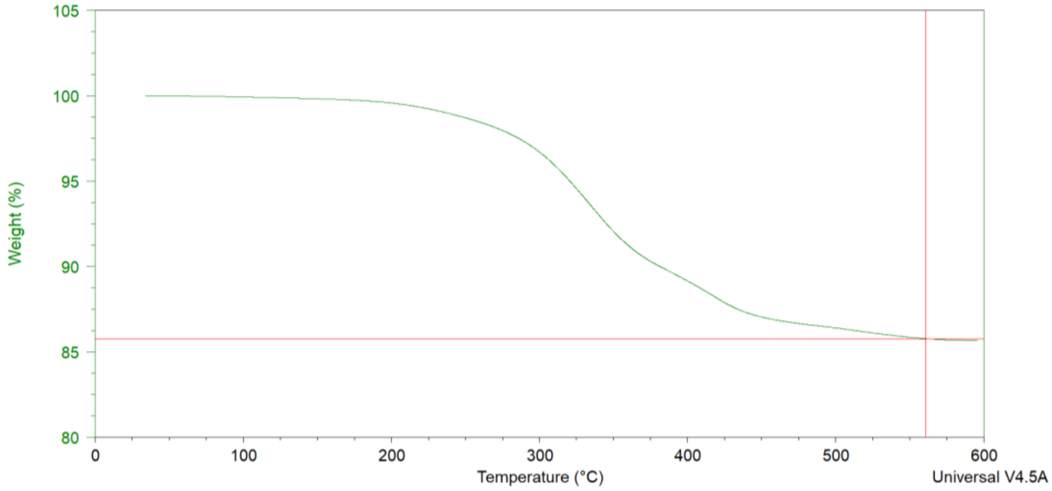


Figure 29: Proportion of binding agent into the zirconia pellets

The second test takes place after the green body has passed the acetone stage and just before it is sintered. The figure 30 demonstrates how effective the acetone step is in removing binder from the green body. In the end, this step manages to remove 8 wt% of binding agent from the 14 wt% total. This represents 60 wt% of the binder. Adding this step before the sintering is indeed very beneficial because it allows to accelerate the sintering because very little polymer remains. After that, the 200 °C step during the sintering has been removed to save time.

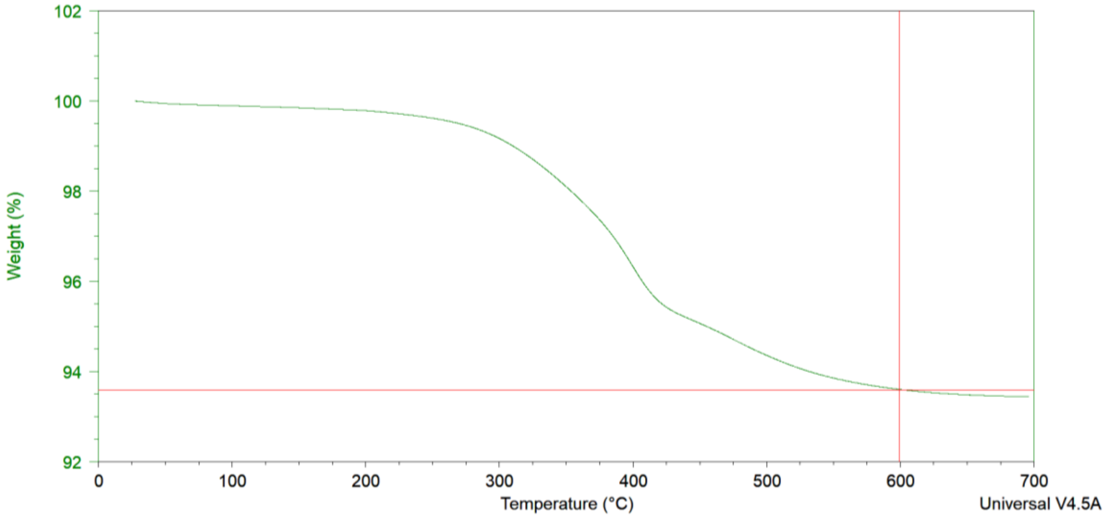


Figure 30: Proportion of binding agent into zirconia sample after the acetone bath

The last graph (figure 31) clearly shows that after sintering the material is composed only of zirconia with 99.76 % purity.

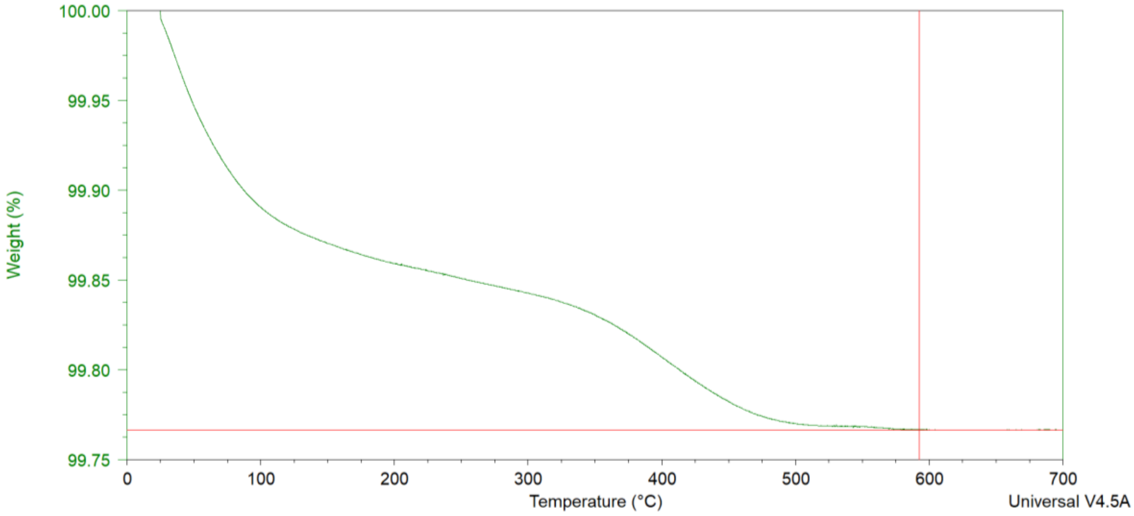


Figure 31: Proportion of binding agent into zirconia sample after sintering

4.2. Sintering

4.2.1. Conventional sintering

During conventional sintering, the first sintering operations were made on zircon samples. As the picture illustrates, the samples were damaged, deformed and barely recognizable. The first mistake was that the temperature rise was far too fast and so during the next sintering a stage was added. However, this was not the only problem as the 40 % sample was not as bad as the others (figure 32 d). he percentage of a sample is the percentage of material that makes up the sample. For example, a 100% sample means that the sample is completely filled, the lower the percentage, the more space there will be between the filaments that constitute the structure. It was noted that the samples above 40 % were of poor quality and that probably the overfilling of a small sample had a bad effect during sintering (figures 32 b), c) and e)).

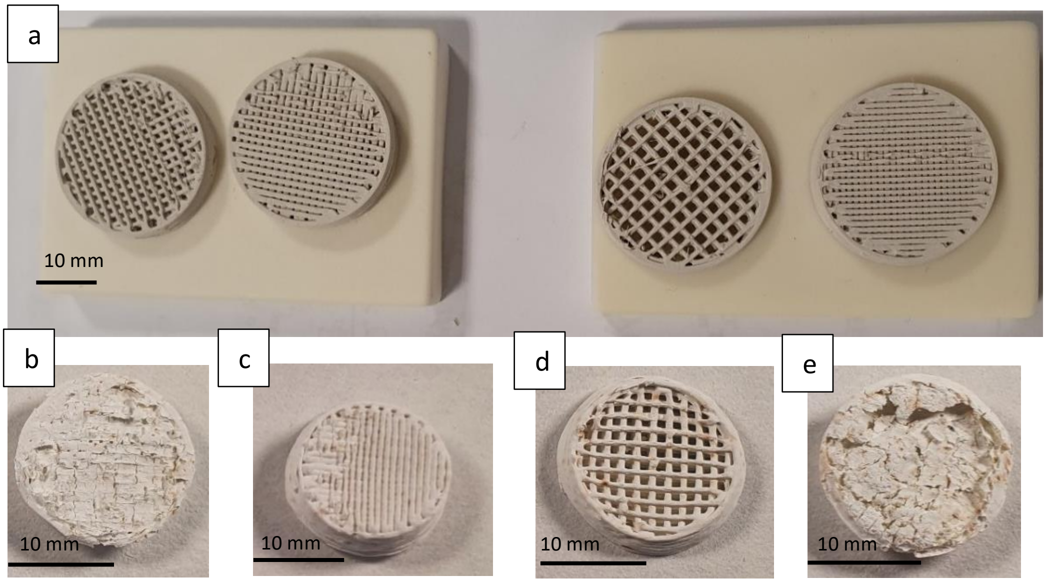


Figure 32: First sintering: a) samples before the sintering 60%, 80%, 40% and 100% of infill; b) 60% infill after sintering; c) 80% infill after sintering; d) 40% infill after sintering; e) 100% infill after sintering

For the second test, it is still zircon but with a much lower filling (20 %, 30 % and 40 %). The result is unequivocal, the less material the structure is filled with, the better the samples are. This time, the worst sample is the one with 40 %, notably because of a bulge in the sample (figure 33 f) g)). The samples are still not usable, the sintering is still too fast.

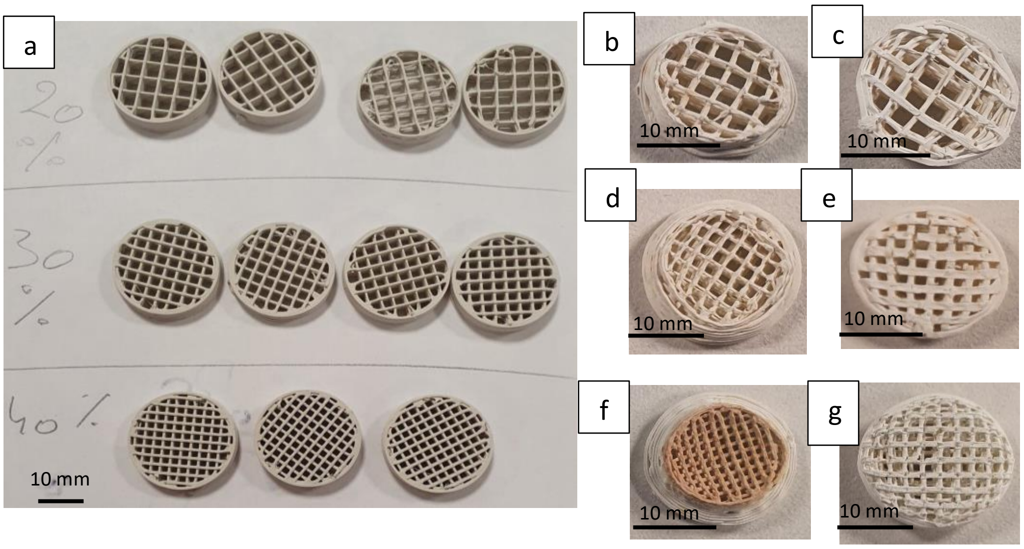


Figure 33: Second sintering: a) samples before the sintering 20%, 30% and 40% of infill; b) c) 2 sides of 20% infill after sintering; d) e) 2 sides of 30% infill after sintering; f) g) 2 sides of 40% infill after sintering; e) 100% infill after sintering

For the third sintering test, the same filling percentages are kept and only the temperature rise is slowed down. The samples are not perfect but are usable (figure 34) and can be analyzed which is a good thing. Now that the right sintering has been found samples can be made of zirconia.

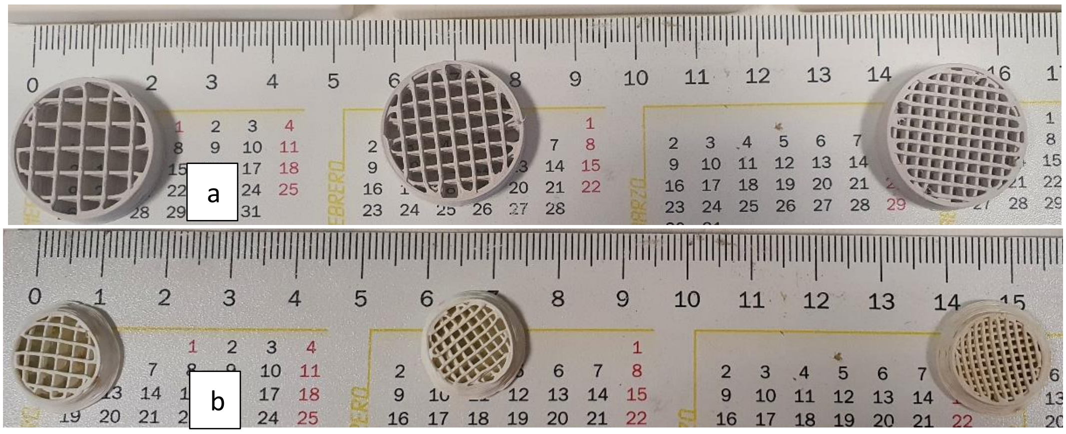


Figure 34: Third sintering: a) samples before the sintering 20%, 30% and 40% of infill; b) 20%, 30% and 40% infill after sintering

Sintering four is the same as the third except for the final sintering temperature which is 1400 °C instead of 1500 °C because zirconia and zircon do not have the same sintering temperature. The samples come out without deformation just with a contraction. However, the samples containing two layers at the bottom ended up cracked, as can be seen in the figure 35 c) and d). One step was forgotten, that of putting the specimens for six hours in acetone to remove most of the binder which is there just to help print the specimen at a lower temperature. The next sintering was done in the exact same way but without forgetting the acetone step and the specimens were in perfect condition (figure 36).

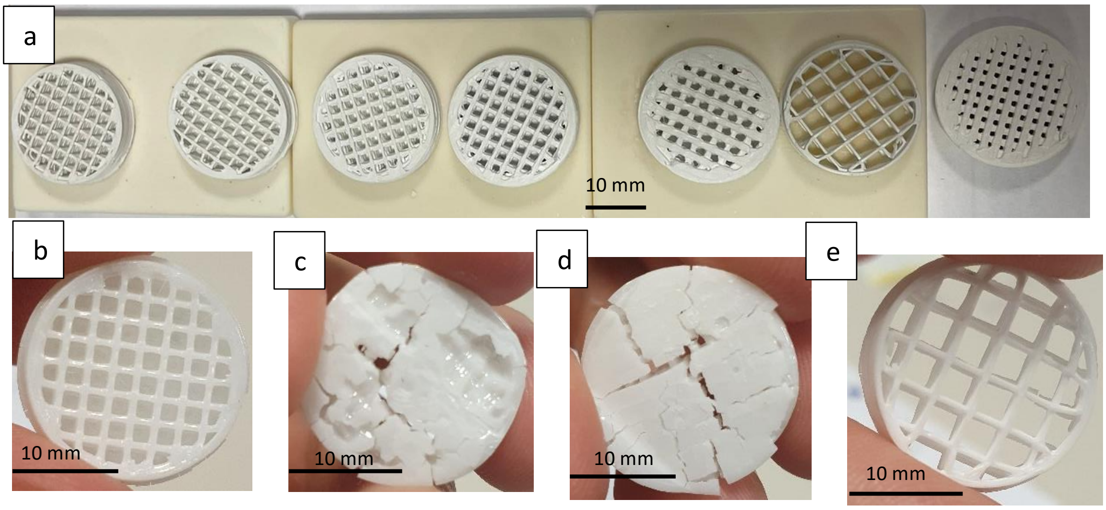


Figure 35: Fourth sintering: a) samples before the sintering 5 of 30%, and 1 od 20% infill; b) 30% infill after sintering; c) 30% infill other side after sintering; d) 30% infill other sample after sintering; e) 20% infill after sintering

The last samples, which were mainly experiments to see how to make more complicated parts (as teeth, square, cross), were made without the 200 °C stage. Once the TGA test has proved that the main part of the binder was removed during the acetone test, one stage was removed to win some time. Finally, no difference has been seen between the sintering four and five.

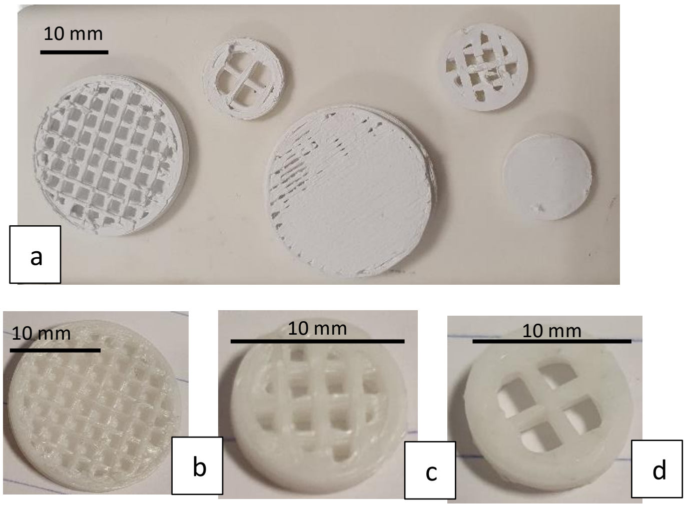


Figure 36: Fifth sintering (+ acetone step): a) small samples before the sintering 20%, 30%, 100%. For large sample, the 2 sides of 30% infill; b) 30% infill after sintering; c) small sample 30% infill after sintering; d) small sample 20% infill after sintering

4.2.2. Microwaves sintering

During microwave sintering, the first sample to be sintered was a disc made of zirconia with a filling ratio of 20 %. For this type of sintering, the sample must be small enough to fit in the cavity. A power of 350 W was deployed during the test and when the 1200 °C value was reached the sintering time was five minutes. Despite the silicon carbide which was supposed to smooth the temperature curve, the temperature rise was too fast and as can be seen in figure 37 b), at the end the sample was in pieces. The hardness test and the density test could still be applied to the sample despite the condition it was in.

The test was repeated a few days later with a 30 % filled zircon sample. The same conditions were applied but the temperature rise was better controlled, and the sample was in good condition. In figure 37 c) and d), the before and after sintering is shown and there is no visible difference with conventional sintering. The mechanical properties can now be tested.

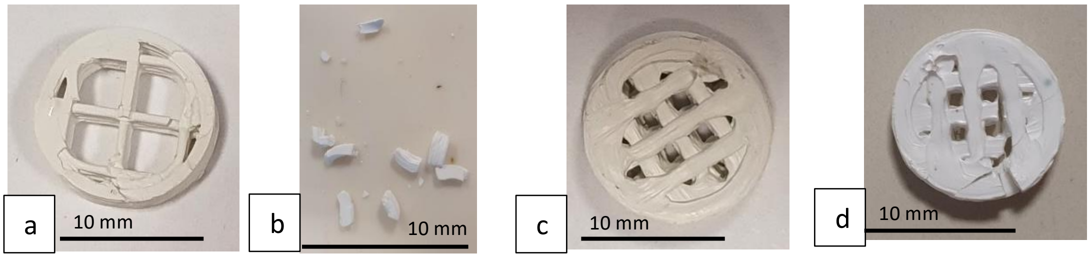


Figure 37: a) before sintering 20% infill; b) after 1200°C MW sintering; c) before sintering 30% of infill; d) after 1300°C MW sintering

4.3. Contraction

Contraction of samples due to sintering is a normal phenomenon. However, it is important to know the percentage of contraction especially when custom parts are to be manufactured. The contraction can change according to different materials or different shapes. The tables below are a summary of all the contractions according to the different parameters. Each sample was measured with a digital caliper.

4.3.1. Disc

Firstly, the discs were measured according to their diameter and height. At first sight, the diameter of the zircon disc underwent a contraction twice as important as the others (30 %). Otherwise, the different diameter contractions for the zirconia seem to be about the same around (15 %). The only exception is ZrO_2-small disk-HC 1300, but this is probably due to a lack of precision on small samples. Every small measurement error is more significant on small samples than on large ones. Concerning the height, it is harder to compare because these are only a few millimeters high so as mentioned above the lack of precision can change the values.

Table 5: Contraction of the disks

Samples	Diameter contraction %	Height contraction %
ZrSiO4-disk-HC 1400	31.9	16.4
ZrO2-disk-HC 1400	16.1	17.3
ZrO2-small disk-HC 1400	16.2	12.0
ZrO2-small disk-MW 1300	14.3	6.5
ZrO2-small disk-HC 1300	19.8	18.1

4.3.2. Square/Angle

Then, come the square and the angle so for these, the height and the two sides have been measured to make an average as shown in the figure 38.

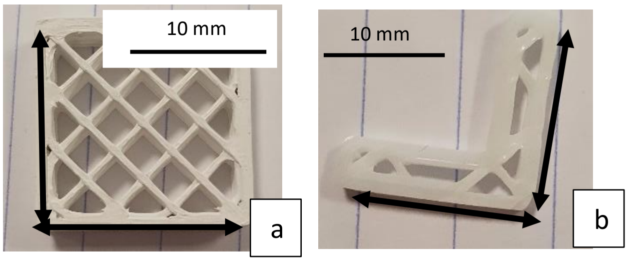


Figure 38: a) Different lengths measure for square sample; b) different lengths measure for angle sample

With the square/angle shapes, the contraction is a bit more important than with the disc. It is around 20 % and for the height even if the values are not completely reliable but they give an order of magnitude which is in the same range as for the other lengths.

Table 6: Contraction of squares and angles

Samples	Contraction (%) of the mean of the 2 lengths	Height contraction %
ZrO2-square-HC 1400	20.5	16.2
ZrO2-small square-HC 1400	20.8	17.1
ZrO2-small angle-HC 1400	18.1	7.3

4.3.3. Cross

For the cross shape, the diameter inside has been measured in addition to the same length as for the square as illustrate on figure 39.

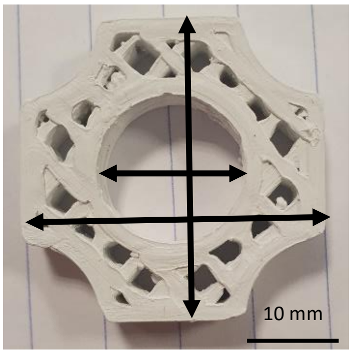


Figure 39: Different lengths measure for cross sample

This time again, table 7 shows that the contraction is around 20% for every parameter.

Table 7: Contraction of the crosses

Samples	Mean of the 2 lengths contraction %	Diameter contraction %	Height contraction %
ZrO2-cross-HC 1400	20.5	21.4	18.7
ZrO2-small cross-HC 1400	20.3	21.2	17.0

4.3.4. Cone/cylinder

For unique parts, it seemed more logical to show in a table all their size variations and finally to show the percentage of contraction during sintering which was done in a conventional way. For the contraction of the cone and the cylinder, only the diameter of the pieces and their height has been measured as demonstrated in the figure 40. Finally, the 2 pieces that look very similar (two large pieces with a circular base) have practically the same percentage of contraction which is coherent. The percentage of contraction is a little less than 20 % as for the other pieces.

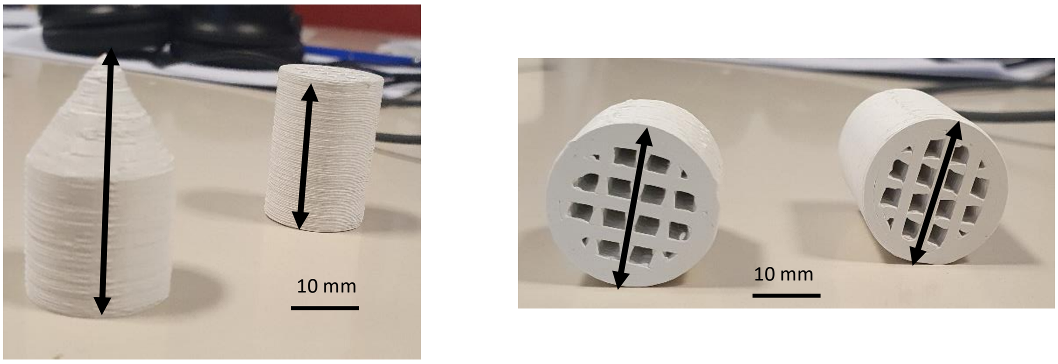


Figure 40: Different lengths measure for cone and cylinder

Table 8: Contraction of the cone/cylinder

	Before sintering		After sintering		Contraction %		
	Height (mm)	Diameter (mm)	Height (mm)	Diameter (mm)	Height	Diameter	Mean
Cone	29.6	20.5	23.7	16.9	19.8	17.4	**18.6 ± 1.7**
Cylinder	33.5	20.6	27.3	16.7	18.5	19.1	**18.8 ± 0.4**

4.3.5. Teeth

Once the long works have been validated, a non-geometric shape has been realized. Indeed, several samples of two teeth were made. To evaluate the contraction several measurements were taken: the width of the two teeth as well as their respective heights.

Table 9: Size of the teeth

	Before sintering			**After sintering**		
	Width (mm)	**Height teeth (mm)**	**Height small teeth (mm)**	**Width (mm)**	**Height teeth (mm)**	**Height small teeth (mm)**
Teeth 1	19.1	15.9	12.4	16.2	12.3	10.2
Teeth 2	19.1	14.8	12.5	15.6	12.6	9.7
Teeth 3	24.8	19.1	15.6	21.4	15.5	12.4

Teeth 1 and 2 were the same size and the last one was made with an increased size of 20 % to get the size of the two real teeth with the contraction and also to have a better finish in the details.

Table 10: Contraction of the teeth

	Contraction %			
	Width	**Height teeth**	**Height small teeth**	**Mean**
Teeth 1	15.3	22.3	17.9	**18.2 ± 3.5**
Teeth 2	18.2	14.4	22.5	**18.1 ± 4.1**
Teeth 3	13.8	19.4	20.2	**17.5 ± 3.5**

The mean of the contraction of the teeth is the same as for the previous forms around 18 % (table 10). So, the shape does not have an impact at all on the percentage of contraction.

4.3.6. Denture

For the last piece, a lot of measurements have been made to get a very precise idea of the contraction. The denture was made 20 % larger to obtain the same piece as the one that was scanned. So, each tooth was labelled, and its length and width were measured. Even the distance between the teeth has been measured (figure 41).

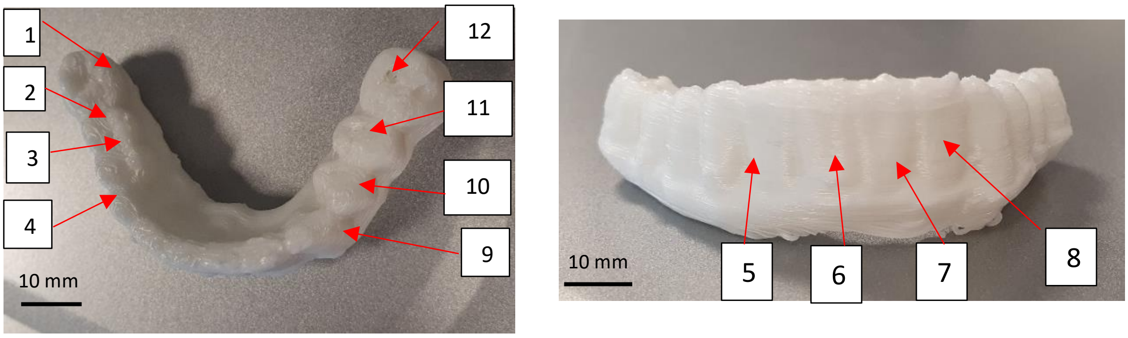


Figure 41: Denture

All measurements have been listed in the following tables (table 11, 12, 13).

Table 11: Contraction of the length between the teeth

Length between	Before sintering (mm)	After sintering (mm)	Contraction %
1-12	45.7	37.8	**17.4**
2-11	38.0	29.7	**21.9**
3-10	30.6	23.7	**22.5**
4-9	26.8	22.8	**14.5**
Mean			**18.8 ± 3.8**

Table 12: Contraction of the height of the teeth

Height	Before sintering (mm)	After sintering (mm)	Contraction %
1	15.4	12.9	**16.5**
2	15.8	13.0	**17.0**

3	18.3	15.0	**17.5**
4	21.3	16.4	**23.0**
5	21.6	17.6	**18.7**
6	20.9	16.8	**19.8**
7	19.9	16.3	**18.1**
8	21.0	16.9	**19.7**
9	21.3	17.3	**19.1**
10	19.7	15.0	**23.5**
11	17.7	13.9	**21.4**
12	16.8	13.2	**21.4**
Mean			**19.5 ± 2.3**

Table 13: Contraction of the width of the teeth

Width	**Before sintering (mm)**	**After sintering (mm)**	**Contraction (%)**
1	12.2	9.7	**20.7**
2	10.4	8.7	**16.4**
3	10.9	8.8	**19.0**
4	10.0	7.8	**21.4**
5	5.5	5.2	**5.7**
6	5.9	5.3	**10.2**
7	7.6	6.2	**18.4**
8	7.8	6.4	**18.4**
9	9.7	7.6	**21.2**
10	10.5	8.7	**17.2**
11	11.7	9.6	**18.4**
12	13.8	10.4	**24.3**
Mean			**16.6 ± 5.1**

According to the tables, width would have been the least affected by the contraction phenomenon with an average slightly below the others (16.6 %). However, the width is the table that contains the smallest values, so as mentioned above, the accuracy errors change more than for the long lengths. If the mean of all values of contraction, it would be the same as the other values and still around 18 %.

To conclude, the material has an impact on the contraction. The difference between the two materials is around 15 %, which is not negligible. However, it seems that the shape does not have an impact on the contraction. Indeed, whatever the form, the contraction has always been around 15-20 %. Nevertheless, if a custom-made piece needs to be done for a specific use, it is better to test before the shape to get the desired dimensions.

4.4.Density

Concerning the density test, almost all the sample have the same density than the theorical one. For zircon, it is 4.46 g/cm^3 and for zirconia it is 6.05 g/cm^3. The samples are not porous at all, and this is sign of quality of the ceramics. The only sample that has it is ZrO_2-HC-1300. The temperature of sintering of the zirconia for conventional sintering is around 1400 °C. However, a test has been made at 1300 °C to compare with the MW sintering at the same temperature. As expected, porous remains in the sample ZrO_2-HC-1300 whereas the sample at same temperature but with microwave sintering is 100 % dense.

Table 14: Density of the samples

Sample	Density of the sample (g/cm^3)	Density (%)	Porosity (%)
ZrSiO4-HC-1500	4.46	100.0	0.0
ZrO2-HC-1400-without acetone step	6.10	100.0	0.0
ZrO2-HC-1300	5.88	97.1	2.9
ZrO2-HC-1400	6.08	100.0	0.0
ZrO2-MW-1300	6.12	100.0	0.0

This test shows that microwave sintering requires less temperature for full density than conventional sintering. By knowing that less time is also required for a microwave sintering, it remains to determine whether the mechanical properties are the same or not.

4.5. Microhardness

Concerning the Vickers test, it can be seen that zircon and zirconia cannot be compared. The three zircon samples tested show that there is a real difference of hardness between these two materials. Vickers test for zircon has been made with a force of 1.961 N while for zirconia the force was 4.903 N except for one exception (ZrO_2-MW-1200).

The results prove it, zircon has reach at maximum 2.4 GPa whereas zirconia is around 11/12 GPa. Moreover, the result of the sample $ZrSiO_4$-HC-1500 (40 %) could be disputed because it has a large standard deviation which is not a sign of reliability. In addition to that, on the three samples only the percentage of filling is different, and it is the same material so there should not be such a big difference. The first two zircon samples have a closer hardness value and with a lower standard deviation. In conclusion, the true value of zircon is probably more around 1 GPa as the theoretical value.

For the zirconia, results change according to the temperature of sintering or the type of sintering. To begin with, the only exception is this sample: ZrO_2-MW-1200. It has a lower hardness value than $ZrSiO_4$ (0.4 GPa). This can be explained by the fact that the sample was completely in pieces after the microwave sintering. Indeed, the heating was too fast, and the sample could not take this temperature gradient. Moreover, it was a sintering at 1200 °C so below the temperature of MW sintering and the sample would have been less hard than the other.

Then, the samples ZrO_2-HC-1400 show that despite the differences in the percentage of infill, the material remains the same and so does the hardness value (12.5 GPa) at the same sintering. If ZrO_2-HC-1400 and ZrO_2-HC-1300 are compared now, they were both sintered in the conventional way but with 100 °C difference. The first one has a higher hardness than the second one, this is due to the fact that the basic sintering temperature of zirconia is 1400 °C, so if you sinter at 100 °C less, the mechanical properties are not at their maximum. The consolidation of the grains is not finished and that can play on the porosity and on the hardness. However, the value of hardness of ZrO_2-HC-1300 stay correct (11.2 GPa) and if the main utilisation does not require the highest mechanical properties, it is possible to sinter with 100 °C less that saves time and energy.

Then the different types of sintering (conventional and MW) are analysed with samples ZrO_2-HC-1400 and ZrO_2-MW-1300. In the density test, no difference could be found but it is not the same with this test. Indeed, ZrO_2-HC-1400 (12.5 GPa) has a higher hardness than ZrO_2-MW-1300 (11.7 GPa). The difference is not that important but the standard deviation of the ZrO_2-MW-1300 (0.8 GPa) shows a greater variation of hardness present in the sample while ZrO_2-HC-1400 is more homogeneous (0.2 GPa).

Table 15: Hardness of the samples

Sample	Hardness (GPa)	Standard deviation (GPa)
ZrSiO4-HC-1500 (20%)	0.8	0.2
ZrSiO4-HC-1500 (30%)	1.0	0.2
ZrSiO4-HC-1500 (40%)	2.4	0.9
ZrO2-HC-1300	11.2	0.3
ZrO2-HC-1400 (20%)	12.5	0.3
ZrO2-HC-1400 (30%)	12.5	0.2
ZrO2-MW-1200	0.4	0.1
ZrO2-MW-1300	11.7	0.8

To conclude, the best hardness is obtained by conventional sintering at 1400 °C. However, not far behind is MW sintering at 1300 °C which has the advantage of time and loses very little hardness compared to ZrO_2-HC-1400. After that, conventional sintering at 1300 °C provides good hardness properties and if the best hardness properties are not required in the application, it is a possibility. However, in this case, MW sintering is a better choice, faster and with a better result.

4.6.FESEM

4.6.1. Size of the grain

The size of the grain of the different sample has been calculated thanks to the FESEM. Several pictures have been taken for each sample at different magnification (x2k, x5k, x10k, x15k, x20k and x30k). After that, the size of a hundred grains was measured by photo with the software *ipwin32*. Moreover, three or four photos have been analyzed to get a real representation of the grain size of the sample. At the end, the mean and the standard deviation has been measured on excel.

As expected, the grain size of the zircon is bigger than the zirconia’s. There is a factor four with the zirconia at 1400 °C and a factor six with the other. This explain the difference of hardness noticed on the Vickers test because more the grain is small, harder is the material.

However, there is an exception because the sample ZrO_2-HC-1400 has a microstructure a bit larger (232 nm) but the sample is a bit harder too (12.5 GPa). This can be explained by the porosity. If there is a comparison between samples with a conventional sintering, the one with the 1400 °C sintering contains no porosity while the one with the 1300 °C sintering contains 3 % porosity. This percent of porosity is enough to lower the hardness.

The grain size of ZrO_2-MW-1300 and ZrO2-HC-1300 are the same and are also the smallest. This explain why their hardness is close (11.7 GPa and 11.2 GPa). Nevertheless, the ZrO_2-MW-1300 should have a better hardness because the ZrO_2-HC-1300 is a bit porous. However, if the standard deviation is taken as the upper limit the sample would reach 12.5 GPa as the sample ZrO_2-HC-1400 and it would have been more expected.

Table 16: Summary of the thermal attacks and the size of the grain

Sample	Thermal attack (°C)	Attack duration (min)	Size of the grain (nm)	Standard deviation (nm)
$ZrSiO_4$-HC-1500	1300	30	957.0	459.3
ZrO_2-HC-1300	1200	30	148.6	65.6
ZrO_2-HC-1400	1300	30	232.1	106.5
ZrO_2-MW-1300	1200	30	156.5	58.9
$ZrSiO_4$-pellets	400	30	1269.7	545.5
ZrO_2-pellets	400	30	155.0	90.4

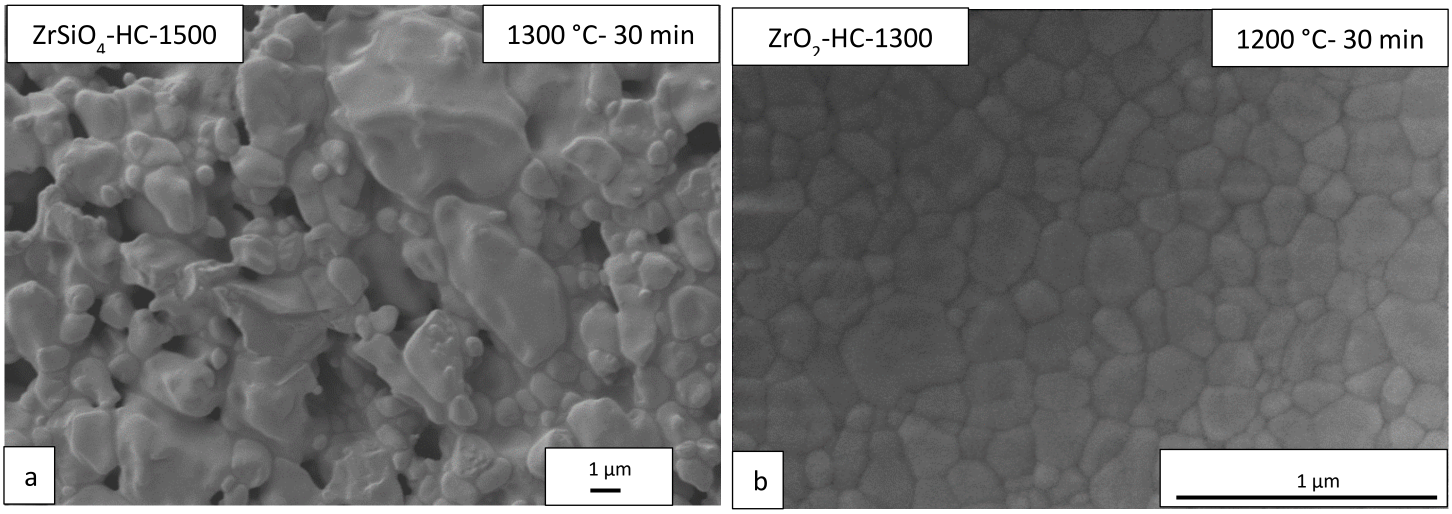


Figure 42: FESEM images a) ZrSiO4-HC-1500 b) ZrO2-HC-1300

The figure 42 a) clearly shows that the thermal attack for zircon was not carried out at the correct temperature. A more beautiful image with more defined grains would have been obtained with a 30 min etch at 1400 °C. Indeed, the grains are barely formed, and it is difficult to calculate the size of the grains. On the other figure 42 b) and 43 a) and b), samples have been attacked correctly and the grain boundary is very apparent which facilitate the measurement of the grains.

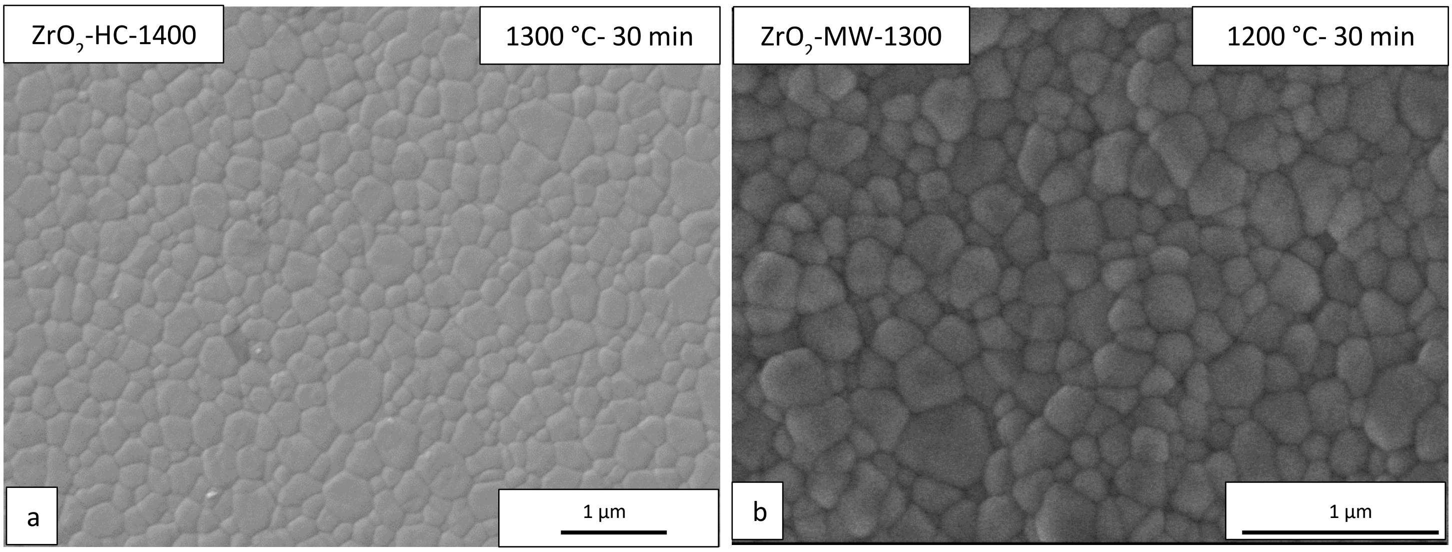


Figure 43: FESEM images a) ZrO2-HC-1400 b) ZrO2-MW-1300

A final analysis was done on zircon and zirconia pellets. Indeed, it is important to know the initial size of the grains of the materials and especially a sintering. During sintering, the goal is to densify the network of grains. However, during heating, the heat often leads to an increase in the size of the grains, which degrades the mechanical properties of the structure. The perfect sintering would be a dense grain network with a grain size of exactly the same size as the initial grains. In the case of zircon, the initial grains are larger than after sintering which is not normal. This is probably due to a lack of accuracy of the grain measurement in figure 44 a). In any case, the order of magnitude is the same, so the sintering is quite efficient. For zirconia, we see that ZrO2-HC-1300 and ZrO2-MW-1300 have the same size as the initial grains (155.0 nm), which is a good thing. In the case of MW sintering, everything is perfect, especially because the density of the sample is at the maximum. For the ZrO2-HC-1300 sample, we see that if we heat less the grain size is the same but there are problems of porosity. If we compare with ZrO2-HC-1400, the size has not increased much, so it is a good sintering too.

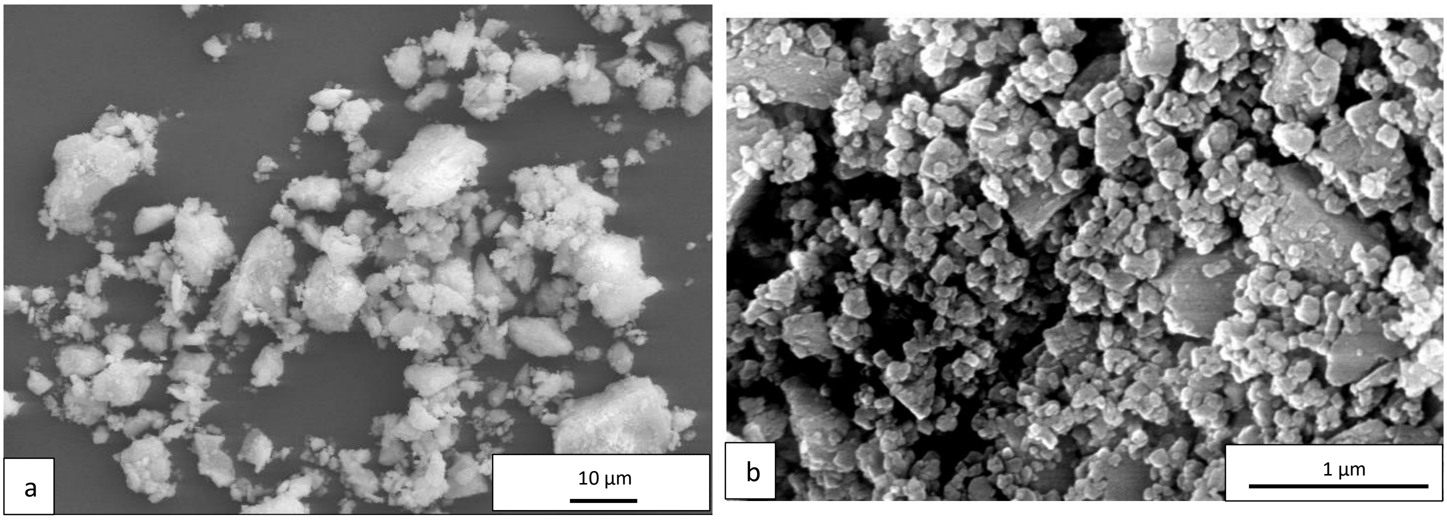


Figure 44: a) ZrSiO4-pellets b) ZrO2-pellets

In the end, as it was announced, the size of the grains does not change after MW sintering thanks to the fact that the heating is uniform and that the heat is released only once the waves have been absorbed. For the conventional sintering, it is more judicious to heat the grains to the indicated heat rather than to have smaller grains but a more porous network.

4.6.2. Fracture

The photos taken at FESEM below show that the fracture of the zirconia is intergranular. It is clear that the fracture follows the grain boundary and does not cut the grains in half. This can be seen very clearly in figure 45 b), c) and d). Thus, the interface between the particule is the weakness of zirconia. For zircon, it seems that the fracture is more transgranular because the grains do not appear clearly on the figure 45 a). The grains were cut in two during the fracture.

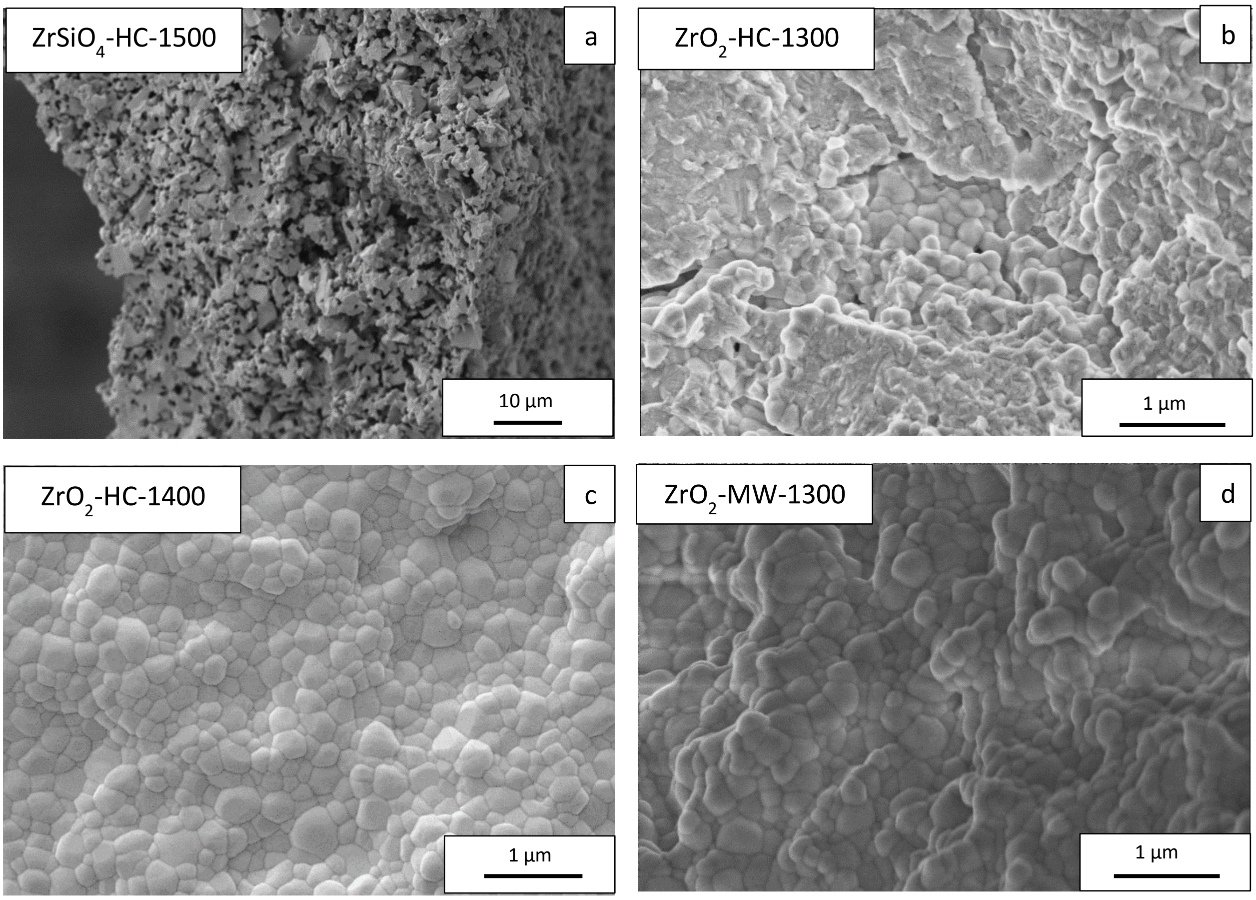


Figure 45: FESEM images a) ZrSiO4-HC-1500 b) ZrO2-HC-1300 c) ZrO2-HC-1400 d) ZrO2-MW-1300

The figure 46 illustrates a facture on the zirconia green body (a) and on a zirconia sample sintered (b) at macroscopic scale.

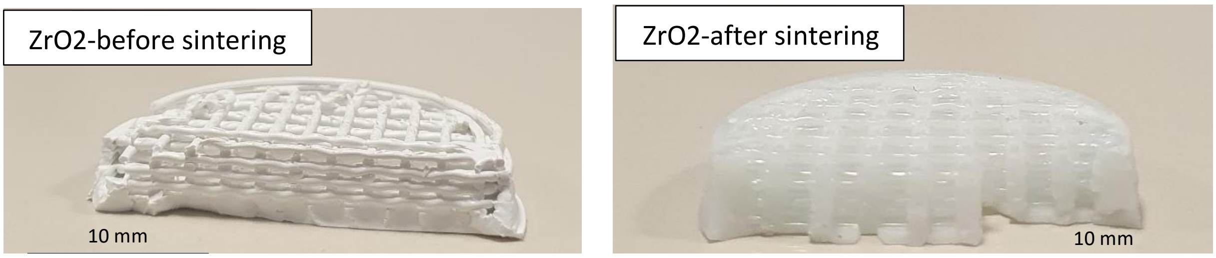


Figure 46: Fracture at macroscopic scale of ZrO2 sample

One of the biggest differences between $ZrSiO_4$ and ZrO_2 sample is the filament which come from the 3D printing. Indeed, the following pictures illustrate the difference: the filament of the zircon is completely empty while the one of the zirconia is full. This plays a role in the hardness of the material with of course the size of the grain. The second thing is that in zirconia, layers are touching each other while in zircon sample, there is a lot of space. The structure is clearly stronger in zirconia sample.

This space between two filaments is here because of to the starting parameters. At the beginning, the space between the layer was 0,4 mm and has been changed for 0.25 mm after few problems of printing. The filament has also been enlarged so that it loses precision and finesse in more complex work.

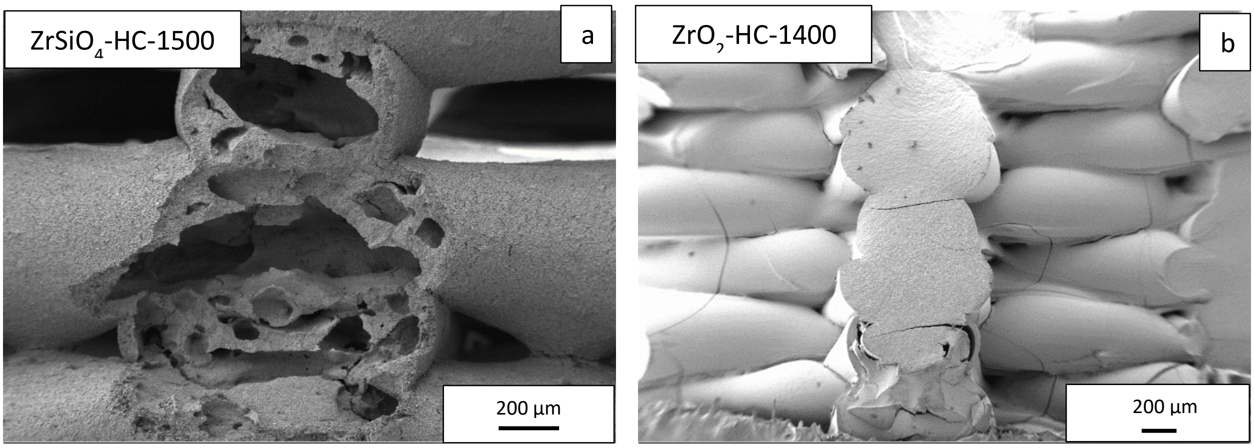


Figure 47: FESEM images; a) ZrSiO4 layers; b) ZrO2 layers

Table 17:Measurements of the zircon and zirconia filament

	Zircon	**Zirconia**
Height layer (µm)	664.0	436.3
Width total layer (µm)	711.7	855.0
Width hole layer (µm)	565.7	0,0
Width material on the layer (µm)	71.9	855.0

As the table shows, the height of zirconia sample is shorter than on the zircon sample. It can be explained by the height between the layers: As the height between the layers has been reduced, the filaments are touching each other, and this create pressure which leads to a reduction in height but an increase in width. However, the interlayer reduction would not have been possible for zircon or at least not on the same scale because in the zircon filament there is almost only vacuum, and this would lead to the collapse of the structure.

These two images represent samples polished for microscopic analysis. In addition of the figure 47, figure 48 with another point of view confirms that the quality of the zircon sample is inferior to the one of zirconia.

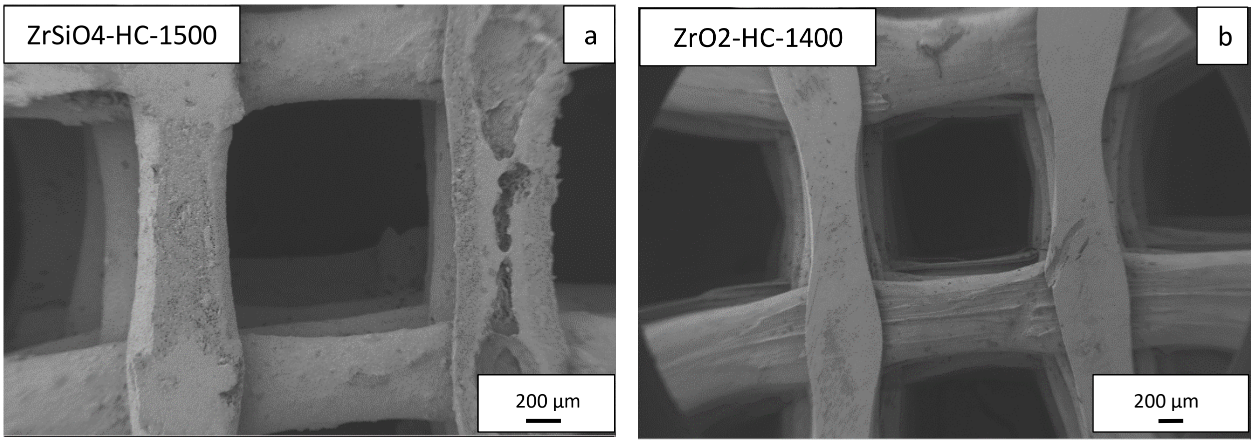


Figure 48: FESEM images ; a) ZrSiO4 30% infill structure ; b) ZrO2 30% infill structure

Shape experiment

After the disc shape, other shapes have been printed to experiment other structure to detect a potential weak point in a certain structure. The first one was the square, printed in several size and several percent of infill. 20 % and 30 % have been tried a 21 mm and 15 mm square (length before sintering). After being sintered the squares look very well as shown in the figure 49. The squares at 20 % fill seem a bit cleaner. At 30 % fill, especially on the large one, the spaces are almost closed due to the width of the filament in the printer. For the angle, only the 10 % infill could be achieved. Beyond this percentage, the filaments were too large and they were no longer accurate. This made the green body deformed. In addition, when the size was increased to try to achieve a higher percentage of fill, the green body broke when it was removed from the printer plate. For this reason, the sample angle was only made with 19 mm sides.

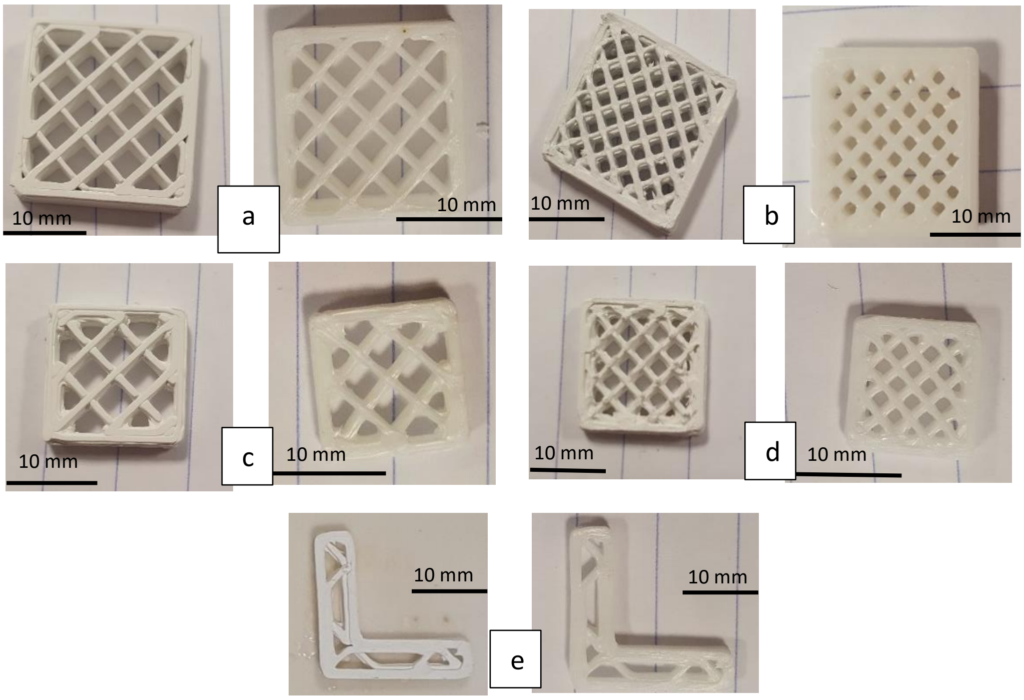


Figure 49: Square and angle shapes; a) before/after sintering 20%; b) before/after sintering 30%; c) before/after sintering 20% small; d) before/after sintering 30% small; e) before/after sintering 10% angle

Then, the cross shape with a hole in the middle has been made. The idea was to see if the samples would remain solid despite the hole in the middle. Two sizes were tried: the large one with 30mm fot the length and 14 mm for the hole diameter and the small one with 21 mm length and a hole diameter of 10 mm (size before sintering). For the 2 sizes, the percentages 10, 20 and 30 % of infill were produced. For both sizes the observation is the same, the higher the percentage, the less correct the sample and the more deformed the inner structure. For large sizes, it can be seen in figure 50 b) and d) that the samples are still of good quality. However, the sample at 30 is not a success (figure 50c)). The size would have to be even larger to make a 30 % fill. Concerning the small sizes, none of them is a success (figure 50 d), e), f)). The filaments are already too big for the 10 % one, so for the others the phenomenon of too much material is even more important.

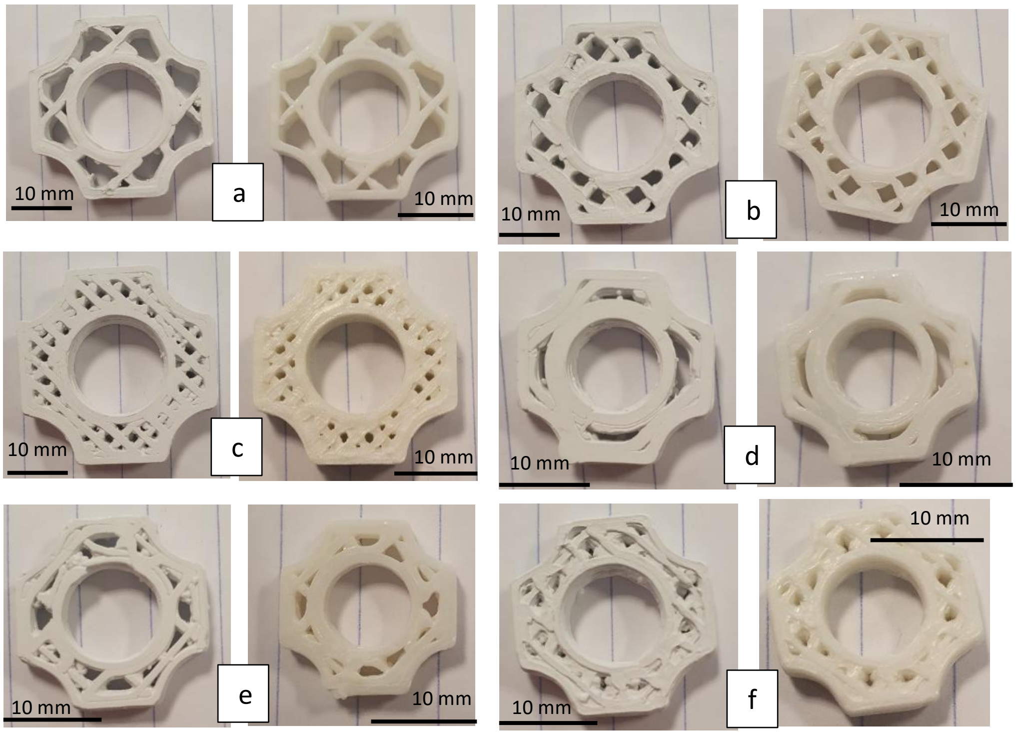


Figure 50: Cross shapes; a) before/after sintering 10%; b) before/after sintering 20%; c) before/after sintering 30%; d) before/after sintering 10% small; e) before/after sintering 20% small; f) before/after sintering 30% small

After that, pieces that can have a specific use were manufactured. Figure 51 shows a bolt at 20 % infill has been print. On the part under, the structure is clean and the 20 % is a good choice. However, on the upper part, this is supposed to have represent a 20 % infill structure. As the figure 51 a) and b) show, it looks like a complete filling. Despite that, the shape stays the same and the piece can still be used.

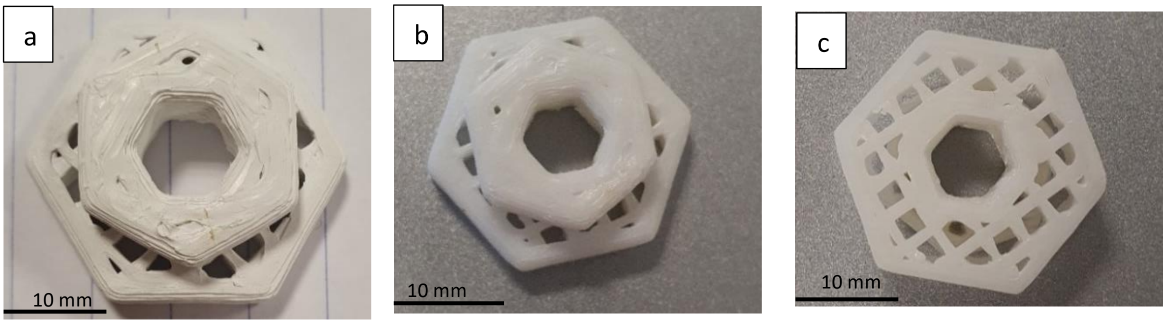


Figure 51: Bolt 20% sample; a) before sintering; b) c) after sintering

To represent a finger with a phalanx, a cone and a cylinder has been constructed. The dimensions are around 30 mm height and 20 mm of diameter and 20 % of infill (before sintering). The structure of the two pieces was well printed. However, after the sintering the two pieces were removed too fast of the oven. A thermal shock occurs and cracks the 2 samples as the figure 52 c) and d) illustrate it. On the cone only, the top has been cracked but the cylinder was cracked from top to bottom.

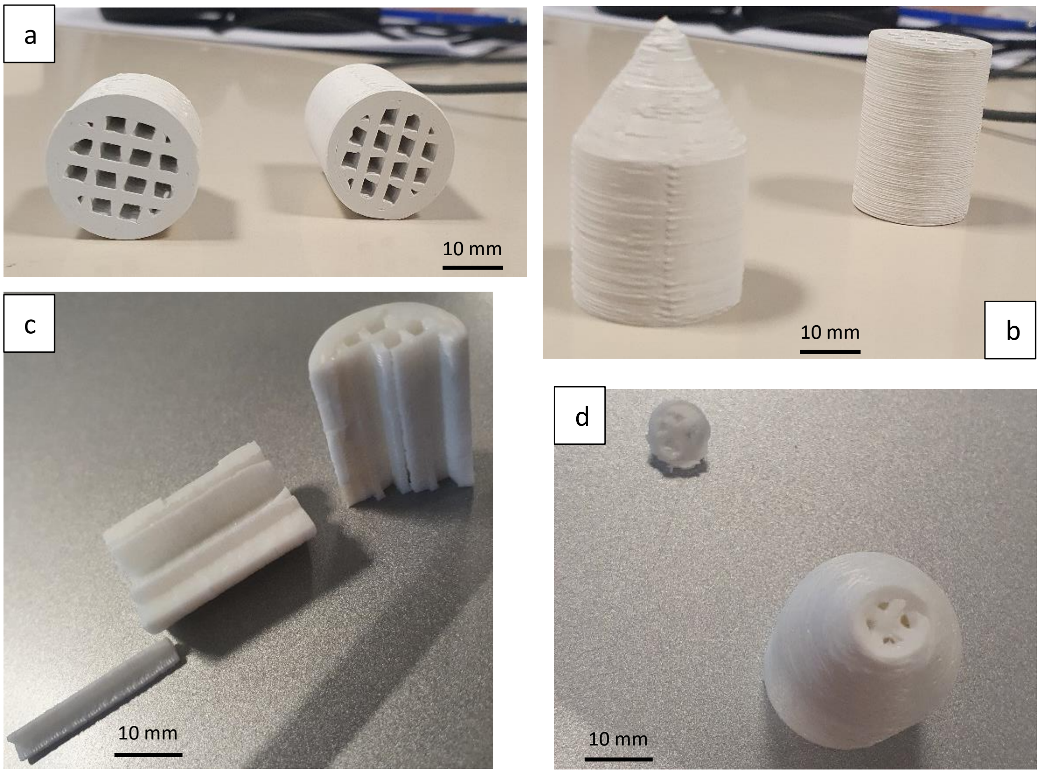


Figure 52: a) b) cone and cylinder before sintering; c) cylinder after sintering; d) cone after sintering

Thanks to a scanner, the g-code of two teeth could be created. Netherveless, the design of the two teeth does not have a plane surface so the question about the direction of the print emerged. The first thought was to print it laid down. The result is visible figure 53. The result did not convince in terms of aesthetics in particular the back part that is shown the figure 53 a). Moreover, the mechanical properties depend not only on the material but also on the orientation of the layers. Here, as can be seen in figure 52, the mechanical properties are not likely to be optimal for someone who should use his teeth to eat due to the orientation of the layers.

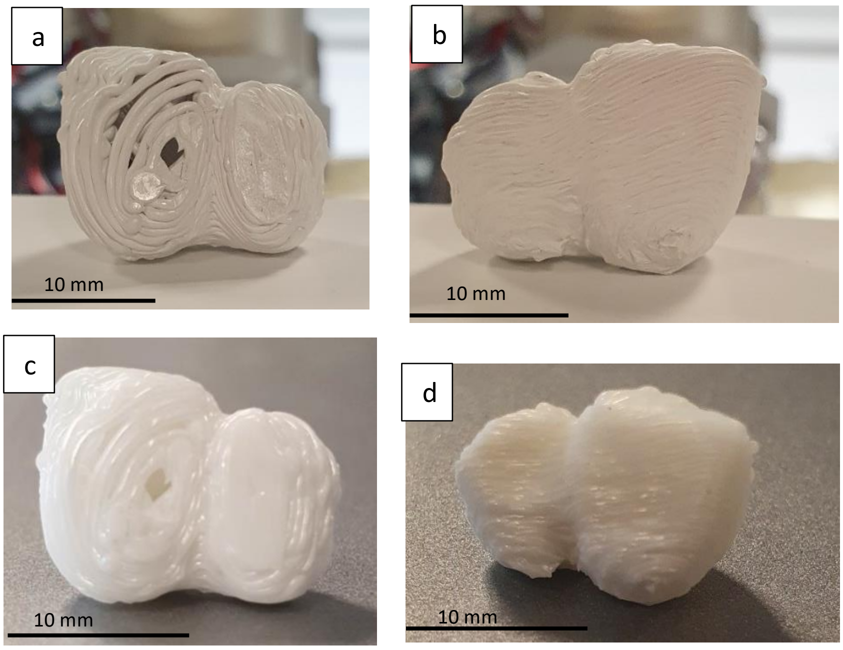


Figure 53: 2 sides of the teeth a) b) before sintering; c) d) after sintering

Another direction of printing has been thinking to avoid that. Even if, the bottom part of the teeth did not have the same starting height, a g-code has been created to print from bottom to top. The result was more convincing in terms of aesthetics (figure 54). Moreover, a tooth are under enormous axial pressure during its use and this way of printing increases the resistance along this axis. Of course, it would be necessary to make several tests to check if these teeth have the required mechanical properties to be used.

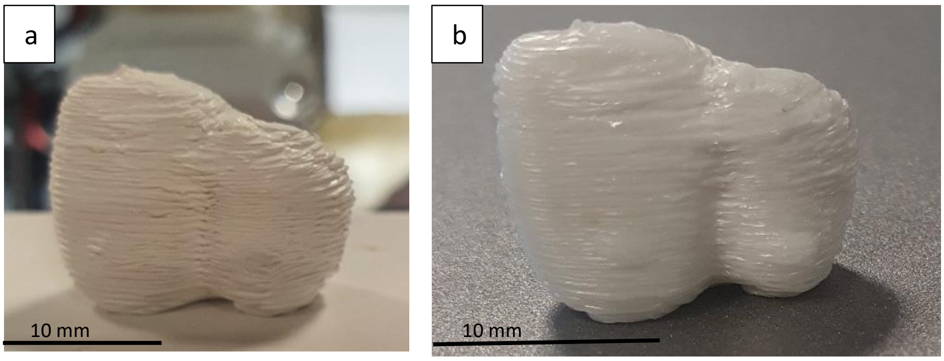


Figure 54: Teeth with another direction of printing; a) before sintering b) after sintering

To go even further, a gypsum denture has been scanned to obtain the g-code. First of all, as it was the most complex piece ever attempted and required a high degree of precision, only the printing position was rethought. 20 % of the infill has been made as usual for complex part. As the figure 55 illustrates, the result is impressive, and the details are well made. All teeth are well detailed and the separations between them are visible. This is a good quality of printing. The only thing is that on the top of the front teeth the nozzle of the printer is a bit too large and at the end it loses accuracy.

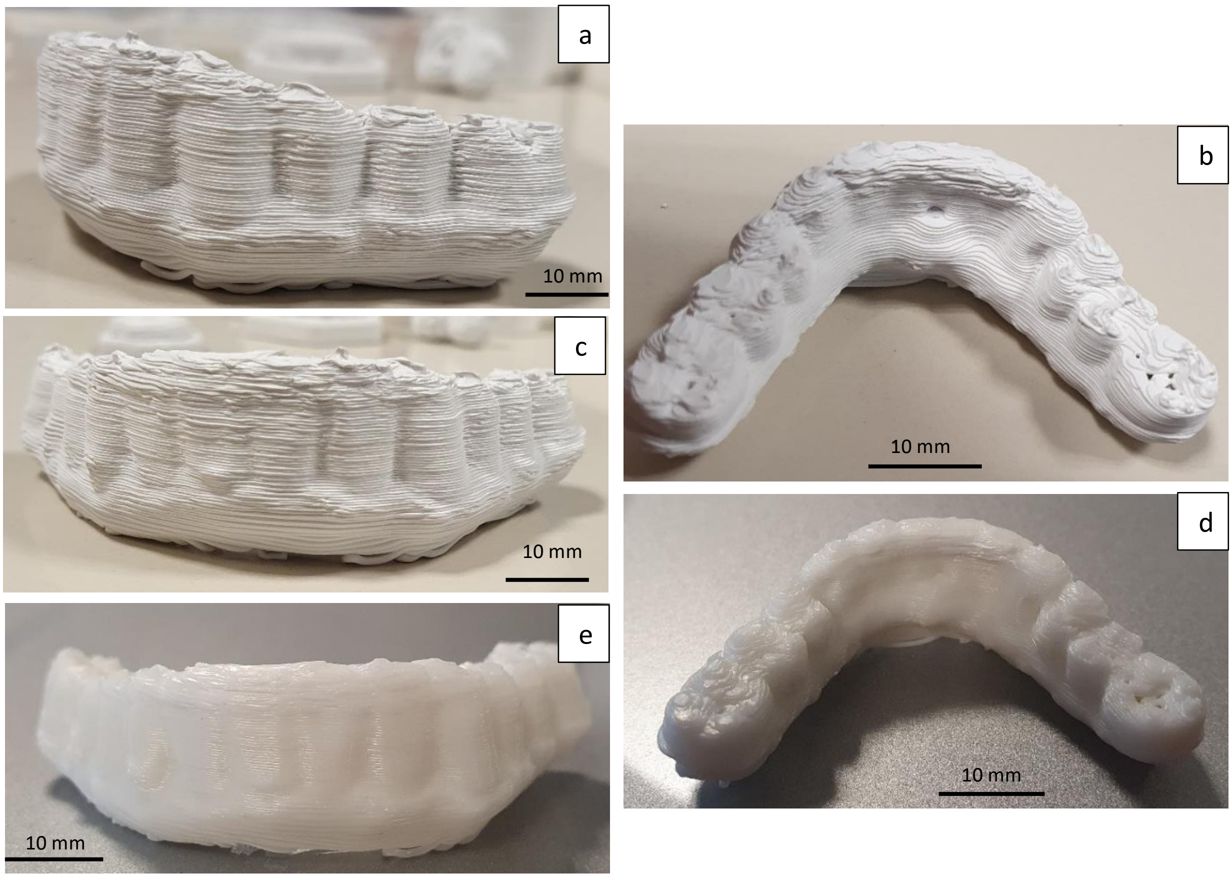


Figure 55: Denture; a) b) c) before sintering; d) e) after sintering

After this successful attempt, another has been made with the same parameters but with a size increasement of 20 %. During the sintering, the green body is contracting, and it loses around 20 % of its size. So, the last attempt was good but after the sintering it was a bit small. Finally, after sintering the same size as the gypsum original is obtained (figure 56). (Abdullah, 2016)

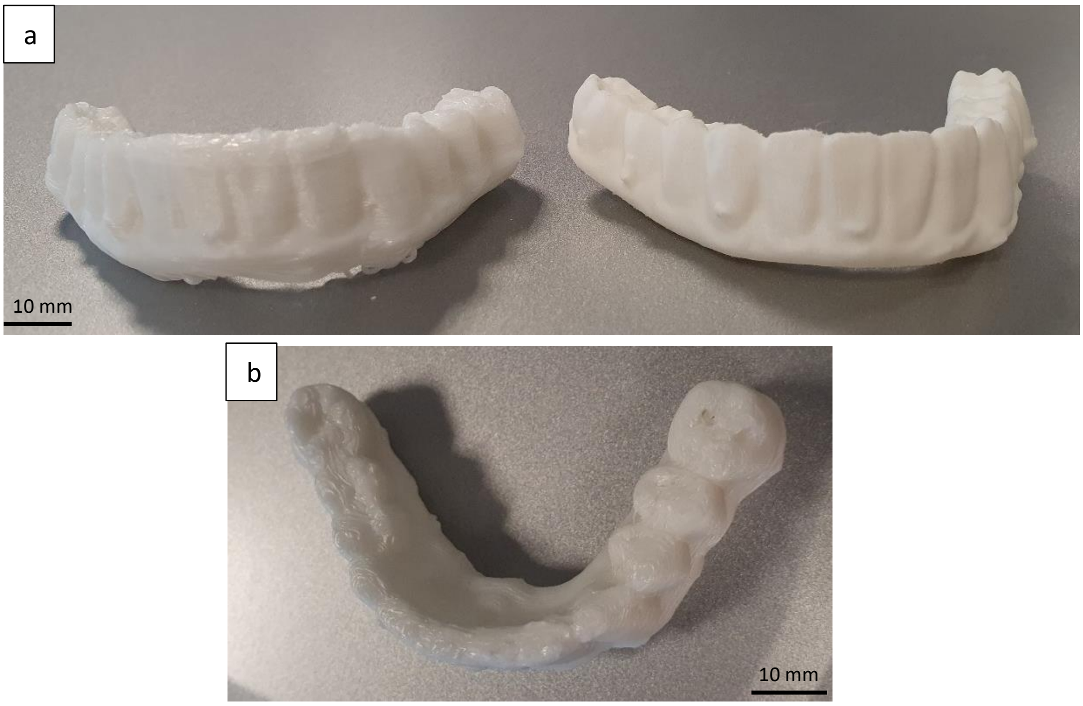


Figure 56: a) zircon denture sintered on the left, gypsum denture on the right; b) view from the top zircon denture

5. Conclusion

Nowadays, ceramics are widely known for their high mechanical strength, their toughness, and their low thermal dilatation. They are increasingly present in the industry, and this is what led to this research topic. At first, the basis of this subject was to manufacture ceramics samples by 3D printer. This allows to discover another manufacture process which win some time, some matter, and some money in comparison with the conventional processes. Then, compacted parts were sintered in different ways. For conventional sintering, it was found that for zircon, the process is mastered, the sample is dense and obtain a hardness of 1.5 GPa. This material suffers from the comparison with zirconia, which is better in every field, even in terms of contraction during the sintering (around 30% for zircon and around 18 % for zirconia). Concerning zirconia, a sintering below it usual sintering temperature (1300 °C instead of 1400 °C) do not result in a fully dense sample and maximum hardness. On the contrary, when the sintering temperature is respected, this create an increasement of the size of grain, but the piece is fully dense and the hardest (12.5 GPa). Nowadays, conventional sintering is well mastered. However, in a society where energy savings are essential, and where production techniques are constantly being improved, new sintering techniques are emerging. Microwave sintering is a relatively new sintering technique that has not yet become established in the ceramics industry, mainly because a technician is still required to carry out the sintering and only small samples can be sintered one by one. However, this technique is the future in the ceramics industry. Indeed, with a microwave sintering, the complete process time is around 30 minutes. Once the sintering temperature is reached (which is 100 °C lower than that for the oven) the time spend for the sintering is 5 minutes only. Results are promising because the samples have a small size grain which is close to the original microstructure and with a density of 100 % unlike the conventional sintering at 1300 °C. In terms of hardness, it does not reach the same value than the conventional sintering at 1400 °C but it stays close at 0.7 GPa. This technique provides mechanical properties that are almost as good as conventional sintering while saving time, energy and therefore money. It would be interesting to continue the research on this sintering process but in particular with bigger and more complex sample to see if it would work on a larger scale like conventional sintering.

6. Budget

6.1.Estimation of the costs

6.1.1. Equipment

In this section, the budget will be discussed. As you can see with table 18, the price of the main equipment is equivalent to 264 453 euros. However, this price is not considered in the final total because most of the time these machines have been used for years or will be used for years, so they are considered depreciated. Table 19, on the other hand, takes into account the small equipment that was used in this study. For the smallest equipment, the cost is 1473.03 euros.

Table 18: Cost of the laboratory equipment

Equipment	Quantity	Unit price (€)
Cutting machine with cutting disk Stamping machine Polishing machine with discs	1	63 000
Drying stove	1	2 350
Grinder	1	50
Microhardness and computer equipment	1	22 900
Oven	1	28 000
Monomodal microwave oven	1	50 000
3D printer	1	4 828
Optical Microscope and computer equipment	1	80 000
Portative durometer	1	5 000
Heating plate	1	325
Precision balance and density measurement equipment	1	8 000
Total		**264 453**

Table 19: Cost of the laboratory small equipment

Small equipment	Quantity	Unit price (€)	Cost (€)
Latex glove box	1	4.39	4.39
Ceramic crucible	6	3.20	3.20
Polishing discs	7	200	1400
Spatula	1	2.89	2.89
Pliers	1	2.55	2.55
Beakers	6	5	30
Quartz tube	1	30	30
Total			**1473.03**

6.1.2. Energy

In this second part, the cost of energy has been calculated with the number of hours spent on each machine and the cost of energy. In the end, table 20 summarizes the number of Wh used while table 21 shows the cost of energy which is 83.53 euros.

Table 20: Electrical energy consumption

Equipment	Power (W)	Time of use (hour)	Quantity (Wh)
Stamping machine	1000	1	1 000
Polishing machine	570	6	3 420
Drying stove	1600	18	28 800
Conventional oven	4500	167.2	752 400
Monomodal microwave oven	700	1	700
Heating plate	1020	48	48960
Precision balance	15.5	1	15.5
Total			**835 295.5**

Table 21: Price of the energy consumption

	Quantity	Unit price (€)	Total energy cost (€)
kWh	835.296	0.103	**83.53**

6.1.3. Characterization costs

Then comes the cost of the hours spent with FESEM (table 21), the price of the materials used during this project (table 22) as well as the time spent teaching us from the project manager.

Table 22: Cost of the characterization

Technique	Time (h)	Price per hour (€/h)	Characterization cost (€)
FESEM	4	20	**80**

6.1.4. Material costs

Table 23: Price of the materials

Material	Quantity (kg)	Price per kg (€/kg)	Material cost (€)
Zircon	1	261.45	261.45

PLA	1	10.97	10.97
Zirconia	0.5	627.9	313.95
Total			**586.37**

6.1.5. Labor costs

Table 24: Cost of the labor

	Time (h)	Price per hour (€/h)	Labor cost (€)
Project director	52	24	**1 254**

6.2. Total of the costs

Finally, the table 23 summarizes all the expenses made during these months of work and it arrives at a sum of 3 474.9 euros.

Table 25: Total of the cost

Category	Cost (€)
Small equipment	1473
Energy	83.53
Characterization	80
Material	586.37
Labor	1 254
TOTAL	**3 476.9**

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