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Altan Alpay Altun

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Abstract

Additive manufacturing (AM) technologies are already established in the plastic and metal industry, but the ceramic production has very rarely used these technologies for their purposes. Nevertheless, there is a strong need for the introduction of AM technologies in the ceramic industry, because no sufficient prototyping technologies have thus far existed and the tools for powder injection molding are very expensive. These are actually perfect conditions for the implementation of AM technologies, but since ceramic materials are usually used where other materials fail, the quality and the reliability of the parts are crucial. In this context, the recently commercially established Lithography-based Ceramic Manufacturing (LCM) process provides new opportunities for the AM of dense and precise ceramic components.

The scope of this work is the development of new photocurable ceramic suspensions as starting materials for the LCM process. These formulations shall be based on tricalcium phosphate as inorganic components and contain a photosensitive organic matrix as binder. The evaluation of these suspensions comprises studies towards their stability and processability as well as the establishment of appropriate processing parameters for the shaping of three-dimensional parts by LCM.

Due to the nature of this process, the initially formed parts are composites consisting of the ceramic particles and the polymer binder. Thus, another central topic of this work is the thermal postprocessing of the structured ceramic/photopolymer composites in order to produce the sintered ceramic bodies as well as their mechanical characterization. Technical parts and scaffolds were fabricated using the developed suspensions and the established shaping and postprocessing parameters.

Zusammenfassung

Generative Fertigungsverfahren sind bereits in der kunststoff- und metallverarbeitende Industrie etabliert, in der keramischen Industrie jedoch werden sie nur sehr selten angewandt. Es herrscht eine starke Nachfrage nach der Einführung generativer Fertigungsverfahren, da keine ausreichenden Prototyping-Technologien existieren und die Werkzeuge für Pulverspritzguss sehr teuer sind. Dies sind ideale Bedingungen für die Verwendung generativer Fertigungsverfahren, wobei bei der Verarbeitung keramischer Materialien Qualität und Zuverlässigkeit wesentlich sind. In diesem Zusammenhang bietet der kürzlich kommerziell etablierte Lithography-based Ceramic Manufacturing (LCM) Prozess neue Möglichkeiten für die generative Fertigung dichter und präziser keramischer Bauteile.

Das Ziel dieser Arbeit ist die Entwicklung von neuen photohärtbaren, keramischen Suspensionen als Ausgangsstoffe für das LCM-Verfahren. Diese Suspensionen basieren auf Tricalciumphosphat als anorganische Komponente und einer lichtempfindlichen organischen Matrix als Bindemittel. Die Bewertung dieser Suspensionen umfasst Studien zu ihrer Stabilität und Verarbeitbarkeit sowie die Etablierung geeigneter Verarbeitungsparameter für die Herstellung 3D gedruckten Teile mittels LCM.

Aufgrund der Natur des Prozesses sind die erstellten Teile anfangs Hybridmaterialien, die aus einem keramischen Anteil und einem polymeren Bindemittel bestehen. Daher ist ein weiteres zentrales Thema dieser Arbeit die thermische Nachbearbeitung des strukturierten Keramik-Photopolymerverbundwerkstoffs, sowie die mechanische Charakterisierung der gesinterten keramischen Bauteile durchzuführen. Abschliessend wurden technische Bauteile und biomimetische Stützstrukturen aus den entwickelten Suspensionen mit Hilfe der erarbeiteten Nachbearbeitungsparameter hergestellt.

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1 Introduction

Skeletal tissue repair or regeneration is one of the current clinical challenge. Musculoskeletal disorders and bone defects are some of the major health conditions that exist today. Trauma, disease and developmental deformity frequently cause bone deficiencies. Bone defect reformation includes surgical techniques as well as replacement implants. A number of implants such as metals, polymers, ceramics and composites have been studied to address these types of bone deformities. Bioceramic materials are significant in bone engineering due to their low density, good chemical stability and similar composition to human bone. More than 50 % of bone replacements involve either ceramics or ceramic composites. One example are calcium phosphates, which are currently available as ceramic based bone graft substitutes[1].

In the case of geometrically challenging defects, it would be desirable if the individual implants could be patient specific. Production by traditional processing techniques, such as slip casting or machining pressed green bodies, is difficult and would require costly and time-consuming production of material matrices.

Through the use of additive manufacturing, however, the approach could be simplified. Patient specific data could be obtained by computer tomography or magnetic resonance tomography. Using existing technology, which is used in the field of prototype manufacturing in mechanical engineering or the automotive industry, this data could be easily processed. Examples include the layer-wise construction of arbitrarily shaped structures by stereolithography, CAD-controlled melt extrusion, selective laser sintering or 3D powder printing process[2]. Application of these techniques for the production of individual implants requires the adaptation of biocompatible materials for the treatment of defect bone areas such as titanium, hydroxyapatite (HA) or tricalcium phosphate (TCP) ceramics. Corresponding approaches are the subject of the current research.

The scope of present work is the production of β -tricalcium phosphate (β -TCP) implants by lithography-based ceramic manufacturing (LCM). The printed structures are characterized by the achievable resolution, the mechanical properties and the composition of the end product.

1.1 Biomaterials and Calcium Phosphate Ceramics

Biomaterials is a generic term that covers a wide range of materials with different applications and requirement profiles. Regardless of material type or application, the unifying element in all cases is that the material is in direct contact with the body, usually to act as an assistant or as a replacement of faulty or damaged biological material. The main application of biomaterials is therefore in the medical field, ranging from skin patches, dental fillings and

contact lenses, to stents, prostheses and organ replacement[3]. In 2009, Williams defined the term as[4],

”A biomaterial is a substance that has been engineered to take a form which, alone or as part of a complex system, is used to direct, by control of interactions with components of living systems, the course of any therapeutic or diagnostic procedure, in human or veterinary medicine.”

1.1.1 Bioceramics

The term bioceramic refers to biocompatible ceramic materials such as alumina, zirconia, hydroxyapatite, tricalcium phosphate or bioactive glass. The medical application of bioceramics can mainly be found in the skeletal system, the bones, joints and teeth. After implantation of a synthetic material, human tissue responds to the material in different ways, depending on the material type. In general, there are four categories to classify biomaterials. They can be bioinert, bioactive, surface active and bioresorbable as shown in Figure 1 schematically.

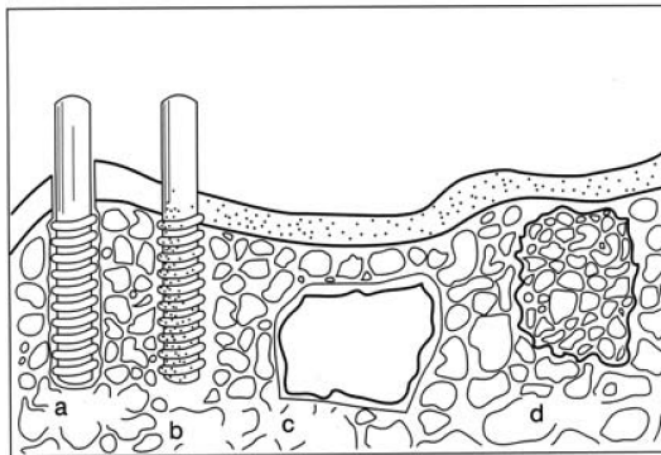


Figure 1: Classification of bioceramics according to their activity (a) bioinert (b) bioactive (c) surface active (d) bioresorbable[5]

The bioionert material (Fig. 1a) can be any material that, once implanted in the human body, has minimum interaction with its surrounding media. Stainless steel, titanium, alumina and partially stabilised zirconia are examples of such biomaterials. The term bioactive refers to a material which, once placed in the human body, interacts with surrounding bone, and occasionally, with soft tissue. Synthetic hydroxyapatite is the prime example of bioactive material (Fig. 1b). As a result of the interactions between the surfaces of these types of materials, these materials, such as bioglass, have been classified as surface active materials

(Fig. 1c). Bioresorbable (Fig. 1d) refers to a material, which upon being implanted within the human body, is resorbed and native bone takes its place. Tricalcium phosphate is important example of bioresorbable materials[5]. Advantages and disadvantages of biomaterial classes are shown in Table 1.

Table 1: Advantages and disadvantages of bioinert, bioactive and bioresorbable ceramics[6]

Property	Advantages	Disadvantages	Example
Bioinert	minimal biological response, high wear resistance	limited mechanical properties in tension	titanium, alumina
Bioactive	enhanced bone tissue response, bone bonding	limited tensile strength and fracture toughness	glass ceramic
Bioresorbable	material is replaced by normal tissue	rate of strength reduction may be too rapid	tricalcium phosphate

1.1.2 Calcium Phosphate Ceramics

In the last 30 years, calcium phosphates have been used as a bioactive coating in orthopedic and dental implants. In addition, they were used as a porous support structure for bone regeneration and as a granulate for the fillings of bone defects. The structure consists of orthophosphate groups $(PO_4)^{3-}$ or pyrophosphate groups $(P_2O_7)^{4-}$. Depending on the desired biological properties, calcium phosphate ceramics can be used with different proportions of calcium and phosphor. The proportion of calcium and phosphor is determined by the molar Ca/P ratio and varies between 1.0 and 2.0. Table 2 gives an overview of different calcium phosphate ceramics.

Table 2: Solubility of the important calcium phosphate ceramics[7]

Name	Formula	Solubility $[-\log K]$	Ca/P
Dicalcium phosphate dihydrate (DCPD)	$CaHPO_4 \cdot 2H_2O$	6.59	1.00
Calcium pyrophosphate(CPP)	$Ca_2P_2O_7$	18.5	1.00
α -Tricalcium phosphate (α -TCP)	$\alpha-Ca_3(PO_4)_2$	25.5	1.50
β -Tricalcium phosphate (β -TCP)	$\beta-Ca_3(PO_4)_2$	28.9	1.50
Stoichiometric hydroxyapatite (s-HA)	$Ca_{10}(PO_4)_6(OH)_2$	116.8	1.67
Tetracalcium phosphate (TTCP)	$Ca_4(PO_4)_2O$	38-44	2.00

The most commonly used calcium phosphate ceramics are β -tricalcium phosphate and hydroxyapatite[8]. The solubility of calcium phosphate ceramics depends on the pH value.

Figure 2 shows the relation between solubility behaviour of Ca^{2+} and pH value in aqueous solutions at 25°C. As the solubility of calcium phosphate ceramics increase, pH value decreases[9]. The most stable phase is HA at $\text{pH} > 4.5$ and dicalcium phosphate anhydrous (DCP) at $\text{pH} < 4.5$. Depending on the pH value, HA and DCP phases can be produced by wet chemical reactions.

By heating to higher temperatures between 450°C and 750°C, additional phases such as CPP, TCP, TTCP and high crystalline HA can be produced. The most important factors to controlling the phase components of high temperature calcium phosphates are the molar Ca/P ratio.

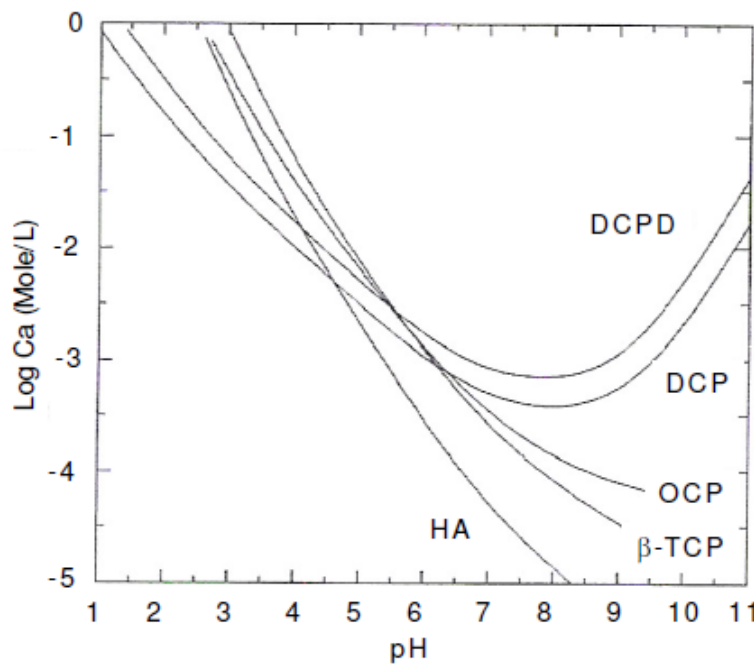


Figure 2: Solubility isotherms of different calcium phosphate ceramics[10]

a) Hydroxyapatite (HA)

Hydroxyapatite is the most commonly used calcium phosphate ceramic due to its close structural relationship to the inorganic part of the human bone[11]. The name apatite refers to a group of solids which have the chemical formula: $\text{M}_{10}(\text{XO}_4)_6\text{Z}_2$ (M: Ca, Ba; X:P, V, Cr, Mn; Z: F, OH). Hydroxyapatite is a compound which occurs naturally, but also can be produced synthetically.

The use of calcium phosphate ceramics as a bone substitute material is currently state of the art[12]. The motivation for the clinical use of calcium phosphate is the result of the fact that it has a chemical composition similar to the mineral phase of bones and teeth. Bones and

teeth comprise of hydroxyapatite nearly 60-70 % and 98 %, respectively[13]. The advantages of using hydroxyapatite coatings clinically are listed here[14];

- no formation of fibrillar connective tissue
- rapid growth of bone tissue
- forming a high strength connection between the implant and tissue
- shorter healing phase of implants with a metallic surface

b) Tricalcium Phosphate (TCP)

The chemical formula of tricalcium phosphate ceramic is $\text{Ca}_3(\text{PO}_4)_2$. These ceramics have been produced synthetically by sintering and exhibit a high porosity. Tricalcium phosphate ceramics can be divided into two groups: α -tricalcium phosphate and β -tricalcium phosphate. The chemical structure of α - and β -TCP are similar ($\alpha\text{-Ca}_3(\text{PO}_4)_2$ and $\beta\text{-Ca}_3(\text{PO}_4)_2$). The difference between the two is in their crystalline structure, which results in different levels of absorption. Consequently, the solubility of α -TCP is bigger than that of β -TCP[15]. The fabrication temperature of α -tricalcium phosphate is over 1100-1200°C and for β -tricalcium phosphate is between 800°C and a maximum of 1200°C[16]. Also with respect to the thermal stability at room temperature, the two groups differ. From a thermo-

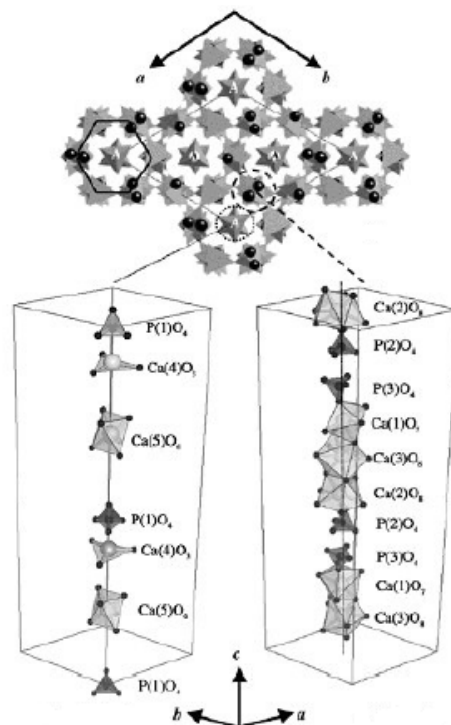


Figure 3: Crystal structure of β -TCP[11]

dynamical point of view, the α -tricalcium phosphate is unstable in the biological environment, whereas β -tricalcium phosphate is stable. Despite the relatively high solubility, α -TCP is quite slowly absorbed and it is either partially or completely hydrolyzed in hydroxyapatite at normal temperatures. The resulting apatite crystals have a unphysiological crystal morphology. Absorption kinetics of α -TCP is unpredictable, which is why it is found in less applications[17]. In addition to hydrolysis, the bridges between the individual particles and the calcium phosphates of the composite are dissolved, phagocytosed by cells and intracellularly degraded. The degradation rate of the ceramics increases with macroporosity. Dense modifications have no signs of degradation or dissolution. The solution strength depends on the solubility product. In vitro studies show a 12-22 times greater solubility as compared to HA and this explains why TCP is mechanically less resilient[18].

1.2 Scaffold Fabrication Techniques

In the body, the structures of cell and tissue are formed in three-dimensional architecture. To produce these functional tissues and organs, scaffolds should aid the cell distribution and mentor their growth into three-dimensional space. The main techniques for scaffold fabrication can be divided into two groups, which are conventional fabrication techniques and advanced fabrication techniques[19, 20].

1.2.1 Conventional Fabrication Methods for Complex Ceramic Components

The starting point for the manufacturing of objects, which are made of ceramic materials, is usually a powder. The conventional techniques include powder preparation, shaping using molds and sintering[21]. It is also possible for the powder to be molded one additional time after sintering. The conventional techniques for complex ceramic materials are wet pressing, slip casting, injection molding and gel casting.

a) Wet Pressing

Wet pressing (Figure 4) enables complex component geometries such as thread, lateral pores, recesses and undercuts. The suspensions used for this purpose generally have moisture in the range of 10 to 15 %. Under uniaxial compressive stress, these compositions become flowable so that a relatively uniform densification can be achieved. The disadvantage is that wet pressing materials can absorb compressive stresses. Additionally, the degree of compression is limited, which is highly dependent on the moisture content of the feedstock and is also lower than that of dry pressed parts. Moreover, drying of green parts before sintering is necessary[22]. This process is similar to the compression molding of plastics due to the flowability where the materials flow into remote side of the mold[23].

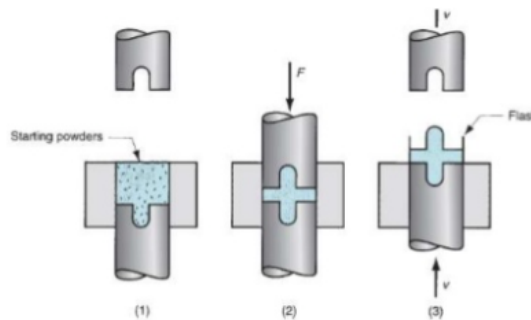


Figure 4: The wet pressing process[24]

b) Slip Casting

For slip casting, powder is dispersed in a liquid (usually water is used) and slurried to a so-called slip. The slurry is poured into a porous mold (usually made of gypsum) which removes the liquid. Here, the ceramic powder particles condense on the mold wall. This method is widely used for the production of hollow bodies, but it is also possible to cast full parts[25].

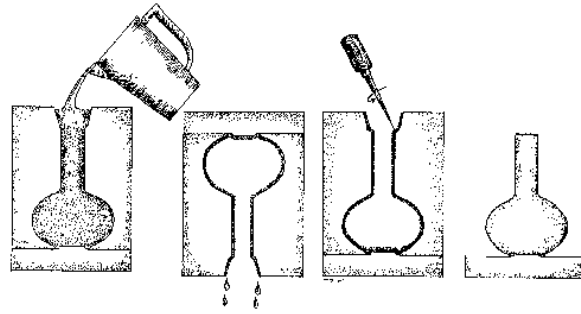


Figure 5: The slip casting process[26]

An advantage of this method is the possibility of producing large volume parts with complex shapes. For the production of individual pieces or small quantities, the requirement of a form is a disadvantage[26].

c) Injection Molding

By addition of a thermoplastic material to the ceramic powder, a flowable plastic mass is produced which is injected into a metal mold. Afterward, the cooled molded part is ejected. The thermoplastic binder material must be removed before the sintering by a thermal treatment[27]. Similar to the plastic injection molding, complicated and small parts can be produced in large numbers with this method. For the production of individual pieces or small numbers, the method is not economically viable due to the need of individual molds for different geometries (Figure 6).

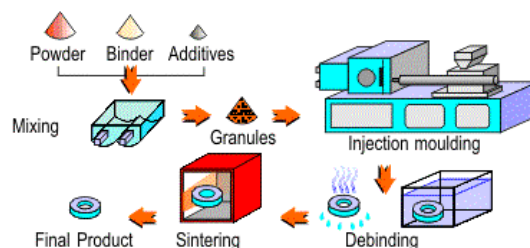


Figure 6: The injection molding process[28]

d) Gel casting

Gel casting (Fig. 7) is a method based on a combination of traditional ceramic manufacturing and polymer chemistry. In gel casting, a slurry is prepared by mixing a ceramic powder and a monomer solution which includes a thermal initiator[29]. The ceramic slurry is casted into a mold. By increasing the temperature, the monomers polymerize to form a green body. After that, the green body is treated first by a thermal process to get rid of the solvent and secondly to remove the binder from the structure. After sintering, full density ceramic materials can be obtained.

In the gel casting process, the ability to achieve a higher density of the final ceramic parts depends on the high powder percentage of the slurry. In addition to this, the viscosity of the slurry should be low to control the solid loading. To obtain good performance, the ceramic suspension should be flowable and with as a high solid as possible[30].

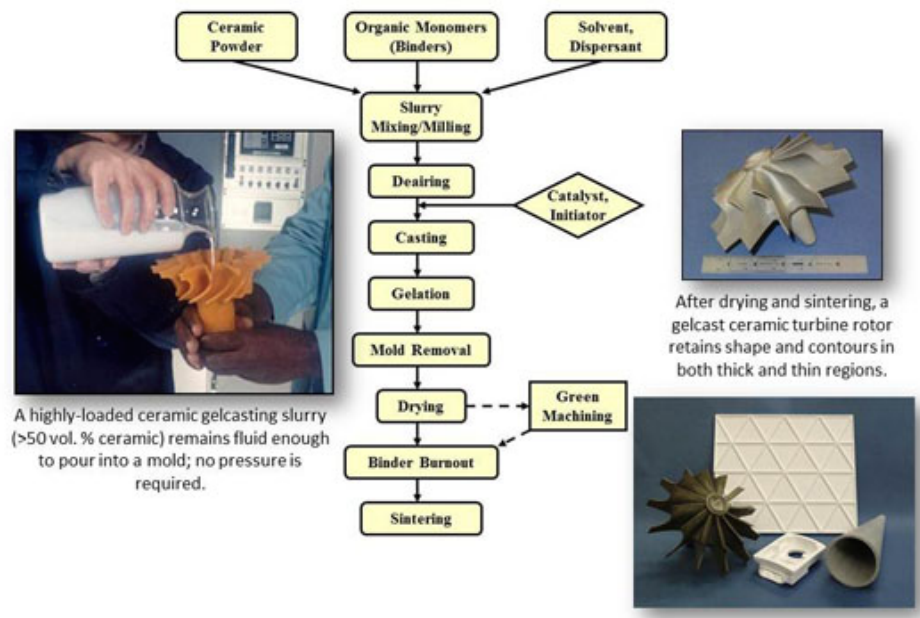


Figure 7: The gel casting process[31]

The summary of the conventional fabrication methods for complex ceramic components can be seen in Table 3.

Table 3: Characteristic of conventional manufacturing techniques for complex ceramic geometries[32]

Master forming techniques	Initial material	+ Advantages/ - Disadvantages
Wet pressing	Aqueous slurry	+ Complex geometries with even density distribution - Compression limited to moisture level - Drying step prior to sintering - Large tolerances
Slip casting	Aqueous slurry	+ Inexpensive molds + Manufacturing of hollow and solid parts - Large tolerances
Injection molding	Thermoplastic slurry	+ Mass production + Complex structures + High green density and stiffness - Furnace burning prior to sintering - Profitable for large lot sizes only
Gel casting	Monomeric slurry	+ Inexpensive molds + Manufacturing of hollow and solid parts + High green density and stiffness - Furnace burning prior to sintering

1.2.2 Advanced Fabrication Techniques

The main advantage of advanced fabrication techniques is that they are able to develop a homogeneous structure and do not require any molds. Therefore, these techniques are practical and beneficial to the manufacturing of the scaffold as required[33].

a) Electrospinning

The electrospinning technique for scaffold fabrication is based upon electrostatic force. In this process, a high intensity electric field is applied between two electrodes. One electrode is connected to the polymer solution containing the ceramic precursor, and the other one is connected to the collector. Normally the solution is charged in forming a drop and then the electric field is applied to produce a force. The collector collects the fibers[34] (Figure 8). The properties of the scaffolds depend on the polymer solution parameters (viscosity, molecular weight of polymer etc.), procedure parameters (voltage, flow rate etc.) and environmental parameters (moisture, temperature).

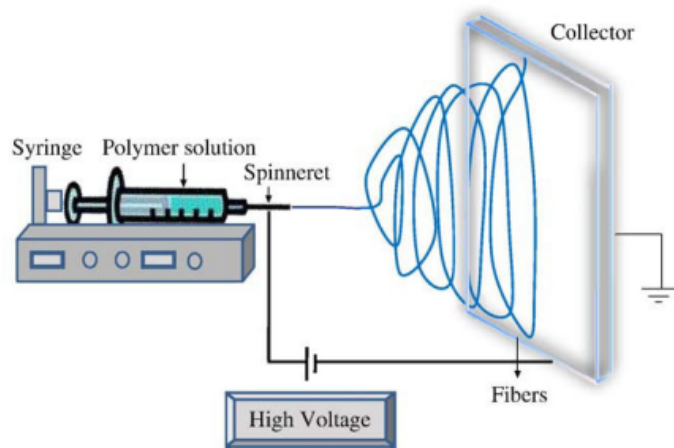


Figure 8: Schematic of electrospinning apparatus[20]

b) Additive Manufacturing

Additive Manufacturing is a class of technologies in which a 3D object is precisely created via a virtual model by adding material in a layer by layer approach and is defined by ASTM F2792 - 12a (Standard Terminology for Additive Technologies) as the "process of joining materials to make objects from 3D model data, usually layer upon layer, as opposed to subtractive manufacturing, such as traditional machining"[35]. Additive manufacturing is a more progressive method for scaffold fabrication. That means highly complex geometries

can be produced with this method. AM is based on the computer-aided design (CAD) and computer-aided manufacturing (CAM) method, where it is easier to control the design of scaffolds as compared to conventional techniques.

The computer generated 3D data also includes the spatial data. The hardware works and controls the exposure in x-y direction and the spatial output builds in z direction. In general, additive manufacturing methods require the steps as shown in Fig. 9[36].

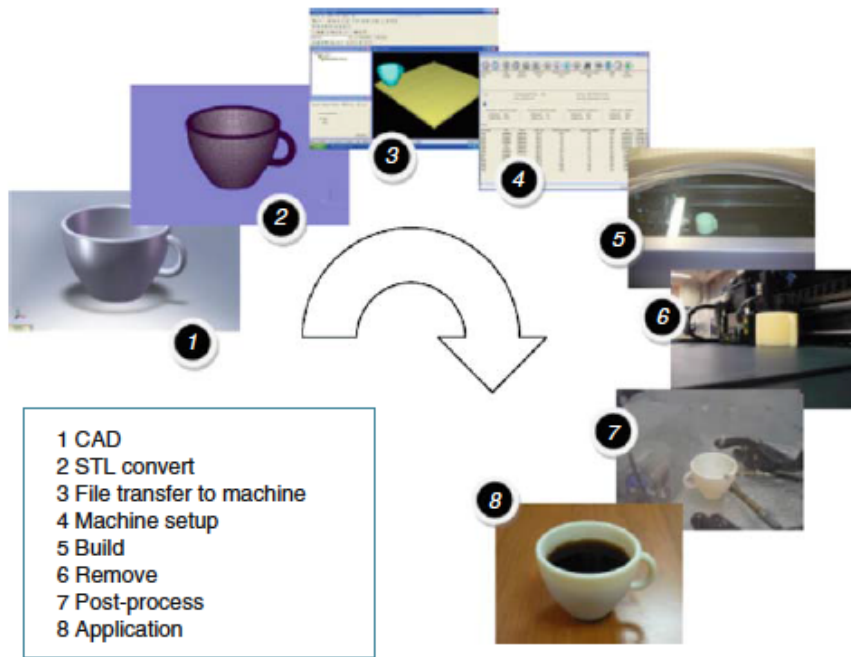


Figure 9: Stages of the additive manufacturing process[36]

- Step 1: CAD

The first step of every production process is design, which is why AM technologies also start with generating CAD (Computer Aided Design) files.

- Step 2: Conversion to STL

The term STL file is derived from **S**tandard **T**riangulation **L**anguage, which describes only the surface geometry of a three-dimensional object without any representation of color, texture or other common CAD model attributes, so it is a basic method of describing a CAD model in terms of its geometry. A STL file represents a 3D CAD model by triangulations. The number of triangles which effects the faceting. Figure 10 shows the difference between the CAD and STL files. Figure 10b is the example of course triangulation, beside this Figure 10c presents fine triangulation.

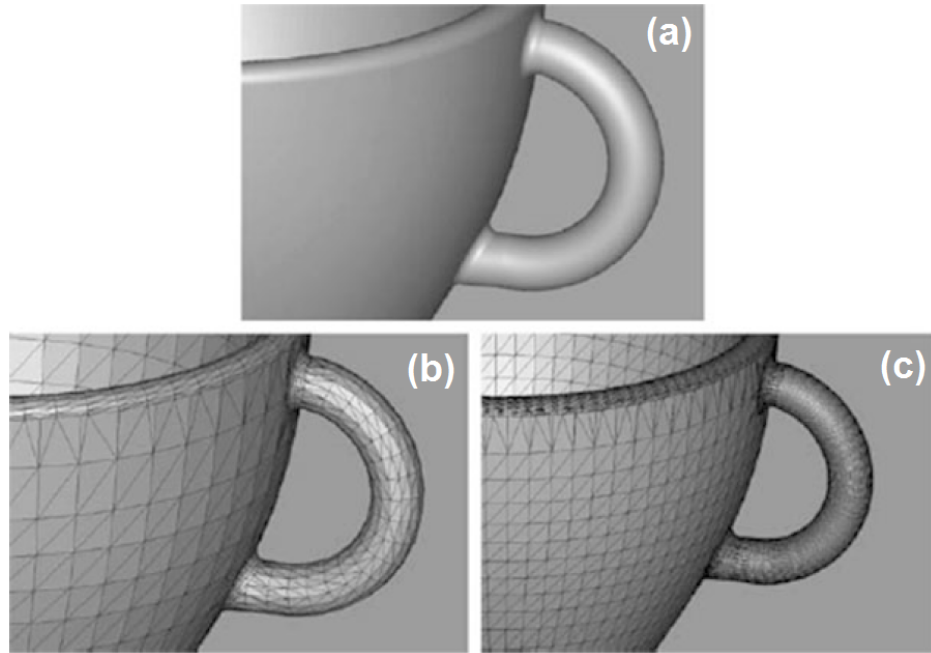


Figure 10: Example of STL and CAD format: (a) CAD model, (b) STL model with course triangulation and (c) STL model with fine triangulation[36]

- Step 3 & 4: Machine Setup & File Transfer to Machine
The additive manufacturing machine must be adjusted to the building parameters. The building parameters would relate to the machine settings like layer thickness, scaling factor, timings, etc.
- Step 5: Build
This step involves manufacturing of the desired sample.
- Step 6: Removal and Cleanup
Once the job has been completed, the parts must be taken off of the building platform on which the part was produced.
- Step 7: Post-processing
This step may contain abrasive processes such as sandpapering. The post-processing is optional, which means some applications may require post-processing, while other applications may require very careful handling of the parts due to their fragility.
- Step 8: Application
Once the post-processing has been completed, the finished parts are ready to use.

The following additive manufacturing techniques have already been used for ceramic materials[37] (see Fig. 11):

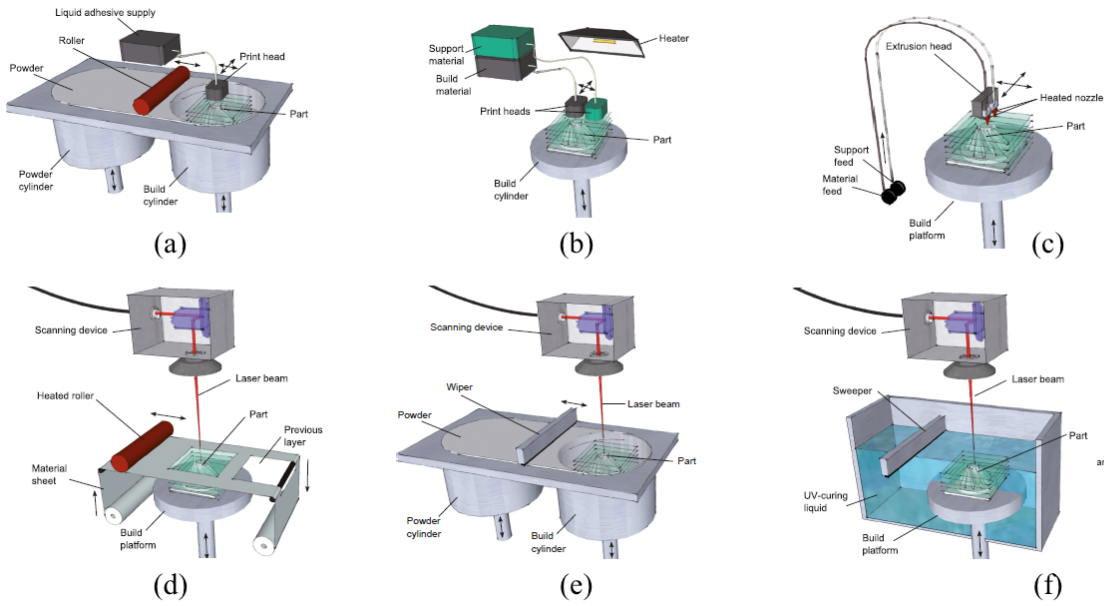


Figure 11: Schematic of additive manufacturing techniques: (a) Three-Dimensional Printing, (b) Ink-Jet printing, (c) Fused Deposition Modelling, (d) Laminated Object Manufacturing, (e) Selective Laser Melting and (f) Stereolithography[32]

Three-Dimensional Printing (3DP):

Classic three-dimensional printing is a powder bed based method (Fig. 11a). After each printed layer of the component, the component is coated by a thin powder layer. A binder in the desired areas of the powder is brought by a print head whereby the powder is solidified. The disadvantage of this method is the high porosity in the component[37]. Due to the powder bed, the tap density of the powder limits maximum solid loadings of the green part[38].

Ink-Jet Printing:

Another type of printing process (see Fig. 11b), often referred to as ink-jet printing, operates without a powder bed. The material supply happens here exclusively by the print head. For this process, supported powder bed is not available, because it is only suitable for the application of individual layers or relief-like structures without overhangs[39]. The applications are limited by the small range of fluid viscosity and surface tension; in general, fluids with a viscosity of less than 20 mPa.s and surface tension of 20-70 mN[40].

Fused Deposition Modelling (FDM):

In Fused Deposition Modelling (Fig. 11c), a plastic filament is pushed through a heated extrusion. Solids are constructed, layer by layer, with the plastic melt track. Ceramic-filled thermoplastic filaments are used for the ceramic manufacturing. The result of the building process is a green body. In a subsequent process, the binder is burned out and the green body is sintered. The surface finish and accuracy of FDM parts are not sufficient for engineering applications. The FDM reduces the surface quality because of staircase effect[41] In this technique, the geometric resolution is limited by the diameter of extruded melt filaments. A reduction of diameter results in less build-up rate and that means a longer production time[39]. As a modification of FDM, Robocasting was developed in 1996 (see Chapter 3.2).

Laminated Object Manufacturing (LOM):

In Laminated Object Manufacturing (Fig. 11d), the part is built through the attachment of individual films. Each film is cut into the required geometry and then bonded with the underlying layer. The film is produced by a rolling process for ceramic materials. The ceramic film also contains a significant number of binder (e.g. 7 % by weight) in addition to ceramic particles. After production of the parts, the parts are sintered in a furnace. Disadvantages of this method are relatively low geometric resolution due to the film thickness which is 0.05 to 0.50 mm. Due to the laminating step, the anisotropy of shrinkage is nearly 34 % in X- and Y- direction and nearly 8 % in Z direction in this method[42].

Selective Laser Melting (SLM):

The principle of SLM (see Fig. 11e) goes back to the year 1986. On a working area, which is called the building platform, a layer of powder material is applied. The powder is solidified by melting using a laser beam according to the cross-sectional geometry of the component. The powder particles are connected to the underlying layer. The principle is based upon the temperature-induced melting of the ceramic materials. The particles are bonded with each other by partial melting and solidification. The tendency of a system is exploited by the state of lowest energy. This is achieved by the reduction of the total surface in the system. As a result, the loose powder particles, which have a larger surface area than solid state, connect to larger structures with lower surface. This effect is called liquid sintering or selective laser sintering[43].

Stereolithography:

Stereolithography (see Fig. 11f) is based upon the principle of photopolymerization. The special photosensitive resin is selectively cured using light. This resin can also contain ceramic particles up to solid loadings of 85 wt%. The green body is built up layer by layer.

In a subsequent furnace process, the cured resin is burned out and then the ceramic particles are sintered in order to achieve a dense ceramic. The content of ceramics must be as high as possible to achieve low porosity after sintering[44].

1.3 Principle of Radical Photopolymerization

The term photopolymerization refers to a polymerization reaction, which is initiated with the aid of photoinitiators in the ultraviolet (UV), visible (VIS) or near infrared (NIR) range. The main advantages of photopolymerization are environment friendly formulations, low energy requirements at room temperature and low costs. Currently, decorative and printing applications are the main use of photopolymers[45, 46]. During photopolymerization the resin formulation is cured in the presence of a photoinitiator. The radical photopolymerization may be divided into the following partial reactions:

Initiation



Figure 12: Mechanism of photoinitiation[46]

The formation of initiator radicals (see Fig. 12) takes place in a process known as photolysis. With the aid of irradiation, cleavage occurs and photoinitiator turns into free radicals. The stability of the radicals and the dissociation energy of the homolytic cleavage are the important parameters in determining the suitability of a compound as an initiator[47].

Start & Propagation

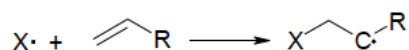


Figure 13: Mechanism of start reaction[46]

After the formation of the free radicals, a radical attaches itself to the double bond of polymerizable monomer to start the reaction (see Fig. 13). Figure 14 depicts the propagation mechanism. In this step, monomer units are added to the growing polymer chain. This step repeats regularly until termination.

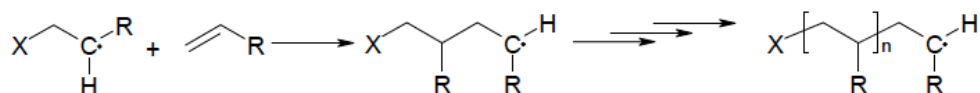


Figure 14: Mechanism of propagation[46]

Termination

In this step, the propagation of the polymer chain is terminated by the disappearance of the reactive centers at the growth end of the macromolecule. In general, three mechanism of termination are most common. These are recombination, addition of radical initiator and disproportionation as shown in Figure 15, 16 and 17, respectively.

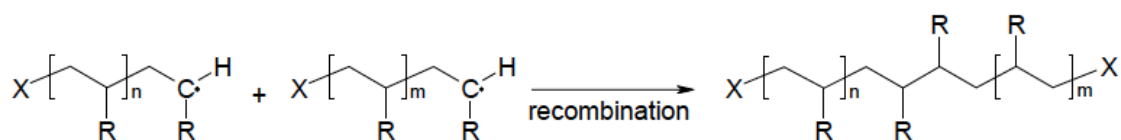


Figure 15: Mechanism of recombination[46]

The term recombination refers to association of two reactive macromolecules to an inert polymer (see Fig. 15).



Figure 16: Mechanism of recombination of macroradical with initiating radical[46]

In Figure 16, the reactive end group is terminated by the addition of a radical initiator.

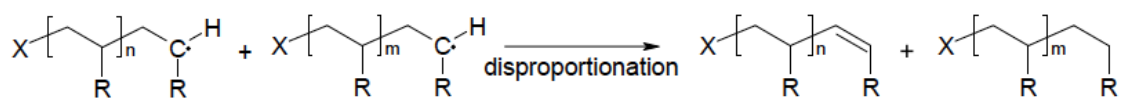


Figure 17: Mechanism of disproportionation[46]

When two reactive heads come together, they interact with the simultaneous transfer of a hydrogen atom to form a saturated and an unsaturated bond. It comes to a termination of the chain growth reaction (see Fig. 17).

The type of the chain termination depends on the monomer type and the temperature. At a lower reaction temperature, the termination occurs by recombination, at higher temperatures by disproportionation.

Photoinitiators

The choice of photoinitiator (PI) is a key factor in adjusting the curing speed and material properties of the polymer. The selection of photoinitiator depends on a number of variables such as chemistry of the monomer, functionality of the monomer, light source and curing speed which is a crucial parameter for Stereolithography[48].

Radical photoinitiators can be divided into two groups according to their photofragmentation. The following photoinitiators can be used for radical photopolymerisation:

a) Type I Photoinitiators



Figure 18: Mechanism of Type I Photoinitiators[45]

Type I Photoinitiators which are known also as unimolecular photoinitiators, are split into two radicals by α -cleavage. Figure 18 depicts the mechanism of photoinitiation of Type I PIs. However, β -cleavage is also possible[49]. Bisacyl phosphine oxide (BAPO) is a typical example of Type I PIs. These types of PIs are synthesized to use the wavelength between near visible region and 430 nm. This results in a higher cure depth.

b) Type II Photoinitiators

Type II Photoinitiators refer to bimolecular photoinitiators such as camphorquinone (CQ)/dimethyl aminobenzoic acid ethylester (DMAB) system. The CQ/DMAB system can be used in biomedical applications. The mechanism is depicted in Figure 19.

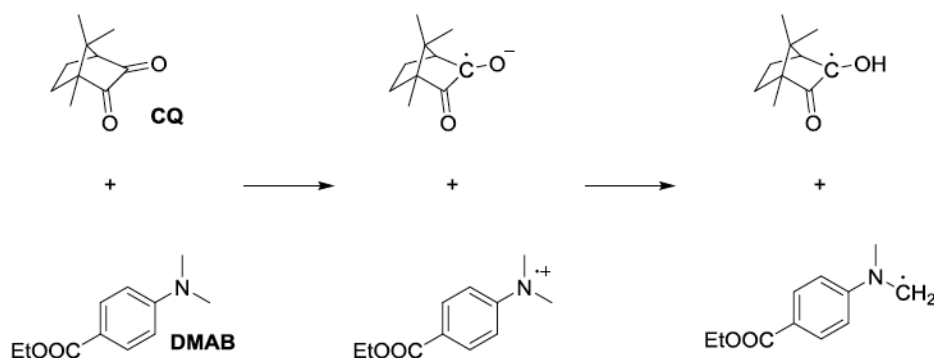


Figure 19: Mechanism of Type II Photoinitiators[45]

The photoinduced radical formation could occur through hydrogen abstraction or electron/proton transfer from a donor molecule. Co-initiator transfers an electron to the PI which

is in an excited state. This leads to the formation of a radical cation and a radical anion. The proton of the cationic structure moves to the anionic structure and the components of the system turn into radicals. Benzophenones, ketocoumarines and xanthenes are other typical Type II PIs[46, 50].

2 Objective

Tissue engineering (TE) is an interdisciplinary research area that applies principles of both engineering and life sciences. The application process involves the development of biological substitutes in order to restore, maintain or improve tissue function of a given organ. The human body is a complex and sensitive biological system which poses an extreme challenge for tissue engineering[50]. Additive Manufacturing (AM) is convenient manufacturing method to prepare parts with controlled dimensions such as macropores, strut thickness and patient specific designs. Photopolymerization based AM methods allow the manufacturing of highly precise structures.

The aim of this thesis is to increase the mechanical strength of tricalcium phosphate ceramics which are already being produced by Lithography-based Ceramic Manufacturing. Figure 20 depicts the desired bending strength with a high porosity. While increasing the mechanical properties, the microporosity of the scaffolds should remain similar. Miao et al. have determined that high porosity is desirable for the scaffolds used for bone tissue engineering[51]. The microporosity is usually proportional to bending strength. Lower relative density provides a higher surface area. For that reason, microporosity is a crucial factor for bioresorbable ceramics due to the absorption by the human body. Due to their non cytotoxic effects, metal oxide dopants such as magnesium oxide, titanium dioxides, zinc oxide and silicon dioxides are therefore preferred for improving the mechanical properties.

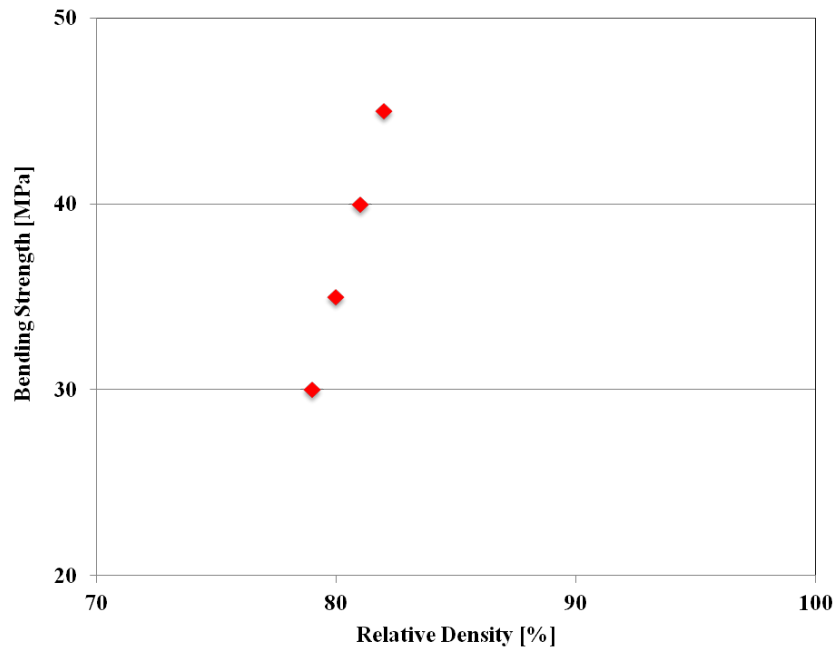


Figure 20: Desired bending strength vs. relative density

In the first part of this thesis, the blending of ceramic powders should be done. For this purpose, pure tricalcium phosphate powder as a reference and tricalcium phosphate powders with metal oxide dopants should be prepared. Furthermore, these prepared powder mixtures shall be used to fabricate 3D structure. Before structuring, light penetration shall be tested to investigate the cure depth. The investigation of material viscosity and the stability of slurries shall be examined by rheometry for fresh and used slurries. Additionally, different sintering temperatures and different sintering times shall be applied after 3D printing of green bodies.

In the second part of this work, a series of tests shall be performed such as: thermomechanical analysis (TMA) to obtain crack free parts after debinding, three point bending test (3PB) for mechanical strength, scanning electron microscope (SEM) for microporosity and fractography, and light microscopy to investigate macroporosity shall be tested.

This work involves interdisciplinary research activities between the Institute of Materials Science and Technology, Vienna University of Technology, the Institute of Applied Synthetic Chemistry, Vienna University of Technology and Lithoz GmbH.

3 State of the Art

Additive Manufacturing (AM) refers to the manufacturing of geometries directly from three dimensional (3D) computer-aided design (CAD) model. AM technologies are already established in the plastic and metal industry. The main advantages are cost savings and lower material consumption, no tooling costs and shaping of materials without any limitations. Nevertheless, additive manufacturing methods are also destined to be used in the ceramic industry. As a result, with the launch of stereolithography technology, a worldwide research and development campaign began, which had to improve and optimize the performance of additive manufacturing processes. For this result, Lithography-based Ceramic Manufacturing (LCM) came into the market. LCM process differs in that single parts and small series can be made in any complexity with the same material properties as in conventional manufacturing methods. In addition to that, some manufacturing methods for complex geometries such as selective laser melting, robocasting and 3D Printing have been also established.

3.1 Selective Laser Melting

Selective laser melting (Fig. 21) (SLM) is working with powdered raw materials which are melted under the influence of a laser. The process was developed in the mid-80s at the University of Texas by Joe Beaman and Carl Deckard. Due to the achievable qualities close to the series material laser sintering in the industry has a great importance. It is used for both the prototype and tool as well as for the direct production of components (direct digital manufacturing)[32].

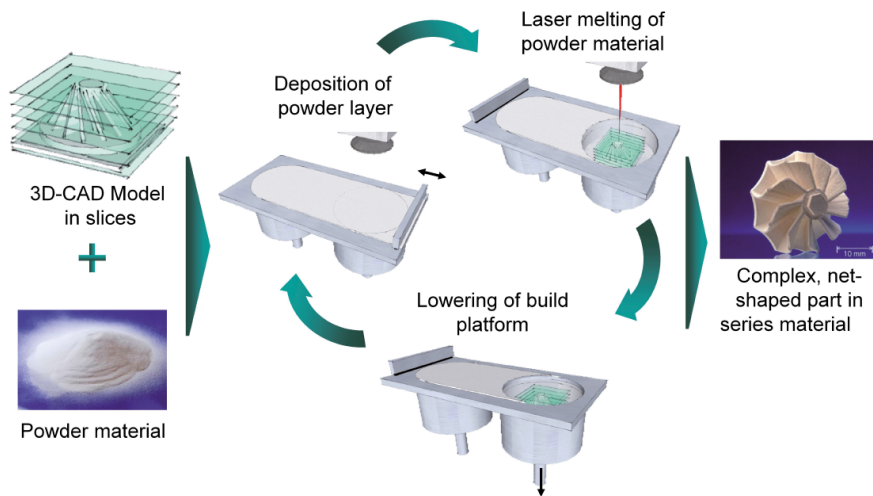


Figure 21: Schematic illustration of the SLM process[32]

The laser melting is based on the local melting and fusing powder material under heat of a laser beam on the basis of 3D CAD data. With a cylindrical coating unit, a thin layer of powder is spread evenly and smoothed on the print bed. Since the solidified material composite is surrounded by loose powder, no support structure is required for the realization of overhangs. However, additional structures are needed to hold the component when working with high-energy lasers in position. To reduce the process time, the entire pressure chamber is heated at most plants to a temperature range below the melting temperature of the material coming to the powder application. Before releasing the finished component from the powder bed, the entire pressure chamber must be cooled evenly over several hours. Unused powder can be reused[43].

Lee et al. have fabricated the HA and TCP ceramics for orthopedic implants via SLM. The fabricated ceramics had the sufficient porosity. However, the mechanical strength has certain limits to be used as an implant[52].

3.2 Robocasting

Robocasting was developed at Sandia National Laboratories for the complex dense ceramics in the 1990s (Fig. 22).

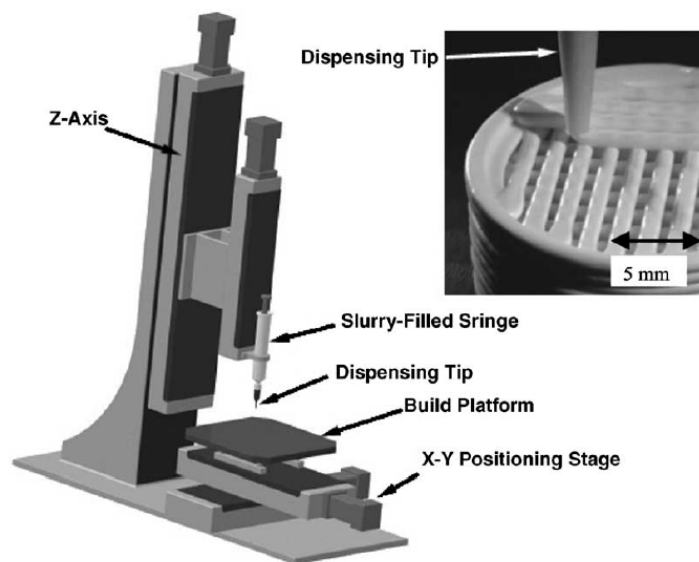


Figure 22: Schematic illustration of the Robocaster[53]

This technique needs less than 2 volume percent of organic binder. The principles of robocasting is based upon the idea of extrusion of ceramic slurry through nozzle. Ceramic slurries are extruded to obtain layerwise deposition via robotics. The highly loaded ceramic

slurries that are typically used by robocasting, contain 50 - 65 vol% ceramic powder, less than 1 vol% organic additives and 35 - 50 vol% volatile solvent (generally water). As a result, a dense ceramic body can be manufactured, debinded and sintered in less than one day[54, 55].

With the aid of this method, HA-based scaffolds have been fabricated for the application of bone implants. Seitz et al. have reported that a pore size of 500 μm is possible for HA scaffolds[56].

3.3 3D Printing

Sachs et al. have developed three-dimensional printing (3DP) at the Massachusetts Institute of Technology (MIT). Before a liquid binder is added by a print head in the desired areas of powders, a thin powder layer of $< 200 \mu\text{m}$ is coated with the aid of a roller. Figure 23 depicts the process sequence of 3DP. An unused powder acts as a support structure and allows one to create more complex geometries.

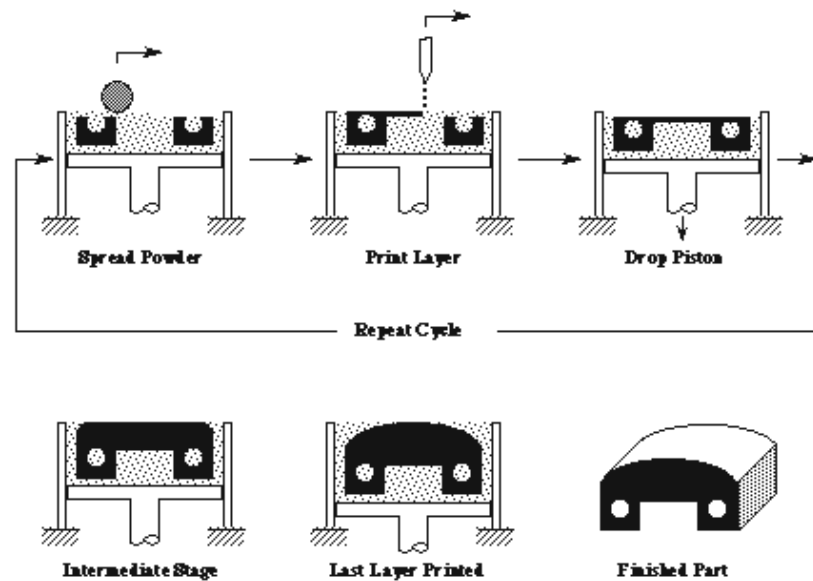


Figure 23: The 3D printing process[57]

The bulk density of the powder bed affects the density of the green part. As a result, sintered parts only reach maximum densities of 95 %. The limitation of this technology is irrelevant for producing porous bioresorbable bone scaffolds of β -TCP and HA[32, 57].

3.4 Lithography-based Ceramic Manufacturing

The LCM method has been developed for highly filled and highly viscous ceramic suspensions by Lithoz (Figure 24). With this technology, highly complex geometries such as scaffolds can be produced in customized designs with high reproducibility.

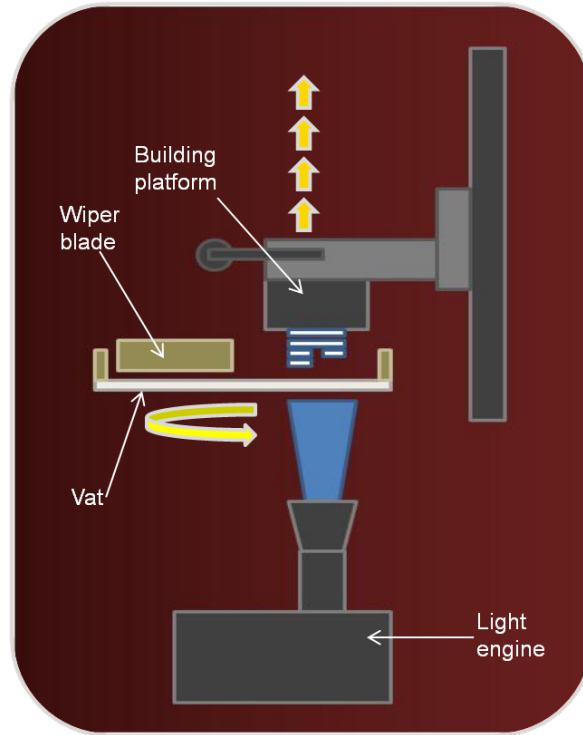


Figure 24: Schematic drawing of LCM process[58]

The LCM process is based upon the idea of photopolymerization, where a photosensitive formulation is cured in the required areas of the slurry via a mask-exposure process.

The system works with light of a wavelength of approximately of 460 nm and is based on the technology of dynamic mask exposure using DLP projection (Digital Light Processing). An essential element of the system is the light engine with specially constructed projection optics. The light source uses powerful light-emitting diodes in combination with a DMD chip (Digital Micromirror Device) from Texas Instruments to give a resolution of 1920 x 1080 pixels. The use of LEDs as a light source provides a much more homogeneous illumination and a more stable light output is achieved as compared to other systems. The resolution and the size of the resulting digital image are determined by the number of mirrors of the DMD chip and the projector optics used. The optics used currently generate pixels with a side length of 40 μm , resulting in a size of a 76.8 mm x 43.2 mm building envelope. Figure 24 shows the schematic system.

In addition to the light engine (DLP projector), included is the z-axis, a tilting mecha-

nism, the building platform with integrated backlight exposure, a rotating mechanism and the wiper blade to the other main components of the developed system. The movement of the building platform in the z-direction is achieved by a high-strength and high-precision linear axis. The linear axis and tilting and rotating mechanism are controlled from a PC via motor drives and stepper motors.

The dedicated software coordinates the various stepper motors and sends the respective layer information in the correct order in the form of bitmaps to the DLP projector. Usually, components with layers of 20 μm to 100 μm thickness are built. The DLP projector projects the layer contour. This is the photosensitive resin system that is located between the building platform and cured material vat solidification. By a tilting movement of the material vat, the separation from the vat of the cured layer is achieved. In addition, this the deposit of hardened resins into the material vat which would further interfere with the construction process. The next step is to feed in the viscous slurry. By a rotational movement of the circular vat, fresh material is resupplied. By means of a wiper blade, which is connected directly to the tilt mechanism, the redelivered material is evenly distributed, smoothed and shaped into the desired material film thickness. Thereafter, the building platform is returned to the defined distance (layer thickness of the single layer) from the vat and the generation of the next layer can begin. In this way, the green body is generated layer by layer[59, 60].

Figure 25 shows the process sequence of LCM. This procedure continues until the last layer is cured.

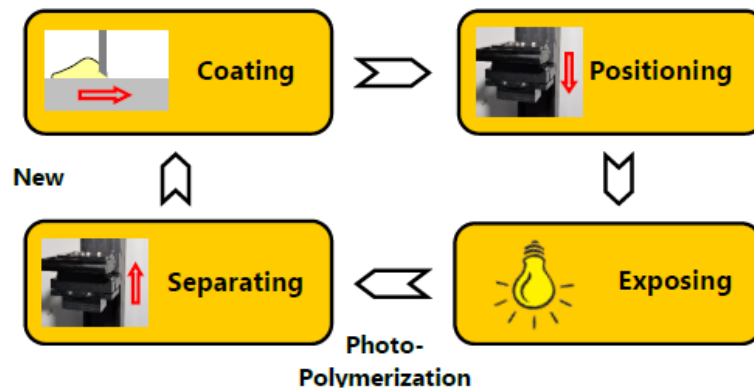


Figure 25: The LCM process sequence[61]

3.5 Metal Ion Dopants

Metal ions are common in biological systems. Metal ions play a crucial role such as energy production, electron transfer and redox activation[62]. However, sintering additives are usually used to improve the sintering behaviour and to manage the change in the microstructure. The addition of MgO to Al_2O_3 is a typical example of a sintering additive. The mechanism of sintering additives is not well known. For that reason, the roles of sintering additives are understood only empirically[63]. Nevertheless, the following dopants are preferred: magnesium oxide, titanium dioxide, zinc oxide and silicon dioxide[64]. The main aim of this study is to characterize the influence these dopants have on the sintering behavior and the resulting mechanical properties. The concentration of the dopants should be kept low in order to preserve the TCP structure.

3.5.1 Magnesium Oxide

Magnesium is one of the crucial minerals for the human body. Magnesium is needed for energy production, glycolysis and oxidative phosphorylation. It aids in the construction of bone and in the synthesis of DNA and RNA. The other role of magnesium is the active transportation of calcium and potassium ions which are critical for nerve impulse and the rhythm of the heart[65]. Moreover, insulin secretion and insulin activity also require magnesium. Magnesium is the fourth most common mineral in the human body and is necessary for its overall health and wellness. Nearly 60 % of the magnesium in the human body is in the bones, where it is believed to constitute a surface from hydroxyapatite mineral. The other 40 % is found in the body tissue and organ cells. There is only 1 % of magnesium in the blood[66].

Table 4: General properties of magnesium oxide[67]

Molecular formula	MgO
Crystal structure	Cubic fcc
Density (g/cm^3)	3.58
Boiling point ($^{\circ}\text{C}$)	3600
Melting point ($^{\circ}\text{C}$)	2852
Young's modulus (GPa)	250
Colour	White
Solubility in water (mg/l)	6.2
Molecular weight (g/mol)	40.30

It has been found that the optimum amount of MgO in TCP, as dopant, is 1 % and this value shows good biocompatibility without any toxic effects in vivo and in vitro testing. It was also determined that Mg^{2+} addition into TCP tends to reduce the degradation rate[6].

3.5.2 Titanium Dioxide

The metal titanium has excellent mechanical properties and is bioinert. As a result of that, it has been widely used as a load-bearing biomaterial due to their bone-compatible modulus, excellent biocompatibility and greater corrosion resistance[68]. Titanium and its alloys are also used as orthopedic and dental implant materials[69]. Titanium metal is produced from the mineral rutile, TiO_2 . If titanium oxide is immersed in a simulated body fluid, titanium dioxide also grows bone-like apatite. Additionally, F. Caroff has showed that titanium dioxide in TCP, as dopant, increases the mechanical strength[70].

Seeley et al. have found that the optimum amount of titanium dioxides is 1 wt%. However, according to Manjubala et al., it has been found that 5 wt% titanium dioxide can also be used in TCP[71, 72].

Table 5: General properties of titanium dioxide[73]

Molecular formula	TiO_2
Crystal structure	Tetragonal
Density (g/cm^3)	4.23 (Rutile) 3.78 (Anastase)
Boiling point ($^{\circ}C$)	2972
Melting point ($^{\circ}C$)	1843
Young's modulus (GPa)	250
Colour	White
Solubility in water	insoluble
Molecular weight (g/mol)	79.87

3.5.3 Zinc Oxide

Zinc has many functions in the human body. One of the important roles of zinc is in growth and cell division, where it is responsible for protein and DNA synthesis, insulin activity, in the testes and ovaries metabolism and in the function of the liver. Zinc takes part in the protein, carbohydrate, lipid and energy metabolism as an enzyme component. In the human body there is nearly 2-3 gr zinc[74]. There is no specific place for zinc storage in the human body, however 60 % of zinc is found in muscle, 30 % in bone and nearly 5 % in skin. The first indications of zinc deficiency are immune reactions and skin problems.

Table 6: General properties of zinc oxide[75]

Molecular formula	ZnO
Crystal structure	Hexagonal Cubic
Density (g/cm ³)	5.63
Boiling point (°C)	1975
Melting point (°C)	1975
Young's modulus (GPa)	250
Colour	White
Solubility in water	insoluble
Molecular weight (g/mol)	81.41

For bone formation, zinc is a crucial trace element. It was found that beta-TCP doped with zinc can help bone generation. If the zinc content is greater than 1.2 wt%, it shows cytotoxic effects[76].

Kawamura et al. have shown that TCP based materials doped with a trace element such as zinc, show superior bioactivity[77]. However, the high Zn concentration may increase the the toxic side effects on cells[78].

3.5.4 Silicon Dioxide

Silicon dioxide which is also called silica, is a trace element in the human body. Silica is found in bones, teeth, skin, eyes and organs. The function of silica in collagen is to give the skin elasticity. Silicon molecules help facilitate tissue strength and provide stabilization. Another function of silicon dioxide in bone, blood vessel and cartilage, is to make them stronger[79].

Table 7: General properties of silicium dioxide[82]

Molecular formula	SiO ₂
Crystal structure	Tetrahedral
Density (g/cm ³)	2.65
Boiling point (°C)	2230
Melting point (°C)	1600 to 1725
Colour	Transparent crystals
Solubility in water (mg/l)	10
Molecular weight (g/mol)	60.1

Carlisle and Schwarz discovered the role of Si as an essential element in the 1970s[80, 81]. Carlisle showed that silicon helps bones maintain calcium and assists with bone growth

in experiments with chickens. In this study, half of the chickens were fed with a very low Si content, and the rest were given sodium metasilicate as a supplementary. As a result, the chickens with low Si content have showed some deformities in the skin and bones. The average mass of the supplemented chickens was bigger than the average mass of non-supplemented chickens[80].

Additionally, Gomez-Vega et al. have worked on bioglass, which is a high Si content biomaterial[83]. Bioglass was the first bioactive ceramic. Consequently, the fields of research projects and development were bone substitutes. The peculiarity and the advantage of Bioglass is the binding property to the bone, in order to unfold its osteoconductive function. This is the basis of the development of bioactive granules. At the present time it may be assumed that Bioglass is an alternative to conventional bone substitutes[84]. The first developed bioglass is composed of 46.1 mol % SiO_2 , 24.4 mol % Na_2O , 26.9 mol % CaO and 2.6 mol % P_2O_5 , later termed 45S5. However, there are different type of bioglasses which show no better biological properties since the invention[85].

4 Experimental Part

Tricalcium phosphate (TCP) is a bioceramic which shows excellent biocompatibility and can be absorbed by the body. Nevertheless, the mechanical properties are known to be quite poor. According to Tampiere et al., fully dense β -TCP without any α -modifications can achieve a maximum strength of 120 MPa[86]. However, fully dense ceramics are not suitable for bioresorbable implants. For this purpose, instead of increasing the densification, the sintering additives can be examined to improve the mechanical strength. The addition of dopants can enhance the mechanical strength of TCP. In this work, tricalcium phosphate was doped with various percentages of different metal ion dopants (Table 8) and manufactured to test specimens (Table 10 and 11) using LCM. After slurry preparation, viscosities were characterized by rheometer and green parts were printed. After sintering, these samples were then analysed to determine how the dopants effect the mechanical properties and the microstructure of TCP. These analyses were density measurements, three-point bending tests, scanning electron microscopy and light microscopy. Before this study began, TCP* (without pre-milling process) was already in use as a standard material by Lithoz. This is the reason that samples of β -TCP* were applied as a reference.

Table 8: Weight percent and combination of dopants

Compositions	Weight (%)
TCP*	N/A
TCP	N/A
TCP*-MgO-1	1
TCP-MgO-1	1
TCP-TiO ₂ -1	1
TCP-TiO ₂ -5	5
TCP-ZnO-0.25	0.25
TCP-SiO ₂ -1	1
TCP-MgO-ZnO-1-0.25	1+0.25
TCP-MgO-TiO ₂ -ZnO-1-1-0.25	1+1+0.25

* without pre-milling process

4.1 Ceramic Manufacturing

In this research high purity materials were used as metal ion dopants. These materials were magnesium oxide ($\geq 99\%$), titanium dioxide ($\geq 99\%$), zinc oxide ($\geq 99\%$) and silicon dioxide ($\geq 99\%$). All were purchased from Sigma-Aldrich except silicon dioxide, which

was used as received from Imerys Fused Minerals (Greeneville, TN USA). β -tricalcium phosphate powder ($\geq 96\%$) was also purchased from Sigma-Aldrich.

In general, the conventional ceramic manufacturing includes powder preparation, shaping and sintering. These steps determine the microstructure. In the shaping stage, lithography-based ceramic manufacturing method has been used in this work.

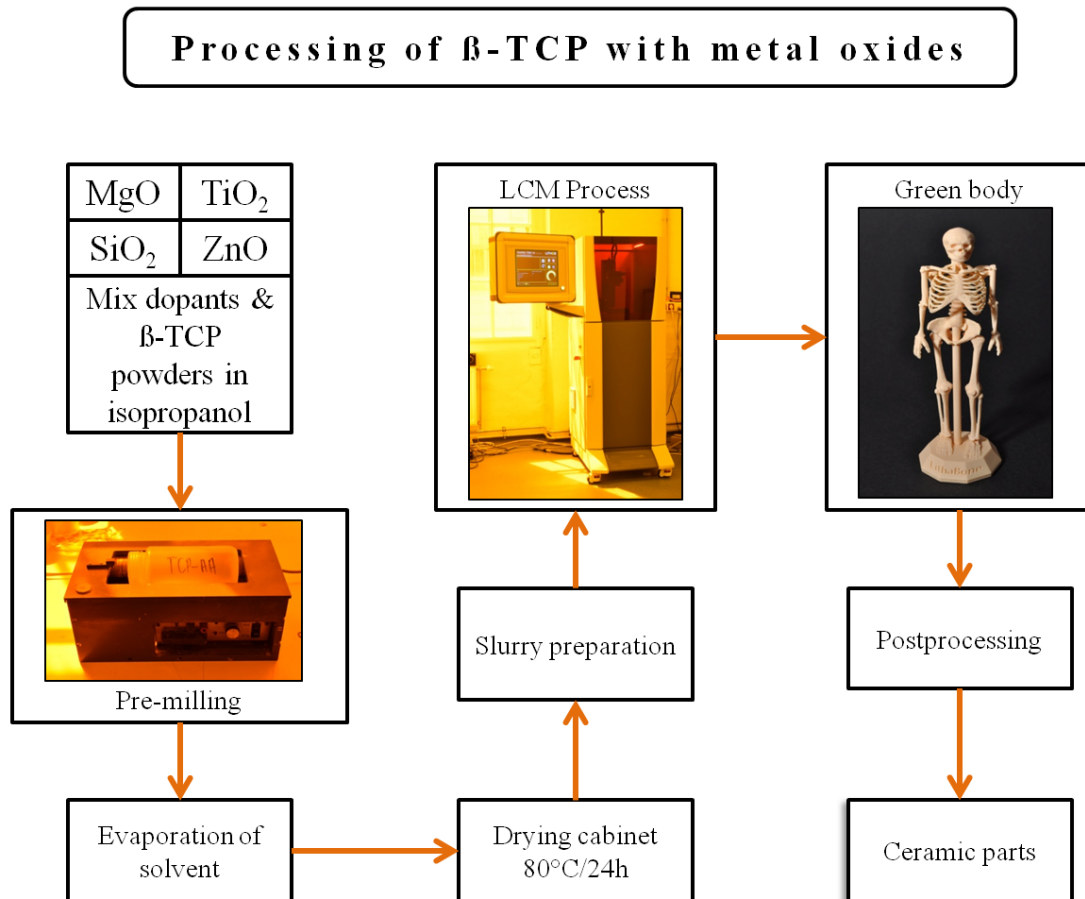


Figure 26: Flow chart for processing of TCP with metal oxide dopants

Powder Preparation

In this work powders were prepared by pre-milling process and direct addition.

a) Pre-milling:

In Figure 26 the standard pre-milling process of this work is shown. The principle of pre-milling process is while rotating the disc in one direction, the bottle rotates in the opposite direction. With the aid of centrifugal forces, the suspension is fractured.

Metal oxide dopants were added to tricalcium phosphate powder in various weight percentages, which were 0.25, 1 and 5. The metal ion dopants used for this job were magnesium oxide, titanium dioxide, zinc oxide and silicon dioxide as shown in Table 8.

Tricalcium phosphate powder, the dopants and dispersant (2.1 g) were weighed and mixed in 500 mL translucent polypropylene bottles. Each of the powder mixtures was based on approximately 150 g of tricalcium phosphate. The dispersing agent was calculated as 1.4 wt% of tricalcium phosphate. Then isopropyl alcohol (IPA) (150 mL) was added as a solvent. As a last step, 50 mL of zirconia milling balls (Zirmil Y ϕ =1.5 mm, Saint-Gobain, France) were added. Table 9 shows the weights that were used to prepare the pre-milling mixtures.

Table 9: Weights for pre-milling process

	Weights of	Weights of Dopants			
	TCP [g]	MgO [g]	TiO ₂ [g]	ZnO [g]	SiO ₂ [g]
TCP	150	0	0	0	0
TCP-MgO-1	150	1.5	0	0	0
TCP-TiO ₂ -1	150	0	1.5	0	0
TCP-TiO ₂ -5	150	0	7.5	0	0
TCP-SiO ₂ -1	150	0	0	0	1.5
TCP-ZnO-0.25	150	0	0	0.375	0
TCP-MgO-ZnO-1-0.25	150	1.5	0	0.375	0
TCP-MgO-TiO ₂ -ZnO-1-1-0.25	150	1.5	1.5	0.375	0

Subsequently, pre-milling process was started and done for 24 hours using a roller mill (self-made). After pre-milling, the suspension and milling balls were separated from each other by a sieve. Isopropyl alcohol was evaporated from the suspension to give the doped tricalcium phosphate powder. As a last step, doped powder was placed into the drying cabinet at 80°C for 24 hours before further use[87].

b) Direct addition:

Beside the pre-milling process, a direct addition procedure was also used. As a metal oxide dopant, magnesium oxide was added directly to the TCP powder. First, 150 g of TCP was weighed in a centrifugal mixer cup. Then, 1.5 g of MgO was added to TCP powder. The powder mixture was used to prepare slurry.

Slurry Preparation

In the LCM process, a photocurable suspension (slurry) is used to manufacture the ceramic parts. The photocurable suspension consists of TCP powder with dopants, which was dispersed in light-sensitive organic matrix (MS13E). MS13E, a proprietary binder system is

developed by Lithoz GmbH. The used binder system was on the basis of multifunctional (meth)acrylates using a visible light photoinitiator and an azo-dye to limit the light penetration. It also contained a dispersing agent which is prerequisite to get a high ceramic loading with a good homogeneity and a low viscosity of the ceramic suspension[88]. Ventura et al. explained that the solid loading usually varies from 45 to 55 vol%[89]. The TCP slurries were consistently 49 vol% in this study.

The slurry was prepared by using a combination of centrifugal mixer (SpeedMixer DAC 400.1 FVZ, Hauschild, Germany) and ball milling. The centrifugal mixer works on the principle of the dual asymmetric centrifuge, which means the spinning arm of the machine is in one direction, while at the same time the basket turns in the opposite direction[90]. First, the organic matrix was placed into the centrifugal mixer cup then the ceramic powder was added. The ceramic suspension was mixed at 1200 rpm for 30 seconds and at 2750 rpm for 30 seconds. Subsequently, the beaker of the ball mill was filled with the obtained ceramic suspension. After filling the beaker, the dissolver disc was mounted and milling balls were added into the milling beaker. The rotation velocity sped up to nearly 3000 rpm in stages over the course of 3 hours.



Figure 27: The doughnut effect during the slurry preparations[90]

The most important thing is to have a doughnut-like shape during the milling procedure (Figure 27), because that means the maximum mechanical power possible is being transferred. The stream is divided into two parts. The first part going down flows back into the middle of the impellers along the bottom of the dispersion beaker and rises up to the disc again. The force of gravity and the rheological properties of the mill base limit the circular path, which is formed by the second part. After three hours, the photocurable ceramic suspension was pressed to the beaker with the aid of air. Lastly, to get a better shelf-life, the stabilization agent was added to the slurry, which is 0.5 wt% of the powder in the slurry.

Fabrication of Samples

The ceramic samples were built on a CeraFab 7500, a printer for LCM which has been developed by Lithoz GmbH.

The designs that were printed had five different geometries. The test cylinder (see Table 10) with 10 mm in diameter and 10 mm in height was used for two purposes: firstly as a cylinder for thermomechanical analysis in green state and secondly for density measurement by a method based on the Archimedean principle as a sintered ceramic sample. The next full geometry is the test bar (see Table 11). The test bars that were used in this work, were manufactured in the dimension of 2 x 2.5 x 25 mm according to DIN EN 843 and used for three-point bending tests to determined the mechanical strength[91].

Table 10: Job details for test cylinder

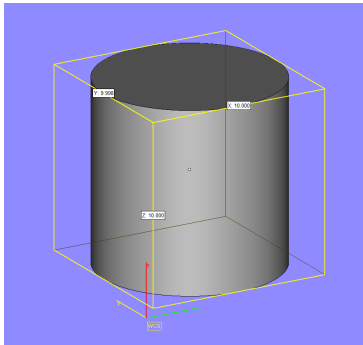
	$\varnothing$ [mm]	10
	H [mm]	10
	Total layers	400
	Layer thickness [μm]	25

Table 11: Job details for test bar

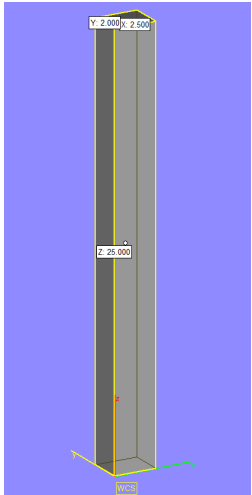
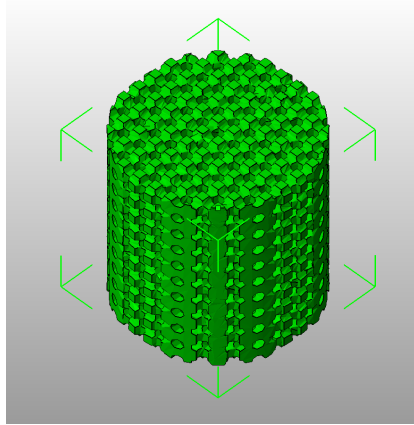
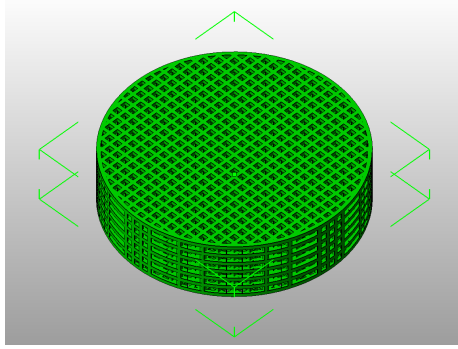
	W [mm]	2
	H [mm]	2.5
	L [mm]	25
	Total layers	1080
	Layer thickness [μm]	25

Table 12: Job details for scaffold I



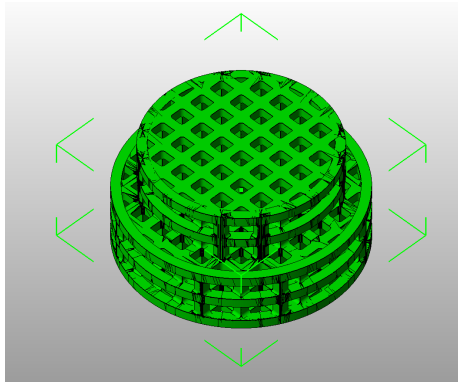
W [mm]	9.98
H [mm]	10
L [mm]	9.99
Pore size [μm]	600
Total layers	400
Layer thickness [μm]	25

Table 13: Job details for scaffold II



W [mm]	20
H [mm]	5.10
L [mm]	20
Strut thickness [μm]	300
Pore size [μm]	500
Total layers	204
Layer thickness [μm]	25

Table 14: Job details for scaffold III



W [mm]	7.5
H [mm]	3.68
L [mm]	7.5
Total layers	148
Layer thickness [μm]	25

In the scaffold fabrication stage, three different structures (see Table 12, 13 and 14) in terms of design, pore size and strut thickness were used. Cell binding, migration, tissue

ingrowth and regeneration are the crucial roles of scaffolds[92]. It was also reported that the optimum pore sizes vary 100 to 400 μm for bone regeneration[93]. These designs were chosen by considering these parameters.

In this work, the thickness per layer was 25 μm .

First, the vat was filled with the slurry and the building platform was adjusted to plane-parallelism to the vat. After choosing the optimum parameters, the optimum energy dose can be measured by light penetration tests. For all parts, the production of one layer of TCP green body takes nearly 50 seconds. Before printing the first layer, the building platform was prepared by curing a primary layer using backlight exposure. The aim of the primary layer is to improve adhesion of the printed part to the building platform so that it does not fall down. After that, the slurry was poured into a rotating vat again and equally distributed with the help of the wiper blade in combination with the vat-rotation. After the rotation, the slurry forms a thin film in the vat and the building platform dunks into the slurry. Once the building platform was in position, the LED light engine cured the required areas of the slurry via a mask-exposure process. The cured slurry adheres to the building platform and gets pulled out of the slurry along the z-axis. Now the vat rotates again to recoat itself and the building platform moves back into the slurry. This process is repeated until all the layers were built.

After the green bodies were manufactured, the printed ceramic parts were removed using razorblade. The excess slurry was removed by compressed air, and then green bodies were cleaned with an appropriate cleaning fluid. Then the green bodies were dried by pressurized air again and left at room temperature before the debinding and sintering process.

Debinding and Sintering

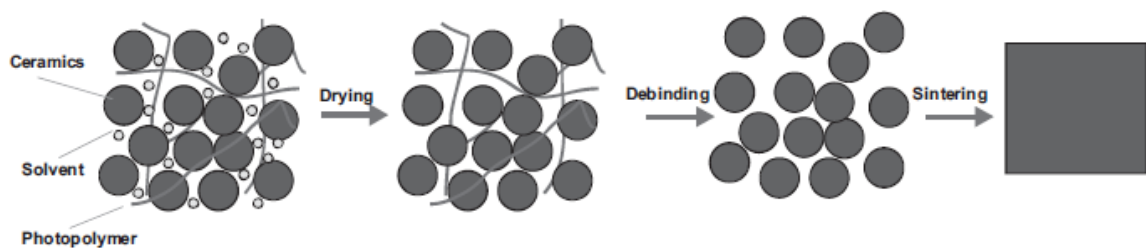


Figure 28: Steps of the thermal treatment from the ceramic green body to the sintered dense ceramic[60]

The post processes after the green body fabrication are debinding and sintering, as shown in Figure 28. The photopolymer is only a binder for the ceramic particles in the green body. For this reason, the concentrations of photopolymer should be minimized[94]. During the debinding step, the photopolymer component gets burned off and the subsequent sintering

step at very high temperatures leads to densification and consequently gives the finished ceramic piece.

The binder formulation affects the debinding process and may even cause shape distortions. Debinding is a time-consuming process and the formulations used in this work specifically will need a very time consuming temperature profile. In a rapid temperature rise, too much gaseous decomposition products are formed and the ceramic structure is damaged. The plasticizer is the first volatile component with a temperature rise, and adds the component to a porous structure. The resulting micro-channels are of great importance in the subsequent transport of the decomposition products of the other organic components. If one of the components is not given enough time, it can lead to destruction of the structure, due to excessive gas pressure of the combustion gases. Using thermomechanical analysis (TMA) optimized debinding conditions were determined.

Sintering is the heat treatment process, during which a relatively loosely bound pressed powder is sufficiently compressed, such that the pore spaces are more or less completely filled[95]. Sintering is a key step in the transformation of the green compact into a denser structure with high strength. It involves heating the component to a temperature at which the particles combine and the necks are increasingly integrated into each other. The formation of these compounds also leads to a reduction in their porosity. The grain size increases and may be much larger than the initial particle size.

After cleaning, the green bodies were placed in a furnace. In our work, four different debinding and sintering cycles were used. These temperatures (see Table 15, 16, 17 and 18) were based on different literature reviews and laboratory works[96, 97]. At the sintering temperature, two different dwelling times were chosen: 1 hour and 2 hours. Debinding and sintering were carried out in a furnace (HTCT 08/16, Nabertherm, Lilienthal, Germany).

Table 15: Debinding & Sintering Programm 1

Heating time [hh:mm]	Temperature [°C]	Waiting time [hh:mm]	Heating rate [K/min]
00:00	25	00:00	
02:00	75	02:00	0.42
04:00	120	04:00	0.19
08:00	205	16:00	0.18
20:00	430	04:00	0.19
06:00	600	00:00	0.47
08:00	850	02:00	0.52
06:00	1200	01:00	0.92
12:00	25	00:00	-1.63

Table 16: Debinding & Sintering Programm 2

Heating time [hh:mm]	Temperature [°C]	Waiting time [hh:mm]	Heating rate [K/min]
00:00	25	00:00	
02:00	75	02:00	0.42
04:00	115	04:00	0.17
08:00	205	16:00	0.19
20:00	430	04:00	0.19
06:00	600	00:00	0.47
08:00	850	02:00	0.52
06:00	1150	01:00	0.83
12:00	25	00:00	-1.56

Table 17: Debinding & Sintering Programm 3

Heating time [hh:mm]	Temperature [°C]	Waiting time [hh:mm]	Heating rate [K/min]
00:00	25	00:00	
02:00	75	02:00	0.42
04:00	115	04:00	0.17
08:00	205	16:00	0.19
20:00	430	04:00	0.19
06:00	600	00:00	0.47
08:00	850	02:00	0.52
06:00	1250	02:00	1.11
12:00	25	00:00	-1.70

Table 18: Debinding & Sintering Programm 4

Heating time [hh:mm]	Temperature [°C]	Waiting time [hh:mm]	Heating rate [K/min]
00:00	25	00:00	
02:00	75	02:00	0.42
04:00	115	04:00	0.17
08:00	205	16:00	0.19
20:00	430	04:00	0.19
06:00	600	00:00	0.47
08:00	850	02:00	0.52
06:00	1150	02:00	0.83
12:00	25	00:00	-1.56

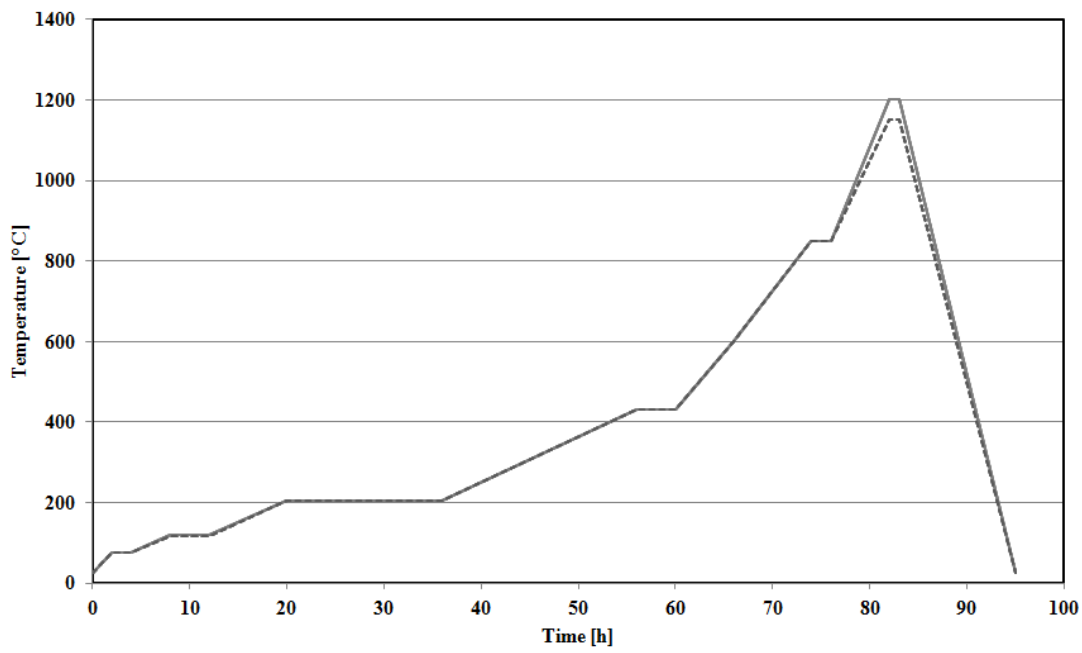


Figure 29: Schematic of the debinding & sintering (1 hour) cycle

Figure 29 depicts 1 hour-sintering cycles at 1150°C (dashed line) and at 1200°C (straight line), Figure 30 shows the 2 hour-sintering cycles at 1150°C (dashed line) and 1250°C (straight line).

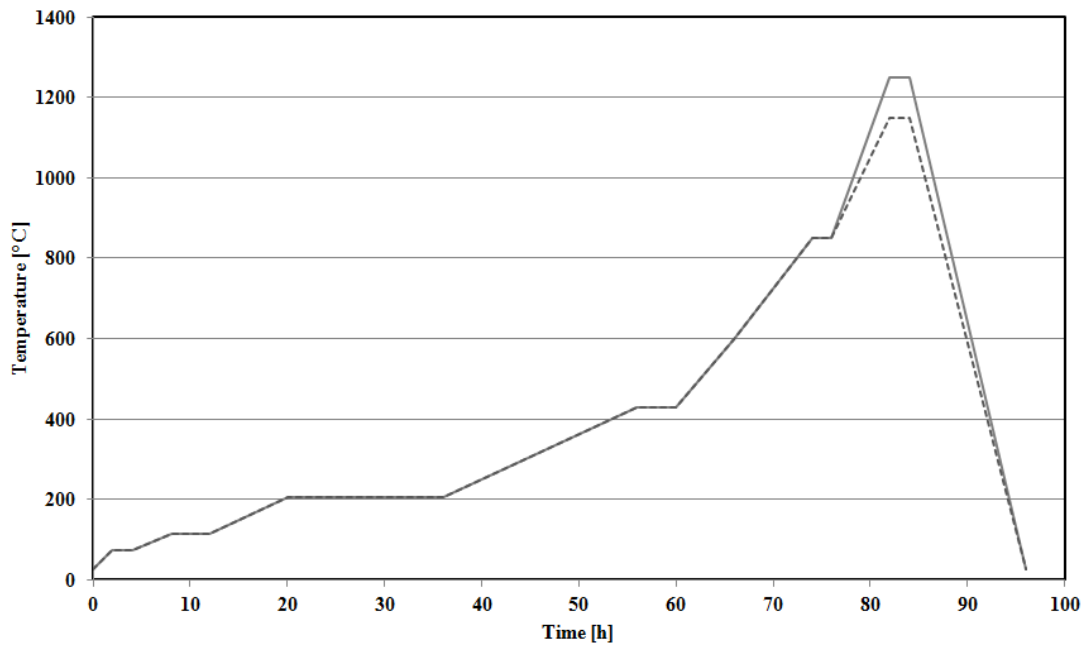


Figure 30: Schematic of the debinding & sintering (2 hours) cycle

4.2 Testing

Penetration Test

The cure depth plays a crucial role for manufacturing samples by LCM. The cure depth is inversely proportional with the refractive index. The higher refractive index of the ceramic lowers the cure depth. As a result, the printing times can be longer or printing can be unsuccessful all together. The refractive indices of tricalcium phosphate powder and the dopants can be seen in Table 19.

Table 19: Refractive Index (n_D) for ceramic powders[99, 100, 101, 102, 103]

Material	Refractive Index
$\text{Ca}_3(\text{PO}_4)_2$	1.626-1.629
MgO	1.7375
TiO_2	2.6142
ZnO	2.0034
SiO_2	1.4585

Griffith and Halloran have discussed that the scattering efficiency term (Q) is a function of the difference of the refractive index between ceramic powder and organic matrix.

$$Q = \beta \Delta n^2 \quad (1)$$

The penetration depth is inversely proportional to $\Delta n^2 = (n_{\text{ceramic}} - n_{\text{solution}})^2$, where n is the refractive index and the term β is relevant to the particle sizes and wavelength[94].

Additionally, Mitteramskogler et al. have shown that the more cure depth the green structure has, the more homogeneous the green body seems. It can reduce the possibility of cracking during debinding and, as a result, it can aid in producing crack-free parts[98].

Rheology

The rheological measurements of the slurries were performed on a rheometer (MCR 301, Anton Paar, Graz, Austria) at a temperature of 20°C with a plate-plate arrangement at the Institute of Applied Synthetic Chemistry, Vienna University of Technology. Using a measuring plate with a 25 mm diameter. The gap between plates was adjusted to 0.5 mm.

In the LCM process, ceramic slurries with viscosity of 12 Pa.s or less are generally used[104].

Thermomechanical Analysis (TMA)



Figure 31: TA 2940 Thermomechanical Analyzer[105]

In this case, expansion of samples is measured as a function of temperature or as a function of time. For this purpose, the samples are exposed to a static or dynamic force. By using a TMA machine, the relative change in length is measured;

$$\varepsilon = \frac{l(T) - l(T_0)}{l_0} \quad (2)$$

Where $l(T)$ is the length at each temperature, $l(T_0)$ is the length at the initial temperature and l_0 is the length of the sample at the initial temperature[106].

TMA (TMA 2940; TA Instruments, USA) (Fig. 31) was performed using a cylindrical sample (see table 10) with approximately 10 mm in diameter and 10 mm in height.

Density

Density of the sintered ceramic parts were measured by a method based on the Archimedean principle (fig. 32) for all compositions.

First, the samples were treated with an impregnating agent (Erdal Protect Aqua Stop). For that purpose, the samples were dipped in impregnating agent and dried. After impregnation, each sample was placed in a sample holder and measured in an air and aqueous media to calculate the density (SI-234A, Denver Instrument, Germany). This change of weight corresponds to the Archimedes force. Five measurements were performed for each sample, and three samples were used for each material.

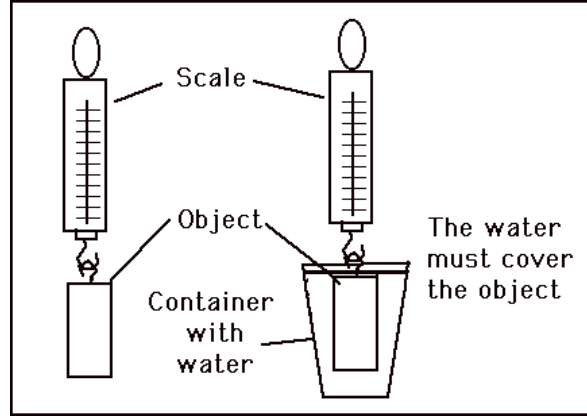


Figure 32: Illustration of Archimedes principle measurement[107]

To calculate the density the following equation was applied:

$$\rho_{sample} = \frac{m_{sample,air} \times \rho_{water}}{m_{sample,air} - m_{sample,aqueous}} \quad (3)$$

$m_{sample,air}$ and $m_{sample,aqueous}$ are the weight of a sample in an air and aqueous media respectively and ρ_{water} is the density of water. The theoretical density of pure tricalcium phosphate is 3.14 g/cm³[108].

Three-Point Bending Test

The Three-point bending test was used to characterize mechanical properties of the brittle TCP samples.

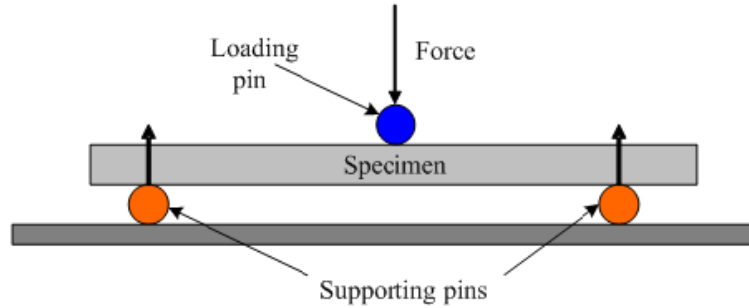


Figure 33: Principle of three-point bending measurement[109]

$$\sigma_f = \frac{3 \times F \times l}{2 \times b \times h^2} \quad (4)$$

In these equation (Eq. 4) the following parameters are used:

- σ_f = stress in outer fibers at midpoint, (MPa)
- F = load at a given point on the load deflection curve, (N)
- l = the distance between the centers of the support rollers, (mm)
- b = width of the test specimen, (mm)
- h = depth of the test specimen, (mm)

The strength of the sintered TCP parts was determined by three-point bending tests. As it can be seen in figure 33, the specimen is placed on supporting pins and the force is applied by a third loading pin, which is placed in the middle of the supporting pins. The dimensions of the specimens (Fig. 11) were 2 x 2.5 x 25 mm and the number of samples that were measured were 8. The tests were performed on a universal mechanical testing machine (Z010: Zwick Roell, Ulm, Germany) at the Institute of Materials Science and Technology, Vienna University of Technology.

Scanning Electron Microscopy

For collecting micrographs, a scanning electron microscope (XL 30, FEI Philips, Eindhoven, the Netherlands) was used at the Institute of Materials Science and Technology, Vienna University of Technology. The microstructure of the sintered TCP samples of the fracture surfaces, the surfaces, the TCP powders and the dopant powders were evaluated via a scanning electron microscopy (SEM). The non-conductive ceramic substrate was previously glued to a sample holder and sputtered with gold.

Light Microscopy

The light microscope (Opto, Graefelfing, Germany) was used to examine the parts for cracks and especially after the temperature treatment during the sintering. In our work, the pore sizes of scaffolds (Fig. 12 and 13) were measured in different magnifications and the light microscope was used to examine the parts for cracks or defects at Lithoz GmbH. Schott KL 1500 LCD was used as a light source.

5 Results

Tricalcium phosphate (TCP) is a bioceramic which shows excellent biocompatibility and can be absorbed by the body. As mentioned before, the mechanical strength is not good enough to use as scaffold in the human body. The maximum strength of fully dense β -TCP without any α -phases is approximately 120 MPa[86]. Nevertheless, fully dense ceramics are not appropriate for scaffolds due to the missing microporosity, which is necessary for efficient bioresorption. For this purpose, the concept of metal oxide dopants were used to improve the mechanical strength while maintaining a porous microstructure. In this work, tricalcium phosphate was doped with various percentages of different metal ion dopants (see Table 8 on page 45) and manufactured to test specimens (see Table 10 and 11 on page 49) using LCM in order to enhance the mechanical strength of TCP. After slurry preparation, viscosities were characterized by rheometer and green parts were printed. After sintering, these samples were then analysed to determine how the dopants effect the mechanical properties and the microstructure of TCP. These analyses comprised density measurements, three-point bending tests, scanning electron microscopy and light microscopy.

Before this study began, TCP* (without pre-milling process) was already in use as a standard material by Lithoz. This is the reason that samples of β -TCP* were applied as a reference.

5.1 Cure Depth

To quantify how far light can penetrate into a given ceramic suspension under conditions such as in the LCM process, so called light penetration tests were conducted. For this purpose, a small amount of ceramic suspension was placed on a glass slide. Subsequently, a defined area of this glass slide was exposed to light of varying intensities for different time periods. To determine how far the light could penetrate into the suspension, the uncured material is removed using a mild solvent and the thickness of the photopolymerized residue is measured using a micrometer screw.

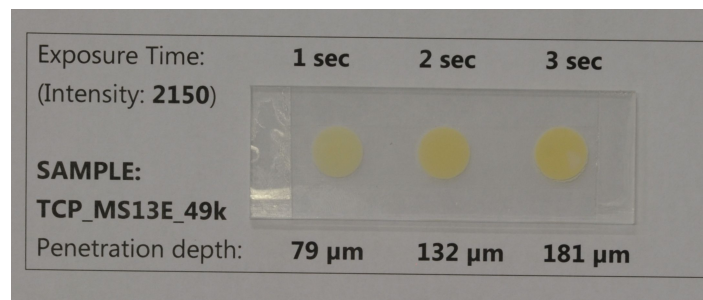


Figure 34: Light penetration test of standard TCP* formulation

Firstly, three different intensities, which were 47.1, 41.7 and 30.7 mW/cm², were used. The typical exposure time for light penetration test is 1 to 3 seconds. Figure 34 shows exemplary glass slides of tricalcium phosphate formulation without pre-milling process from penetration depth experiments. The obtained thickness of polymerized material is noted below the samples. The results of the penetration tests can be also seen from Table 20.

Table 20: The results of the penetration test for standard TCP* formulation

I = 47.1 mW/cm ²		I = 41.7 mW/cm ²		I = 30.7 mW/cm ²	
Energy dose [mJ/cm ²]	Penetration depth [μm]	Energy dose [mJ/cm ²]	Penetration depth [μm]	Energy dose [mJ/cm ²]	Penetration depth [μm]
47.1	79	41.7	57	30.7	27
94.2	132	83.4	123	61.4	88
141.3	181	125.1	160	92.1	126

More than 3 seconds of exposure, which is equal to 141.3 mJ/cm², can cause an irregular shape. Due to so-called over-polymerization, which is caused by light scattering that occurs when light interacts with particles in suspensions. Over-polymerization should be avoided since it limits the possibility to print precise and accurate structures. The respective result is shown in Figure 35.

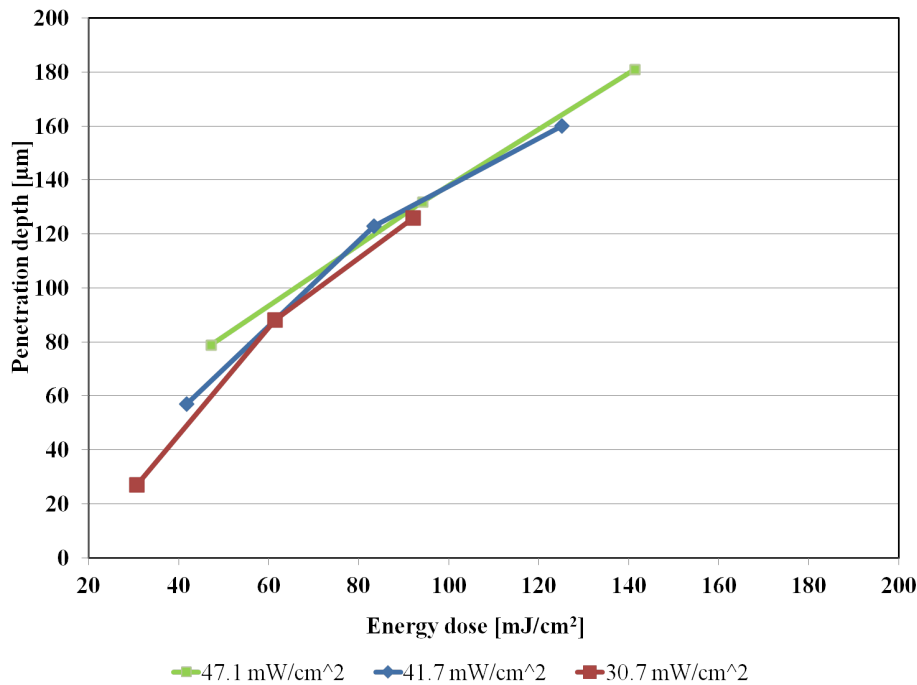


Figure 35: Light penetration for TCP slurries with different dopants and different energy doses

Secondly, to investigate how far the light penetrate into a given ceramic suspension with different dopants, the same procedure were repeated as used in the penetration depth of pure TCP.

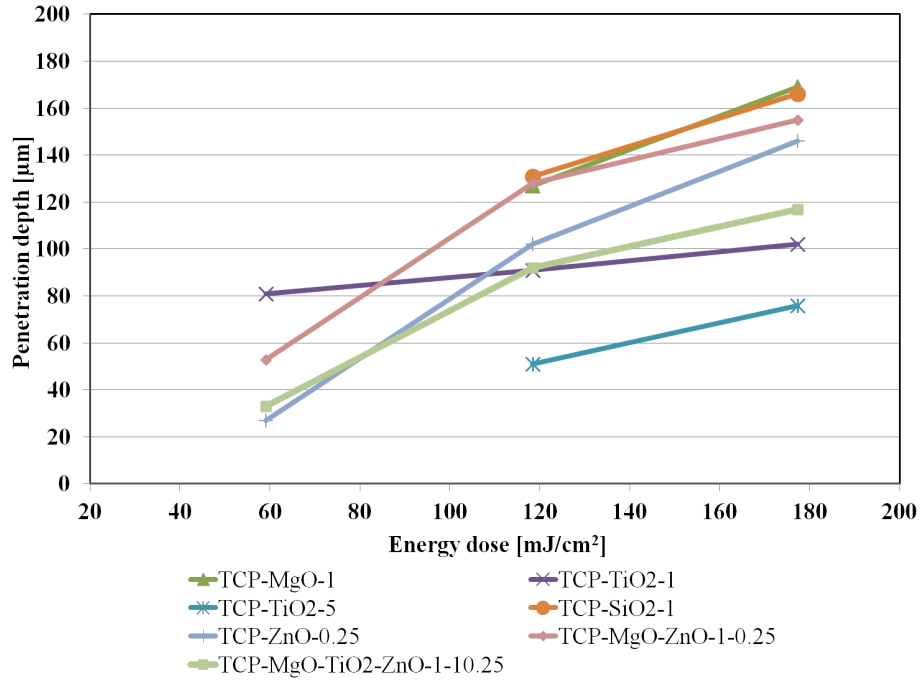


Figure 36: Light penetrations for different light intensities and different energy doses

Figure 36 shows that different dopants have different cure depths. As mentioned in Table 19 (see on page 55), the cure depth is inversely proportional to refractive index. TiO_2 has the highest refractive index and TCP- TiO_2 -5 formulation has also the lowest cure depth as expected. On the other hand, SiO_2 has the lowest refractive index and due to the scattering and absorption of light by the particles, the slurry based on TCP- SiO_2 -1 has the highest depth of cure found in this work.

Consequently, all this values show that energy doses between 100 to 120 mJ/cm^2 are suitable to print at a layer thickness of 25 μm . In this work, the specimens were printed at the intensity of 41.7 mW/cm^2 and every layer was irradiated for 2.88 seconds.

5.2 Rheology

To evaluate the influence of dopants on the suspension in respect to the flow behavior with and without pre-milling process, rheological measurements were performed in this work. For this reason, the same suspensions as used in the penetration test were used. The rheological measurements were operated with a plate-plate arrangement at a temperature of 20°C. Approximately 1 gr of the slurry was placed on the plate and the gap between plates was adjusted to 0.5 mm. The measurement of viscosity was performed in three steps with the following shear rates; 1) at a constant shear rate of 5 s⁻¹, 2) from 5 to 200 s⁻¹ shear rate 29 measurements linearly and lastly again at a constant shear rate of 200 s⁻¹.

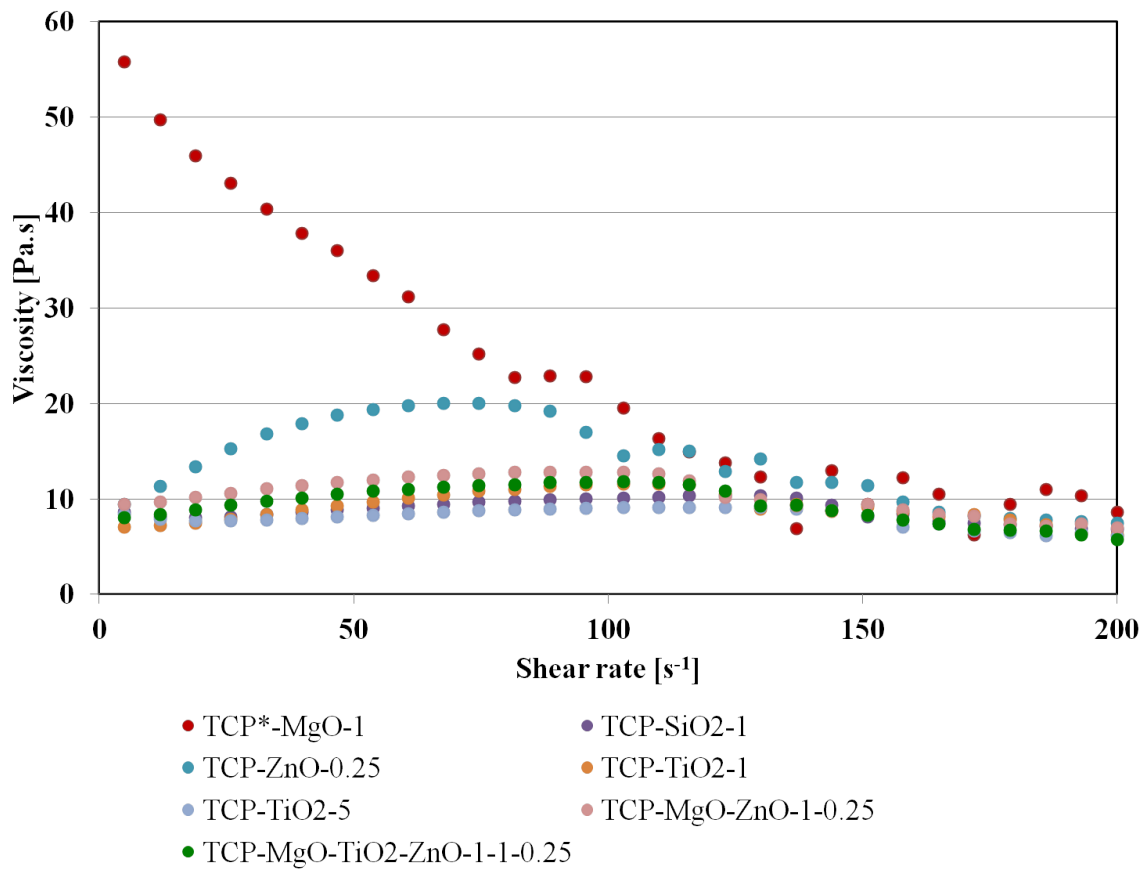


Figure 37: Viscosity of the photocurable TCP suspensions with different dopants as a function of the shear rate

Figure 37 depicts the viscosity measurement of the TCP slurries with different dopants and different dopant loading were performed. The viscosities change at different shear rates. All the dopants were pre-milled with TCP powder, except MgO. MgO dopant was directly added to the TCP powder. TCP*-MgO-1 ceramic suspension shows extraordinary flow behavior for LCM technology (see Fig. 37 with red curve). At the shear rate until 50 s⁻¹,

the viscosity is over 40 Pa.s. Due to grain sizes and inhomogeneous powder dispersion in a photosensitive formulation, agglomeration leads to increasing the viscosity of the slurry. Consequently, the direct addition of the dopant changes the typical flow behavior and suspensions are not within the usable limit for LCM technology. To overcome this problem, the pre-milling process have been applied. According to this process, the viscosity curves show an ideal flow behaviour. Unlike this ceramic suspension, the rest of the photocurable TCP suspensions were ideal for lithography-based ceramic manufacturing. At shear rates between 50 and 150 s⁻¹, the viscosities range between 10 and 20 Pa.s, which is reported by Stampfl et. al as an ideal value for structuring by LCM[104].

5.3 Thermomechanical Analysis

To investigate the thermal behavior of the green parts during debinding process, TMA experiments were performed. During TMA experiments the dimensional change of the green parts can be measured as a function of temperature or time. Thermomechanical analysis was performed using cylindrical sample with 10 mm in diameter and 10 mm in height. The used TMA samples can be seen in Table 10 on page 49. In this work, the same binder system was used to print the green parts. The binder itself has the predominant influence in the temperature range of 25 to 600°C. For this reason, TMA measurements were not conducted for all samples.

The complete elimination of the binder is achieved in two stages: the evaporation of the solvent and the thermal debinding of the polymer network. During the first stage, at 130°C, the solvent will be vaporized at the surface of specimen as well as through the pore channels. During the second stage, once soluble component of the green body is evaporated and/or decomposed, the binder will be burned off and pore channels will allow to transport of pyrolysis products. However, very fast heating rates cause thermal expansion and delamination of the parts. This deformation may result in the damage of the mechanical properties. For this reason, the most critical step is the removal of the binder from green body when temperatures range between 90 and 300°C.

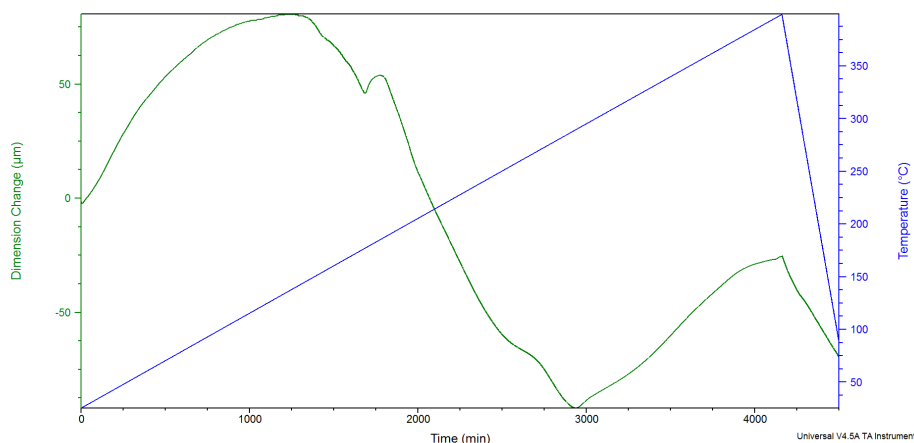


Figure 38: TMA result for TCP without pre-milling process

Exemplary TMA results can be seen in Figures 38 and 39. Figure 38 depicts a debinding profile of TCP* (without pre-milling process) with a heating rate of 0.16°C/min to 400°C and cooling rate of 0.92°C/min. TMA curve shows only 0.01 % expansion until 130°C. The reason is thermal expansion by the solvent evaporation. Temperature increase causes the thermal expansion and occurs slightly. After evaporation of the solvent, during the relaxation due to the weight and volume loss, the shrinkage starts at relatively low temperatures between

130 and 150°C as shown in the left side of the figure.

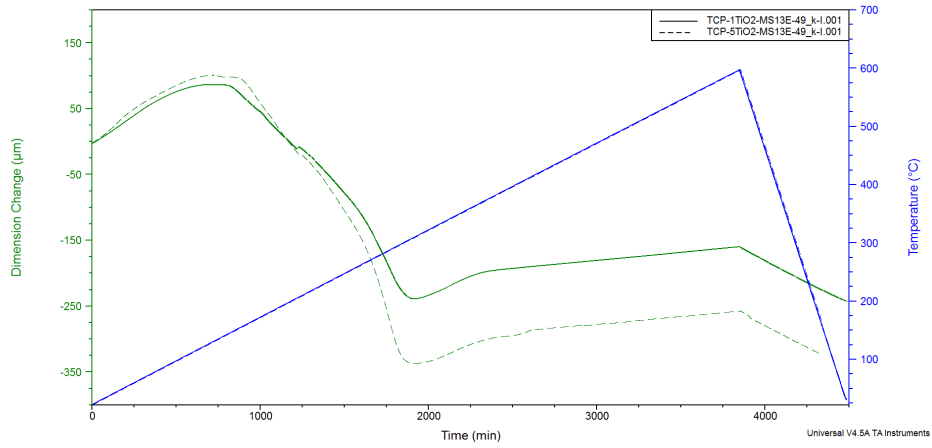


Figure 39: TMA result for TCP-TiO₂-1 (straight line) and TCP-TiO₂-5 (dashed line)

To further investigate the behavior of the binder system at high temperatures, TMA experiments were performed for TCP-TiO₂-1 and TCP-TiO₂-5. In this work, TiO₂ was the only single dopant at two different concentrations. Therefore, TCP-TiO₂-1 and TCP-TiO₂-5 were analysed, in order to determine the influence of low and high concentrations on thermal behavior. The same temperature profile, with the heating rate of 0.16°C/min and the cooling rate of 0.92°C/min, was used to get rid of the polymer network. The thermal behavior for the green parts based on TiO₂ were almost the same. Figure 39 shows that the TMA result for TCP-TiO₂-1 and TCP-TiO₂-5. Due to the reason of the a slight temperature increase, both TMA curves show 0.01 % expansion until 130°C. During the heating to 600°C, the dimension change of TCP-TiO₂-5 (dashed line) is more than TCP-TiO₂-1 (straight line). The overall shrinkages of TCP ceramics with titanium dioxide are about 2-2.5% at 600°C.

Consequently, the exemplary crack-free TMA cylinder can be seen in Figure 40 after the TMA measurement.

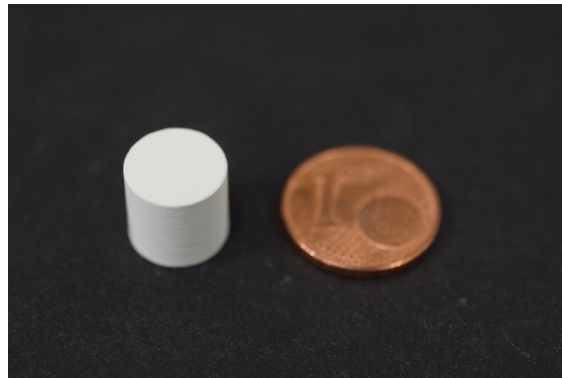


Figure 40: TCP-TiO₂-1 crack-free test cylinder after TMA measurement

5.4 Density Measurements

In order to determine the influence of dopants on the relative density, density measurements were performed by using the Archimedes method. Despite the high densification results regarding biomaterials, the bioresorbable ceramics shall exhibit a certain level of micro- and macroporosity. Nevertheless, the achieved densification of ceramic is the confirmation of microporosity. For that reason, only sintered ceramics were measured for this work. The test geometry had 10 mm in diameter with a height of 10 mm (see Table 10 on page 49). Every layer was cured for 2.88 seconds at the intensity of 41.7 mW/cm^2 .

Figures from 41 to 44 depict the results of the density measurements. The samples were obtained from the reference TCP slurry, without dopant and without pre-milling process. The sintering temperature varied from 1150 to 1250°C with the sintering time from 1 to 2 hours.

a) Pure TCP

As it can be seen in Figure 41a, with the aid of the pre-milling process, the density of tricalcium phosphate ceramics was increased nearly by 14 %. Unlike at low temperatures, sintering at 1250°C for longer dwelling times did not help to increase the value of density. Figure 41a depicts that there is about 2 % difference.

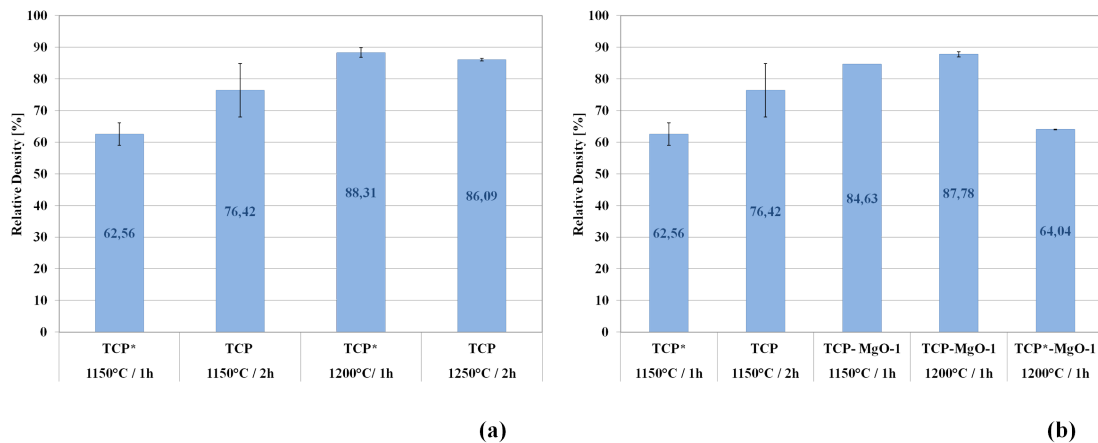


Figure 41: (a) Theoretical density of standart TCP versus pre-milled TCP sintered ceramics, (b) Theoretical density of standart TCP versus TCP-MgO-1 sintered ceramics

b) Single Dopant System

Figure 41b shows the density measurements of TCP ceramics with MgO. As depicted, TCP*-MgO-1 has almost the same theoretical density with pure TCP*. If the slurry was prepared without pre-milling process, the ceramic parts tend to less dense. Probably, the reason

was the neck formation. The loss of neck areas between particles leads to gain growth. In comparison with TCP-MgO-1, TCP*-MgO-1 has a lower density of 64 % of the theoretical density (T.D.), as expected. In addition to that, no increase on density was observed after adding MgO for higher sintering temperatures at 1200°C.

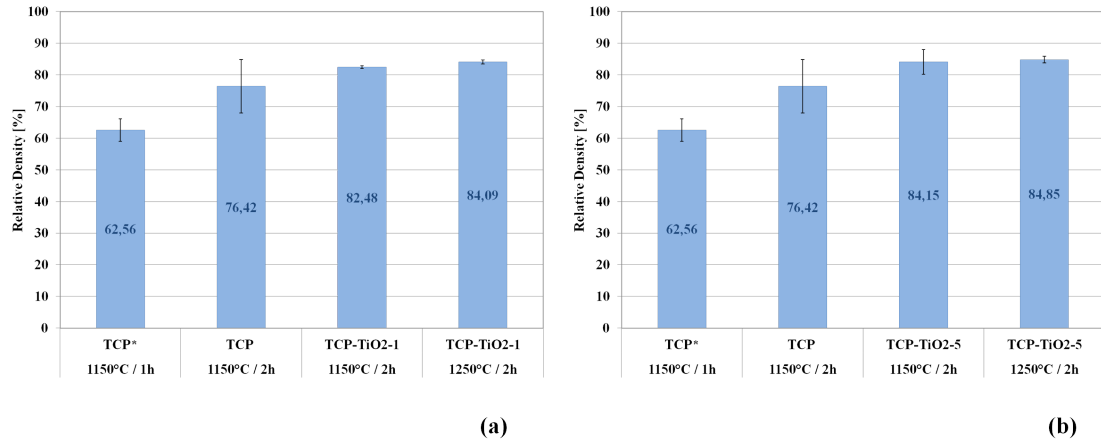


Figure 42: (a) Theoretical density of standart TCP versus TCP-TiO₂-1 sintered ceramics, (b) Theoretical density of standart TCP versus TCP-TiO₂-5 sintered ceramics

Figure 42a and 42b depict the density measurements of TCP-TiO₂-1 and TCP-TiO₂-5, respectively. According to these results, there are no significant changes after adding a high amount of titanium dioxide. The low sintering temperature at 1150°C for two hours effects the density not in a positive manner and nearly 2 % difference was obtained.

The addition of zinc oxide (Fig. 43a) and silicon dioxide (Fig. 43b) led to the same behavior as TiO₂, both at high and low temperatures. However, the standard deviation depicts more accurate results for zinc oxide and silicon dioxide dopants.

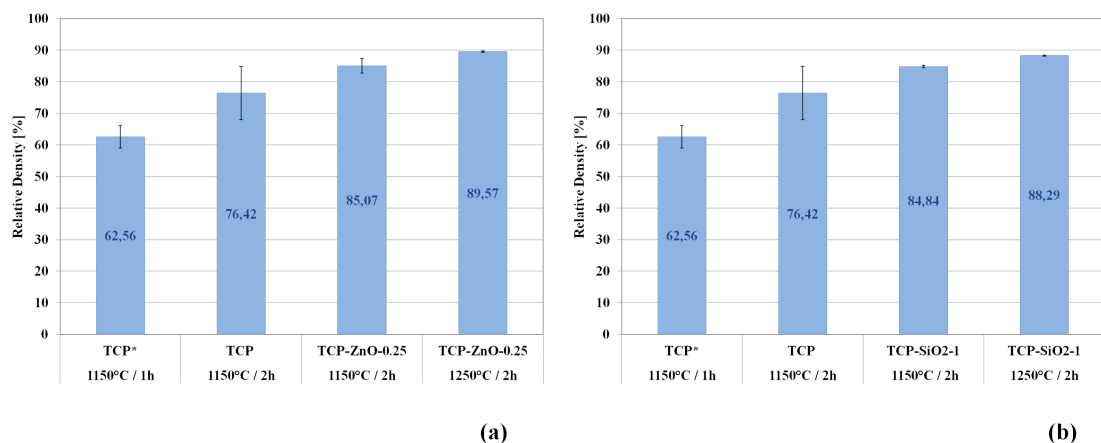


Figure 43: (a) Theoretical density measurements of standart TCP versus TCP-ZnO-0.25 sintered ceramics, (b) Theoretical density of standart TCP versus TCP-SiO₂-1 sintered ceramics

c) Binary Dopant System

In this study, the highest measured density belonged to the mixture with TCP-MgO-ZnO-1-0.25. The sintering of TCP ceramics of the dopant mixture at high temperature probably helps the particles to decrease in porosity. There was a significant increase in the densification. The 94.96 % was the highest obtained density for this research and can be seen in Figure 44a.

d) Ternary Dopant System

TCP ceramics with ternary dopants system (MgO-ZnO-TiO₂) demonstrated a negative effect on densification. The lowest densification was recorded for the ternary system at 1150°C with 59 % (Fig. 44b). The reason can be low sintering temperature. Considering the densification at 1250°C, series of tests for densification can be done to clarify between 1150°C and 1250°C.

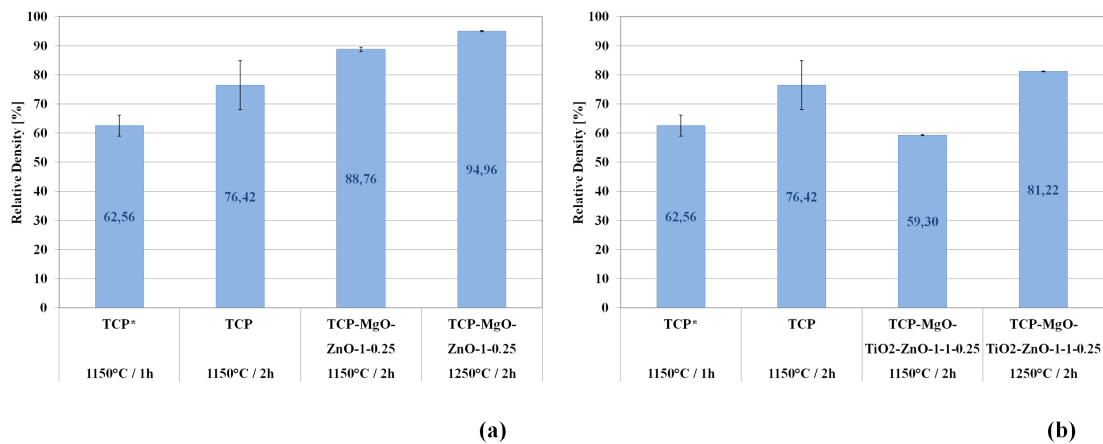


Figure 44: (a) Theoretical density of standart TCP versus TCP-MgO-ZnO-1-0.25 sintered ceramics, (b) Theoretical density of standart TCP versus TCP-MgO-TiO₂-ZnO-1-1-0.25 sintered ceramics

Table 21: Theoretical density measurements of sintered ceramics

Material	Sintering temp./ Dwelling times	Density [g/cm³]	Relative density [%]	Standard deviation
TCP*	1150°C/ 1h	2.0	62.6	3.6
TCP*	1200°C/ 1h	2.8	88.3	1.5
TCP	1150°C/ 2h	2.4	76.4	8.4
TCP	1250°C/ 2h	2.7	86.1	0.4
TCP-MgO-1	1150°C/ 1h	2.7	84.6	0.1
TCP-MgO-1	1200°C/ 1h	2.8	87.8	0.8
TCP*-MgO-1	1200°C/ 1h	2.0	64.0	0.1
TCP-SiO ₂ -1	1150°C/ 2h	2.7	84.8	0.4
TCP-SiO ₂ -1	1250°C/ 2h	2.8	88.3	0.2
TCP-TiO ₂ -1	1150°C/ 2h	2.6	82.5	0.4
TCP-TiO ₂ -1	1250°C/ 2h	2.7	84.1	0.7
TCP-TiO ₂ -5	1150°C/ 2h	2.7	84.2	3.9
TCP-TiO ₂ -5	1250°C/ 2h	2.7	84.9	1.1
TCP-ZnO-0.25	1150°C/ 2h	2.7	85.1	2.4
TCP-ZnO-0.25	1250°C/ 2h	2.8	89.6	0.2
TCP-MgO-ZnO-1-0.25	1150°C/ 2h	2.8	88.8	0.8
TCP-MgO-ZnO-1-0.25	1250°C/ 2h	3.0	95.0	0.2
TCP-MgO-TiO ₂ -ZnO-1-1-0.25	1150°C/ 2h	1.9	59.3	0.2
TCP-MgO-TiO ₂ -ZnO-1-1-0.25	1250°C/ 2h	2.6	81.2	0.1

* without pre-milling process

The densities of the sintered ceramics were calculated according to the Archimedean principle. The measured densities, with the respective relative densities and standard deviations can be seen in Table 21.

5.5 Mechanical Characterization

To indicate the influence of dopants on the flexural strength, three-point bending tests were performed. Felzmann and her colleagues have reported that the test bars were printed in different directions, they have exhibited anisotropic mechanical strength in the applied layer[60]. In this work, all specimens were manufactured in an orientation which is perpendicular to the direction of the applied load during 3PB (Fig. 45). As a result of the layer by layer structure, the direction was the weakest possible direction in this work.

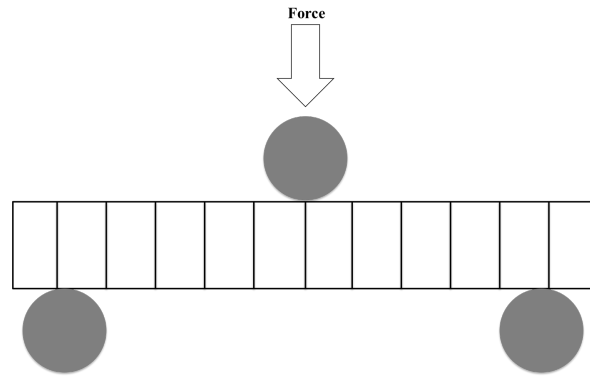


Figure 45: The orientation of the individual layers for 3PB

Mechanical properties of pure TCP ceramics and TCP ceramics with various dopant combinations were evaluated. Three-point bending machine was used for this aim, test bars with length of 25 mm, width of 2 mm and height of 2.5 mm were used (see Table 11 on page 49). Sintered ceramics with TCP-MgO-1, TCP-ZnO-0.25, TCP-TiO₂-1, TCP-SiO₂-1, TCP-TiO₂-5 were tested for their strength and compared with pure TCP ceramics with and without pre-milling process under the same conditions. Eight samples of each variation were tested. Results of these bending tests are illustrated from Figure 46 to 48.

For better comparison, TCP* ceramics (sintering temperature at 1150°C for one hour) and TCP ceramics (sintering temperature at 1150°C for two hours) were chosen as references.

In Figure 46a, the pure TCP ceramics are depicted. The highest mechanical strength was recorded for the pure TCP ceramics with pre-milling process at 1250°C. The strength was increased from 19 MPa to 33 MPa, when the sintering temperature was performed at 1250°C instead of at 1150°C.

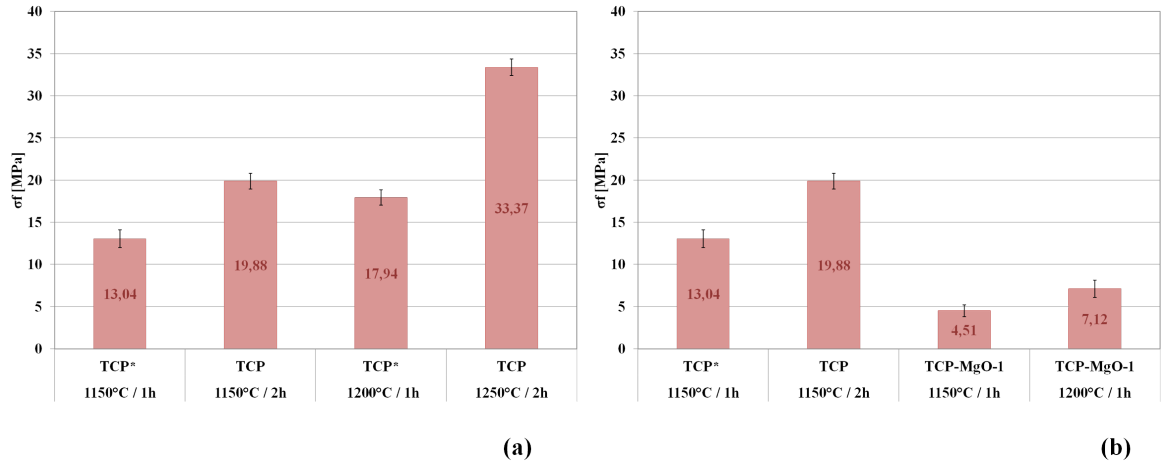


Figure 46: (a) Mechanical properties of standart TCP versus pre-milled TCP sintered ceramics, (b) Mechanical properties of standart TCP versus TCP-MgO-1 sintered ceramics

Unlike pure TCP ceramics, TCP-MgO-1 ceramics have decreased their strength from 13 MPa to 4 MPa at 1150°C as can be seen in Figure 46b. In addition to magnesium oxide, the effect of zinc oxide on mechanical strength was negative. There was an observable decrease in mechanical strength for the test bars to 6 MPa as shown in Figure 47a. In TCP doped with ZnO, due to the interactions of Zn-O and Ca-O bonds, ZnO may hinder the stabilization of TCP and thus may decrease its mechanical strength.

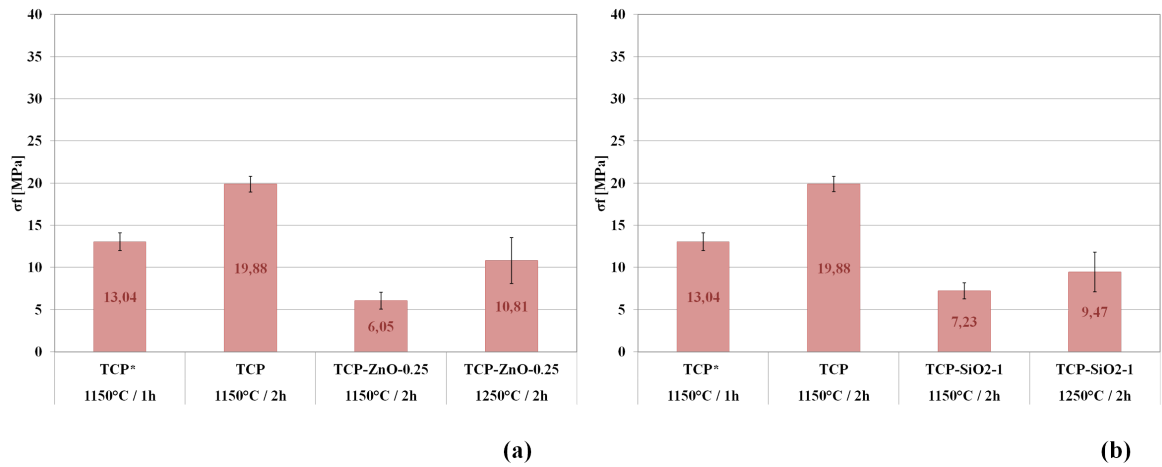


Figure 47: (a) Mechanical properties of standart TCP versus TCP-ZnO-0.25 sintered ceramics, (b) Mechanical properties of standart TCP versus TCP-SiO₂-1 sintered ceramics

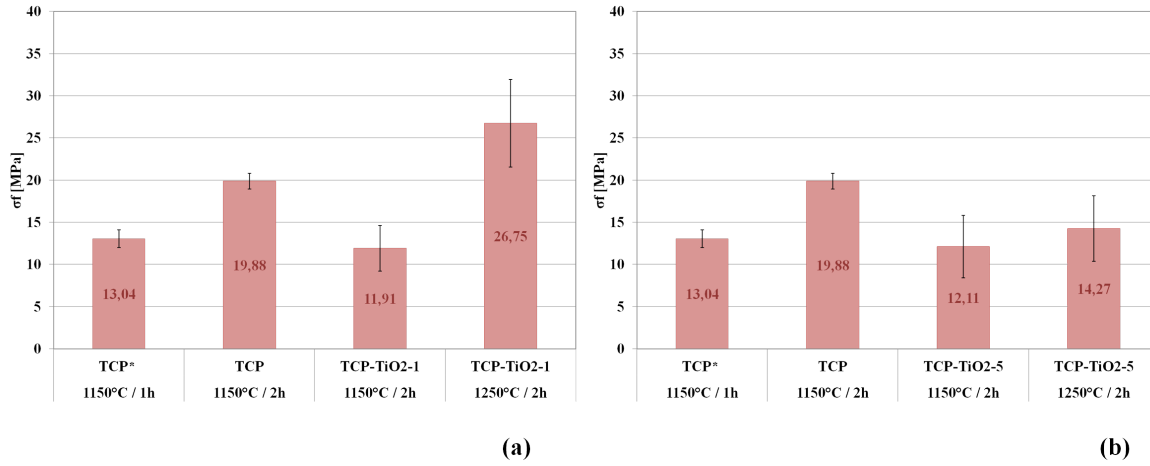


Figure 48: (a) Mechanical properties of standart TCP versus TCP + 1 % TiO₂ sintered ceramics, (b) Mechanical properties of standart TCP versus TCP + 5 % TiO₂ sintered ceramics

In this work, titanium dioxide was used in two different varitions, which were 1 % and 5 %, Figure 48a and 48b are the relevant depictions. Besides the pure TCP ceramics, TCP ceramics with addition of 1 % titanium dioxide had a positive effect at 1250°C, as shown in Figure 48a. However, the standard deviation was also noticeably high. On the contrary, TCP ceramics with 5 % TiO₂ exhibited decreased mechanical strength from 26 to 14 MPa, as depicted in Figure 48b.

Consequently, the highest bending strength was recorded 33.4 MPa for the pure TCP ceramics at 1250°C. Additionally, the second highest bending strength was 26.8 MPa for the TCP with 1 wt% TiO₂ ceramics, which was noted as the highest bending strength for TCP + metal oxide systems.

Table 22: Mechanical properties of TCP ceramics

Material	Sintering temp./ Dwelling times	σ_f [MPa]	Standart deviation
TCP*	1150°C/ 1h	13.0	1.1
TCP*	1200°C/ 1h	17.9	0.9
TCP	1150°C/ 2h	19.9	0.9
TCP	1250°C/ 2h	33.4	0.9
TCP-MgO-1	1150°C/ 1h	4.5	0.7
TCP-MgO-1	1200°C/ 1h	7.1	1.0
TCP-SiO ₂ -1	1150°C/ 2h	7.2	6.3
TCP-SiO ₂ -1	1250°C/ 2h	9.5	2.4
TCP-TiO ₂ -1	1150°C/ 2h	11.9	2.7
TCP-TiO ₂ -1	1250°C/ 2h	26.8	5.2
TCP-TiO ₂ -5	1150°C/ 2h	12.1	3.7
TCP-TiO ₂ -5	1250°C/ 2h	14.3	3.9
TCP-ZnO-0.25	1150°C/ 2h	6.1	0.9
TCP-ZnO-0.25	1250°C/ 2h	10.8	2.7

* without pre-milling process

The summary of the mechanical strength of TCP ceramics with various dopant combinations can be seen in Table 22.

5.6 Microstructural Analysis

Powder

In order to examine the particle size distributions of the powders, SEM scans were performed. SEM images were made in different magnifications for the following powders: TCP powders before and after pre-milling process, the used pure metal oxide dopant powders and the used TCP powders with different metal oxide. The powders were glued onto the sample holder and the images were taken by SEM.

In this study, four different metal oxide powders were used as dopants. These were MgO, ZnO, TiO₂ and SiO₂. The metal oxides powder particles show regular particle size distributions except for the SiO₂ dopant (Fig. 49). Figure 49d is the SEM image of silicon dioxide. As it can be seen from the micrographs, the powder particles are very irregular. The particle sizes are in the range between 3 to 5 μm with a small number of larger particles of 15 to 20 μm .

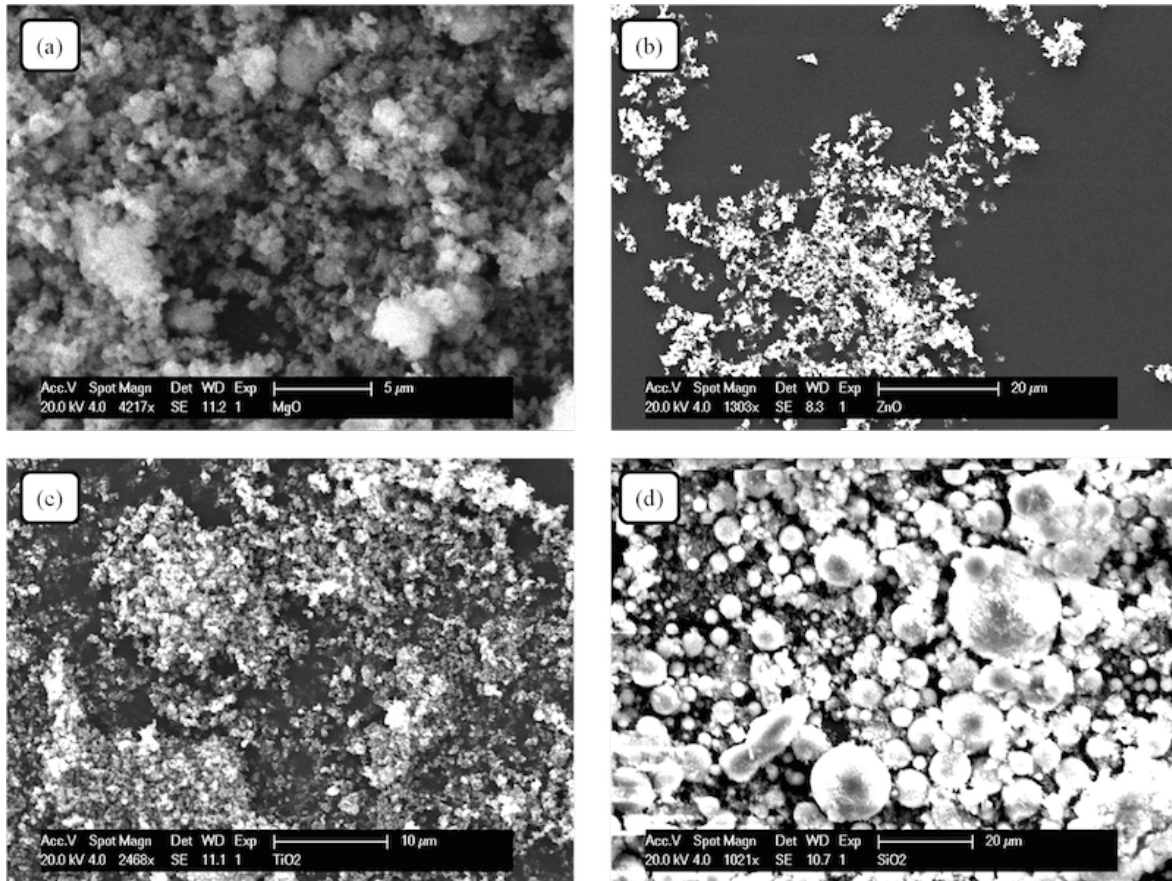


Figure 49: SEM micrographs of the metal oxide dopants in different magnifications: (a) MgO, (b) ZnO, (c) TiO₂, (d) SiO₂

Figure 50 shows SEM images of the tricalcium phosphate powder. The powder particles show irregular particles sizes and the majority of the particles is about 2 to 5 μm with a few particles of about 10 to 15 μm . After pre-milling process, the TCP powders show a more homogeneous distribution in comparison to the powder without pre-milling.

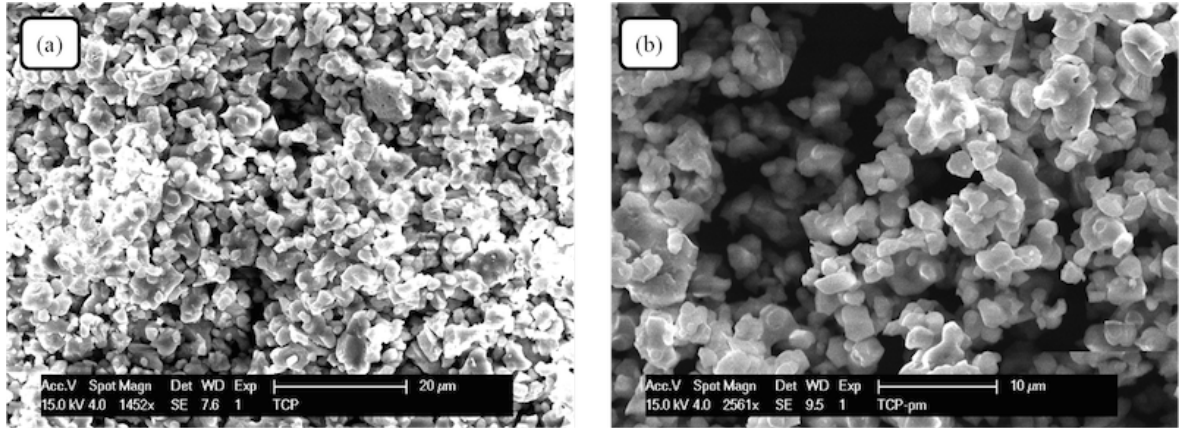


Figure 50: SEM micrographs of the tricalcium phosphate powders in different magnifications: TCP powder (a) without pre-milling process, (b) with pre-milling process

In addition to pure tricalcium phosphate and metal oxide ceramic powders, Figure 51 depicts the combination of the TCP powder with different dopants after pre-milling. The aim of pre-milling process was to hinder the agglomeration and to increase the homogeneity of the particles. After pre-milling process for 24 hours, the powder particles seem homogeneous in matter of particle size, as predicted (see Fig. 51). The size of the particles are about 2 to 4 μm .

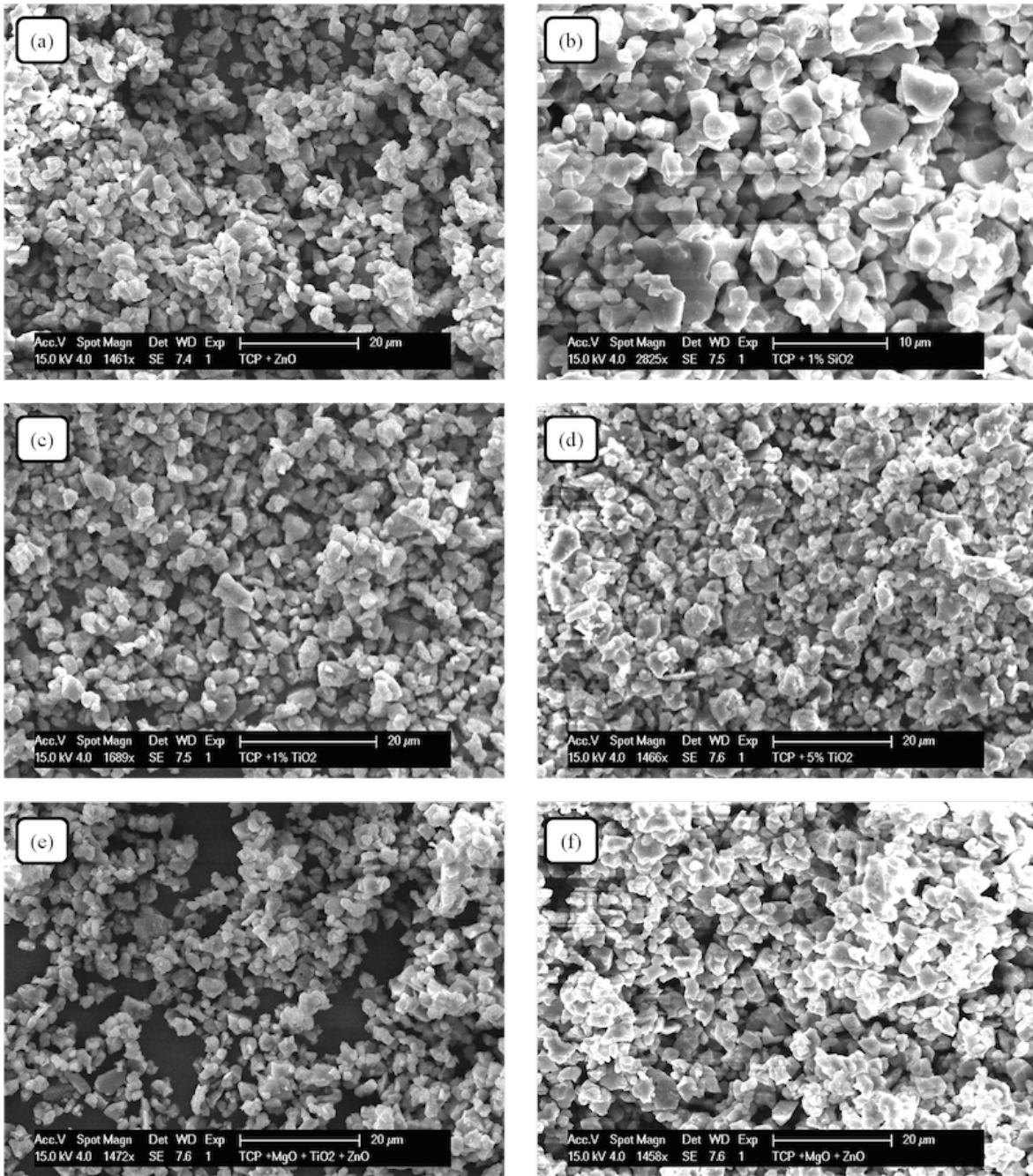


Figure 51: SEM micrographs of TCP powders with different metal oxide dopants in different magnifications: TCP powders with (a) TCP-ZnO-0.25, (b) TCP-SiO₂-1, (c) TCP-TiO₂-1, (d) TCP-TiO₂-5, (e) TCP-MgO-TiO₂-ZnO-1-1-0.25, (f) TCP-MgO-ZnO-1-0.25

Fractography

To investigate the fractography and to observe morphology and microporosity in the interior of the samples, SEM scans were performed. For this reason, SEM images were taken after test bars were broken in the 3PB test. First of all, all specimens were glued onto the SEM sample holder. As a second step, gold particles were sputtered onto the samples for ordinary SEM imaging. Lastly, the SEM micrographs were taken for all specimens.

SEM micrographs illustrate the surface of the fracture. Surfaces are shown from Figure 52 to Figure 56. The fracture surfaces resemble each other morphologically when the theoretical density is similar. The mean value of micropores differ from 3 to 6 μm . The values depend on the relative density. The homogeneous micropore distribution is reflected in the mechanical properties.

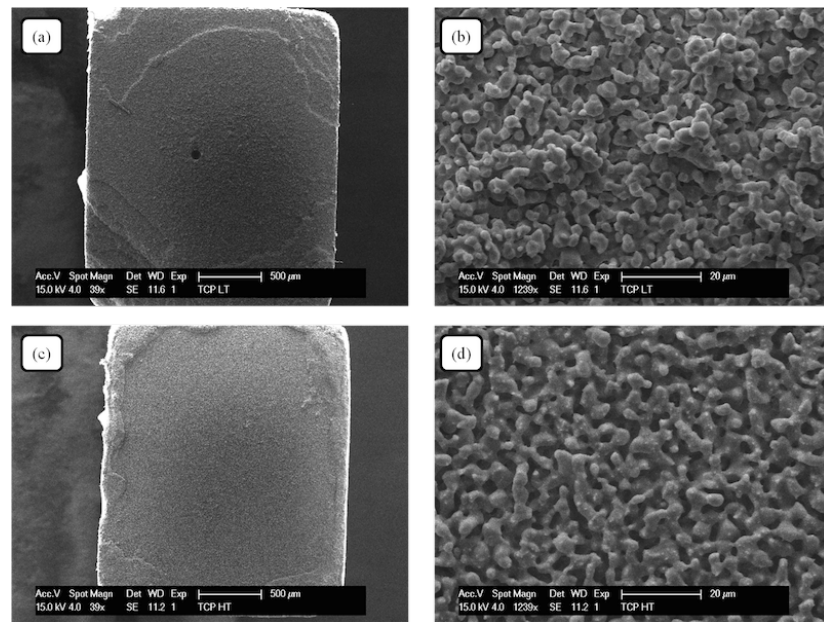


Figure 52: SEM micrographs of the 3PB fracture surface microstructures of standard TCP* ceramics, sintering temperature at 1150°C (Fig. (a) and (b)) for 1 hour (62.6 % of T.D.) and at 1200°C (Fig. (c) and (d)) for 1 hour (88.3 % of T.D.) in different magnifications

In Figure 52, test bars of the pure TCP ceramic without pre-milling process are depicted. As it can be seen in Figure 52a and 52b, the test bars were sintered at two different temperatures, 1150°C and 1200°C, respectively. In Figure 52d, with the temperature changes to 1200°C neck formation areas also increase. Therefore, the relative density at high sintering temperature is greater than the relative density at low sintering temperature. Additionally, the micropore sizes are approximately 6 μm in Figure 52b, and 4 μm in Figure 52d.

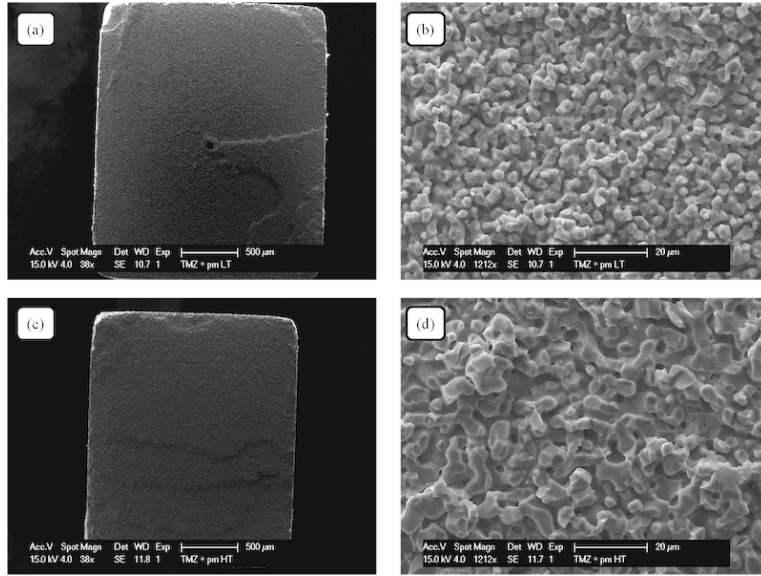


Figure 53: SEM micrographs of the 3PB fracture surface microstructures of TCP ceramics, sintering temperature at 1150°C (Fig. (a) and (b)) for 2 hours (76.4 % of T.D.) and at 1250°C (Fig. (c) and (d)) for 2 hours (86.1 % of T.D.) in different magnifications

Figure 53 depicts the SEM micrographs of pure TCP ceramic. At high sintering temperature, TCP and TCP* ceramics have similar relative densities, 88.3 % and 86.1 %, respectively. However, the bending strength of TCP* (17.9 MPa) is greater than the bending strength of TCP. This increase can be explained by increased neck and grain growth in the microstructure that can be seen in Figure 53d.

Figure 54 depicts the SEM micrographs of TCP-MgO-1 ceramics. The fracture surface of test bars shows smooth gradient on the corner, however, the rest fracture surface microstructures have flat surfaces (see Figure 54c). Microcracks can be the possible reason for this type of surfaces. These may decrease the mechanical strength to 4.5 and 7.1 MPa at low and high sintering temperatures, respectively. As predicted, the size of micropores changed nearly from 5 to 3 μm because of the higher sintering temperatures (see Figure 54b and 54d).

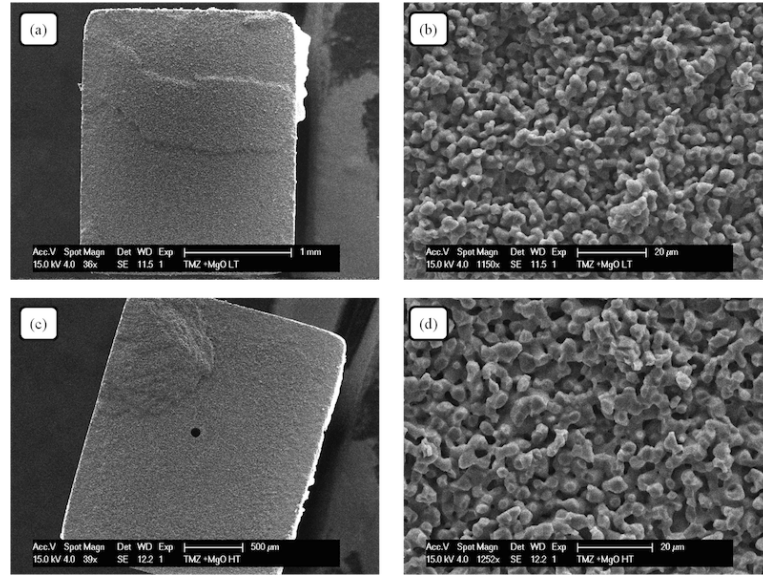


Figure 54: SEM micrographs of the 3PB fracture surface microstructures of TCP-MgO-1 ceramics, sintering temperature at 1150°C (Fig. (a) and (b)) for 1 hour (84.6 % of T.D.) and at 1200°C (Fig. (c) and (d)) for 1 hour (87.8 % of T.D.) in different magnifications

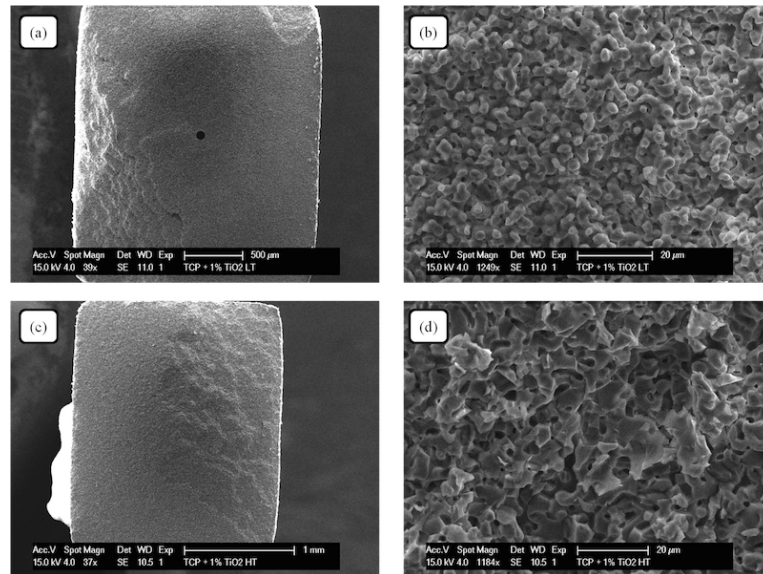


Figure 55: SEM micrographs of the 3PB fracture surface microstructures of TCP-TiO₂-1 ceramics, sintering temperature at 1150°C (Fig. (a) and (b)) for 2 hours (82.5 % of T.D.) and at 1250°C (Fig. (c) and (d)) for 2 hours (84.1 % of T.D.) in different magnifications

After three-point bending test, fractography of TCP-TiO₂-1 shows a smooth surface. The relative densities of TCP ceramics with TiO₂-1 dopants show similar porosity of 15 % as TCP ceramics. Nevertheless, the bending strength is lower than pure TCP ceramics. As depicted in Figure 55d, the increased neck and grain growth may lead to better mechanical strength than TCP-MgO-1 which do not show same microstructure. The micropore sizes seem almost

the same. However, the higher sintering temperature lead to deformation in microporosity (see Fig. 55).

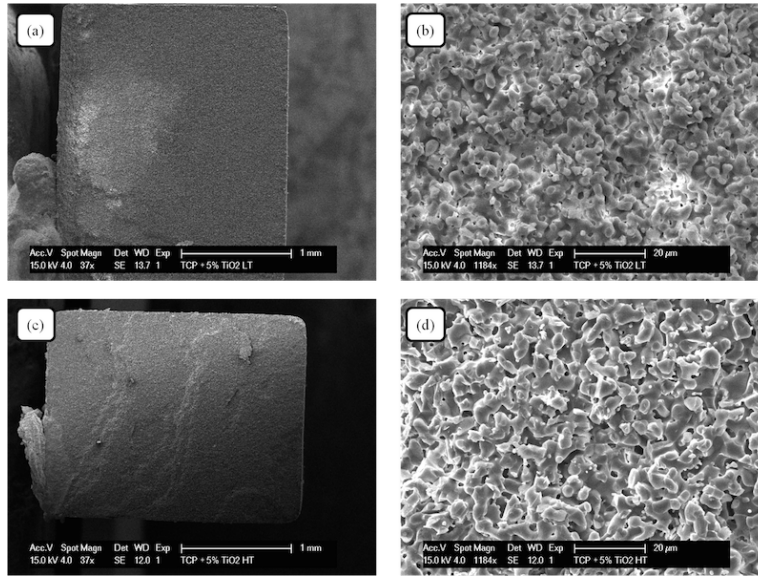


Figure 56: SEM micrographs of the 3PB fracture surface microstructures of TCP-TiO₂-5 ceramics, sintering temperature at 1150°C (Fig. (a) and (b)) for 2 hours (84.2 % of T.D.) and at 1250°C (Fig. (c) and (d)) for 2 hours (84.9 % of T.D.) in different magnifications

Sintering at 1150°C and at 1250°C, the depicted SEM images show same porosity in terms of sizes. The high dopant concentrations like TCP-TiO₂-5 have a negative effect on bending strength. This reason can be explained by the between interactions of Ca-O and Ti-O and thus may decrease the mechanical strength of TCP-TiO₂-5. Figure 56 depicts some particles on fracture surface which probably belongs to TiO₂ powder and may result in microcracks.

In Figure 57, the difference of TCP-ZnO-0.25 micrographs is between low sintering temperature (see Figure 57b) and high sintering temperature (see Figure 57d) is too distinctive, although the difference of relative densities is not enormous. The microphores has a more rounded shape at lower sintering temperature. As seen in Figure 57d, the size of micropores is nearly 3 μm at 1250°C.

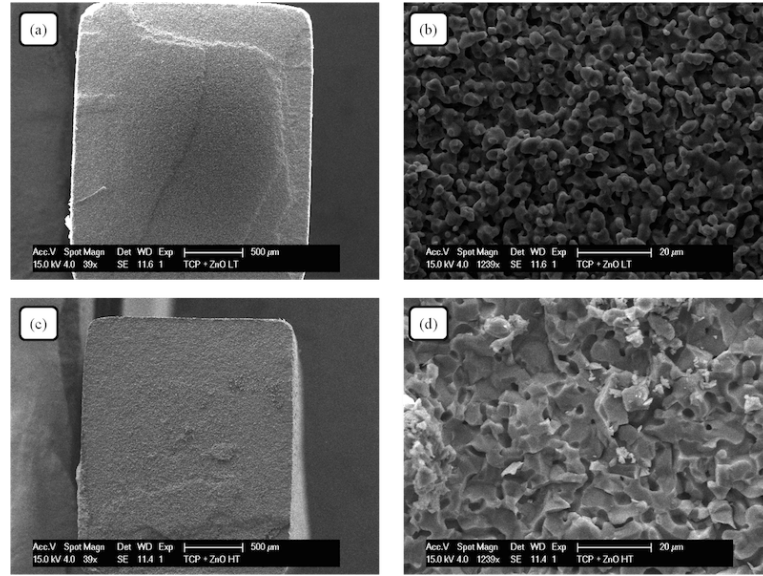


Figure 57: SEM micrographs of the 3PB fracture surface microstructures of TCP-ZnO-0.25 ceramics, sintering temperature at 1150°C (Fig. (a) and (b)) for 2 hours (85.1 % of T.D.) and at 1250°C (Fig. (c) and (d)) for 2 hours (89.6 % of T.D.) in different magnifications

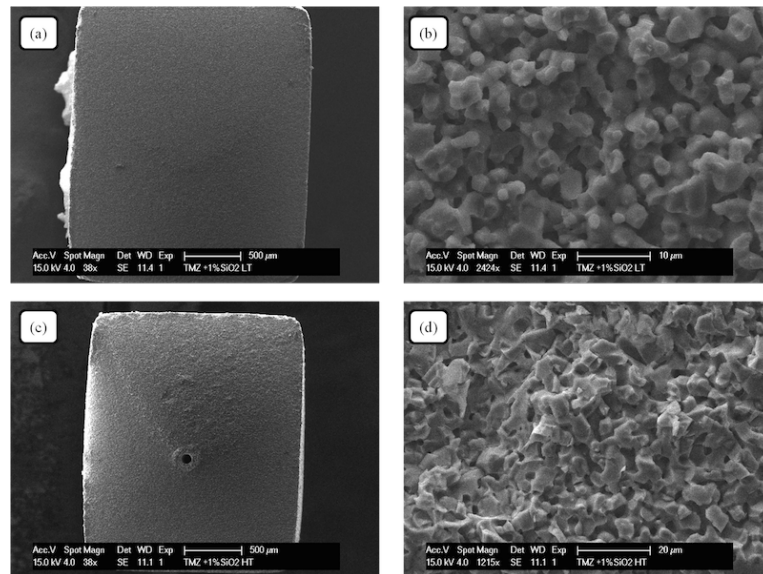


Figure 58: SEM micrographs of the 3PB fracture surface microstructures of TCP-SiO₂-1 ceramics, sintering temperature at 1150°C (Fig. (a) and (b)) for 2 hours (84.8 % of T.D.) and at 1250°C (Fig. (c) and (d)) for 2 hours (88.3 % of T.D.) in different magnifications

The TCP-SiO₂-1 behave almost same at 1150°C and 1250°C in terms of porosity and fractograph, as depicted in Figure 58. The relative density is directly proportional to bending strength.

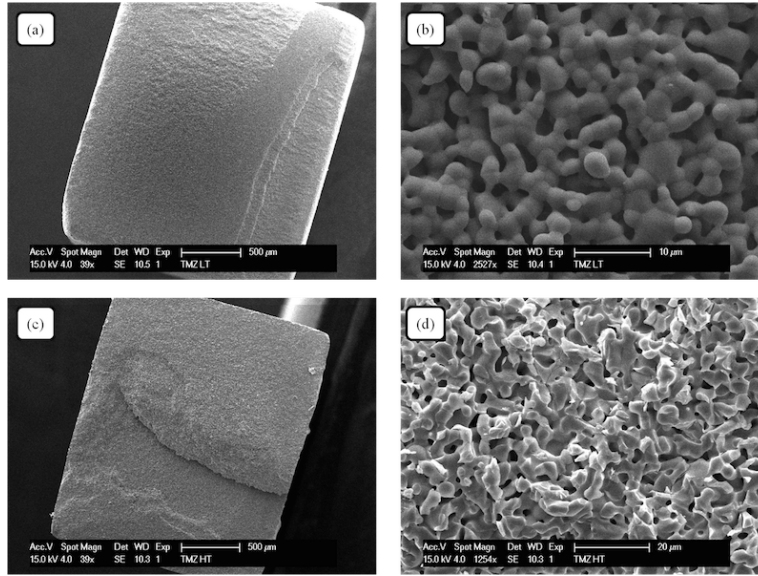


Figure 59: SEM micrographs of the 3PB fracture surface microstructures of TCP-MgO-TiO₂-ZnO-1-1-0.25 ceramics, sintering temperature at 1150°C (Fig. (a) and (b)) for 2 hours (59.3 % of T.D.) and at 1250°C (Fig. (c) and (d)) for 2 hours (81.2 % of T.D.) in different magnifications

After sintering of TCP with ternary dopants, the dense ceramic test bars are full of cracks and the depicted Figures 59a and 59c. The test bars are broken exactly from the crack formation and this can be clearly seen in Figure 59c. The reason can be explained by the interaction of metal-oxide (M-O) bonds. The M-O may decrease Ca-O interactions in TCP and thus may lower the bending strength. In terms of microporosity, the difference is quite high. The microporosity are approximately 41 % and 29 %, respectively. The size of micropores reaches the highest value of 7 μm .

Surface

To investigate further the surface quality and the microcracks of the sintered ceramics, SEM scans were also performed at different magnifications. Therefore the same test bars as used in the SEM scans for fractography, were used. However, specimens were scanned in an orientation of the applied load during 3PB, which is so-called z-direction.

Figures from 60 to 68 show the side surface of three-point bending test bars.

The layer thickness of the specimens were 25 μm and the side surface was fabricated in layers. Test structures have smooth surface generally.

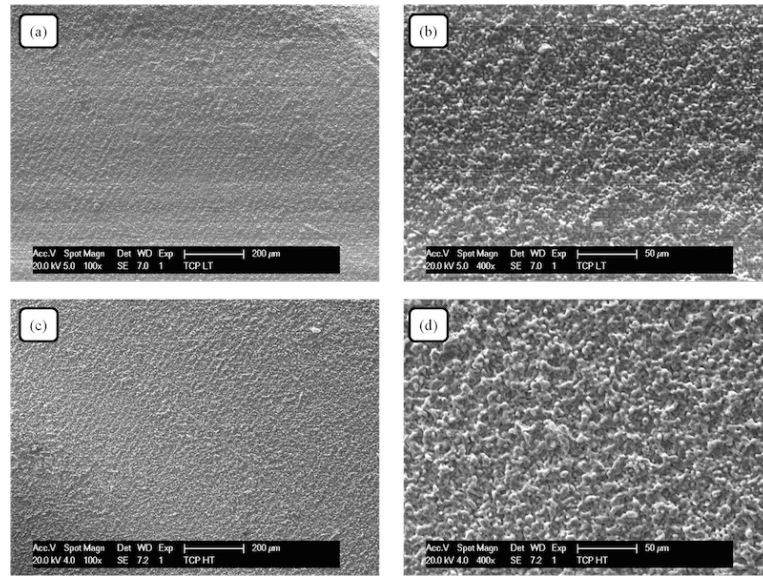


Figure 60: SEM micrographs illustrating surface microstructures of standard TCP* ceramics, sintering temperature at 1150°C (Fig. (a) and (b)) for 1 hour and at 1200°C (Fig. (c) and (d)) for 1 hour in different magnifications

Standard TCP* ceramics and pre-milled TCP ceramics show obviously same surface microstructure quality at different sintering temperatures (see Fig. 60 and 61). In these specimens there were no visible microcracks on the surfaces.

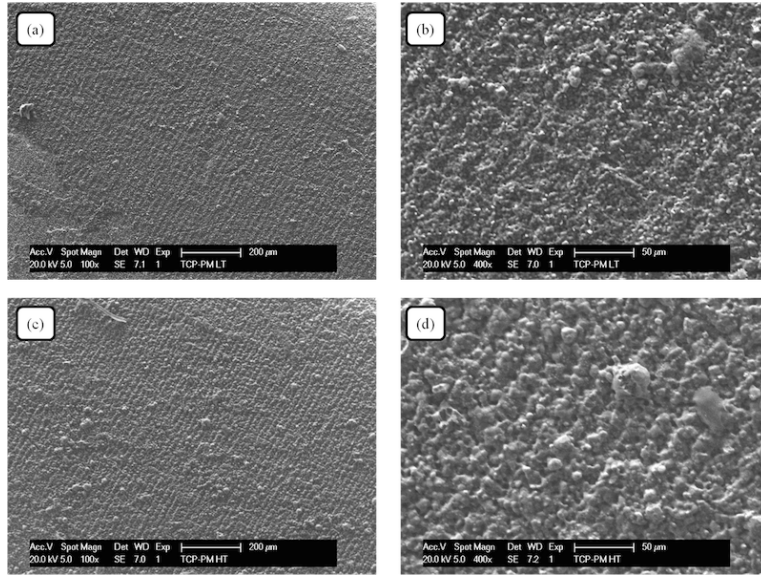


Figure 61: SEM micrographs illustrating surface microstructures of TCP ceramics, sintering temperature at 1150°C (Fig. (a) and (b)) for 2 hours and at 1250°C (Fig. (c) and (d)) for 2 hours in different magnifications

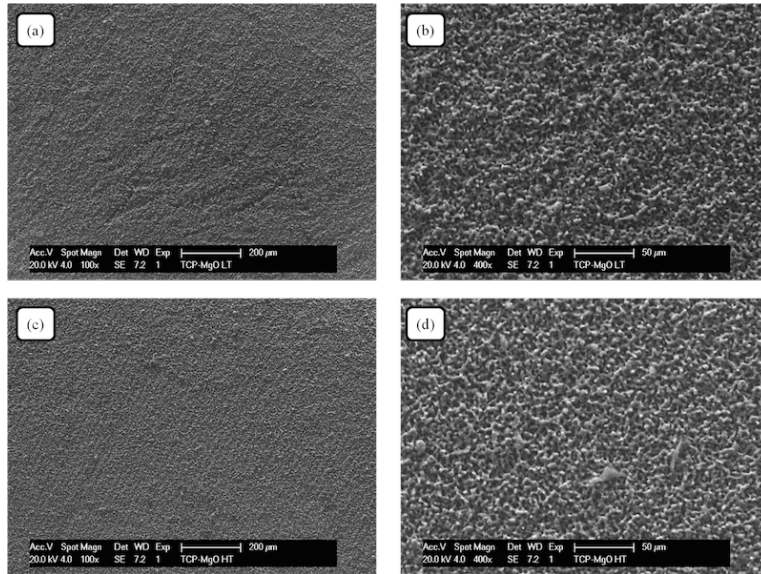


Figure 62: SEM micrographs illustrating surface microstructures of TCP-MgO-1 ceramics, sintering temperature at 1150°C (Fig. (a) and (b)) for 1 hour and at 1200°C (Fig. (c) and (d)) for 1 hour in different magnifications

TCP-MgO-1 ceramics have no noticeable sign about the layer-by-layer structuring, as depicted in Figure 62. Additionally, no visible microcracks were observed.

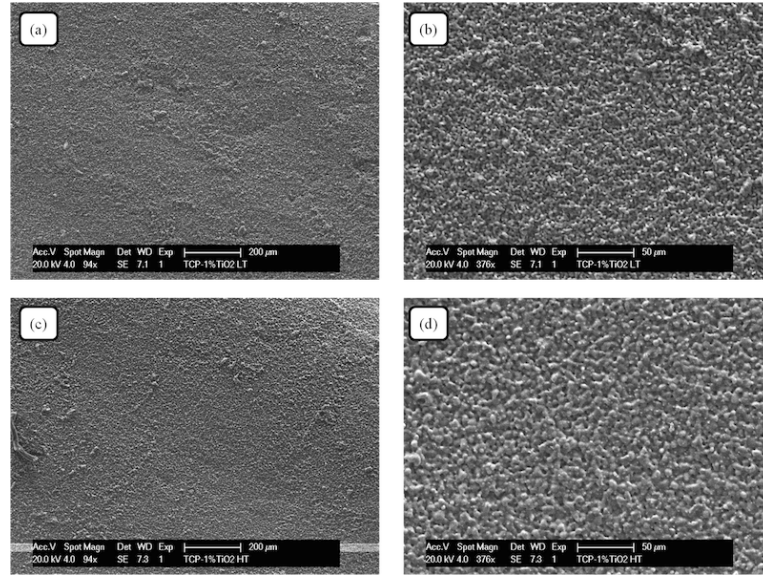


Figure 63: SEM micrographs illustrating surface microstructures of TCP-TiO₂-1 ceramics, sintering temperature at 1150°C (Fig. (a) and (b)) for 2 hours and at 1250°C (Fig. (c) and (d)) for 2 hours in different magnifications

The surface microstructures of TCP-TiO₂-1 and TCP-TiO₂-5 ceramics have no obvious difference. As it can be seen on the Figure 63 and 64, the test structures have smooth surfaces. No microcracks were visible.

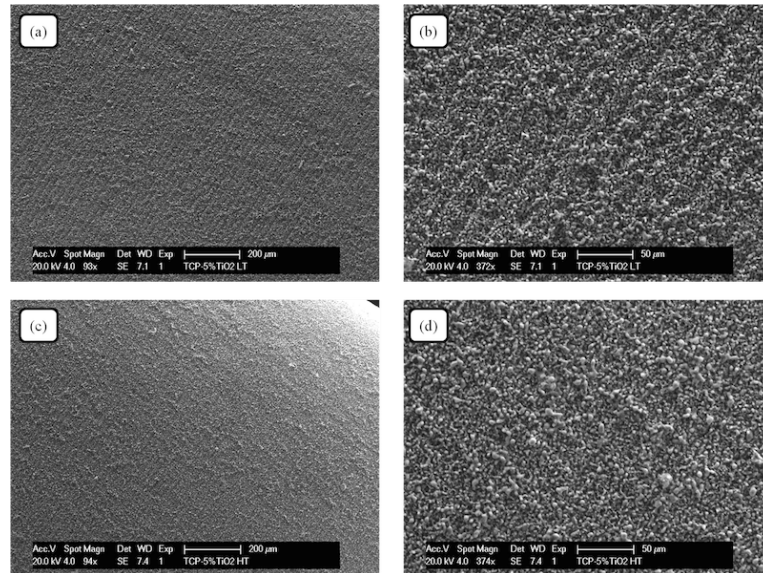


Figure 64: SEM micrographs illustrating surface microstructures of TCP-TiO₂-5 ceramics, sintering temperature at 1150°C (Fig. (a) and (b)) for 2 hours and at 1250°C (Fig. (c) and (d)) for 2 hours in different magnifications

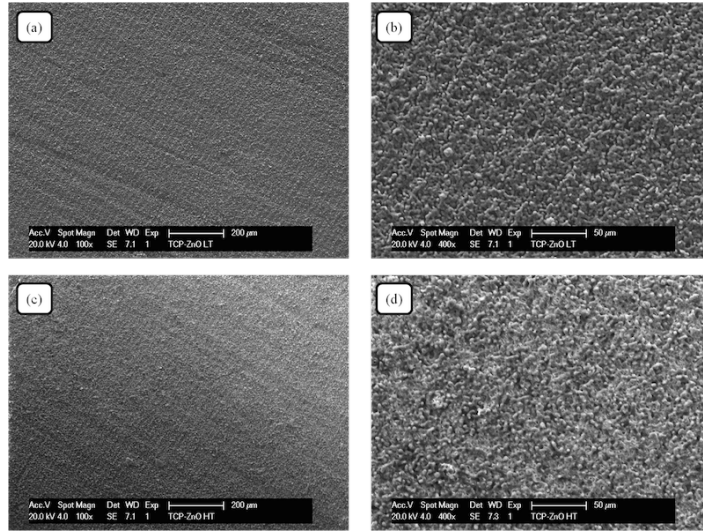


Figure 65: SEM micrographs illustrating surface microstructures of TCP-ZnO-0.25 ceramics, sintering temperature at 1150°C (Fig. (a) and (b)) for 2 hours and at 1250°C (Fig. (c) and (d)) for 2 hours in different magnifications

The addition of ZnO-0.25 in TCP is negligible in terms of surface microstructure. As seen in Figure 65, the microstructure seems like the TCP ceramics without dopants. TCP-ZnO-0.25 ceramics have no visible microcracks on the surface.

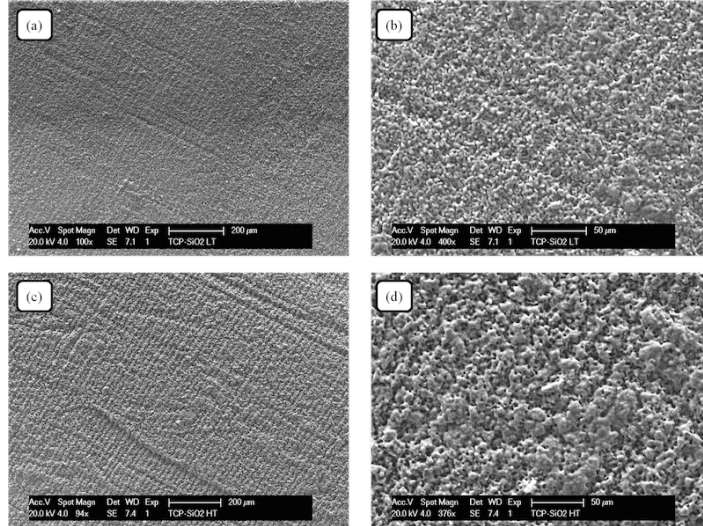


Figure 66: SEM micrographs illustrating surface microstructures of TCP-SiO₂-1 ceramics, sintering temperature at 1150°C (Fig. (a) and (b)) for 2 hours and at 1250°C (Fig. (c) and (d)) for 2 hours in different magnifications

TCP-SiO₂-1 ceramics have also show same surface microstructure quality at low and high sintering temperatures. There is no distinctive sign about the layer-by-layer manufacturing (see Fig. 66).

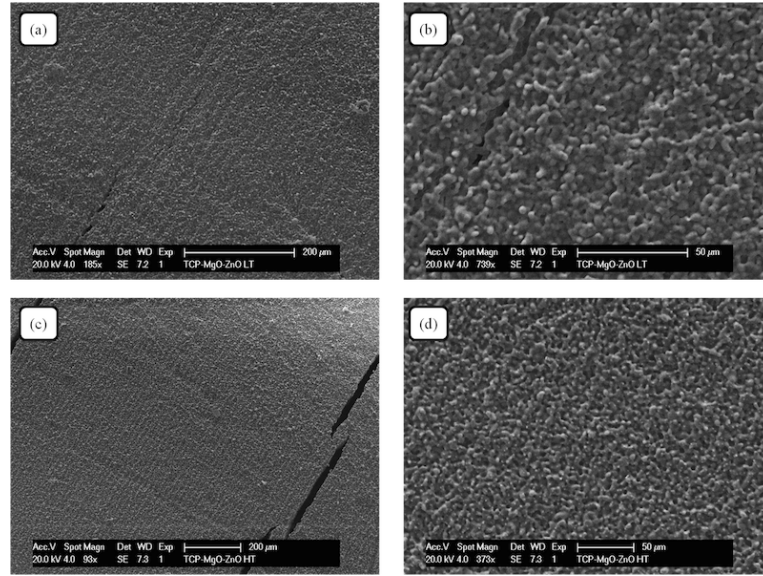


Figure 67: SEM micrographs illustrating surface microstructures of TCP-MgO-ZnO-1-0.25 ceramics, sintering temperature at 1150°C (Fig. (a) and (b)) for 2 hours and at 1250°C (Fig. (c) and (d)) for 2 hours in different magnifications

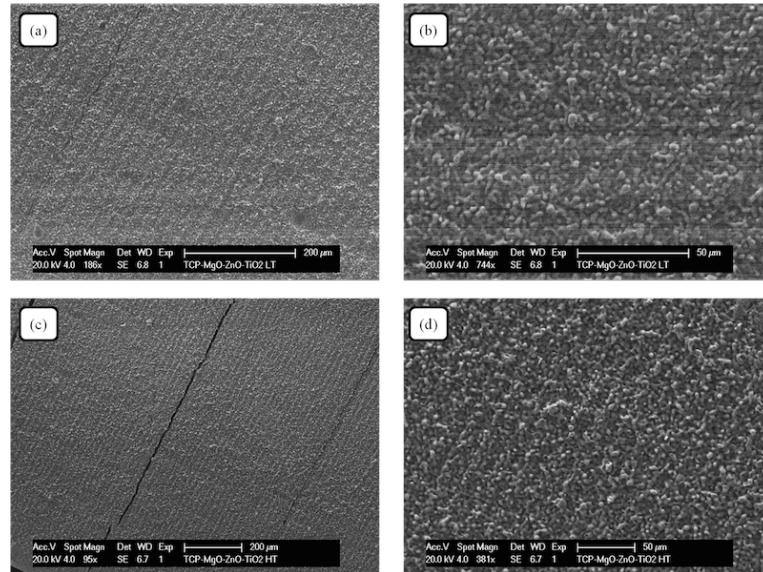


Figure 68: SEM micrographs illustrating surface microstructures of TCP-TiO₂-MgO-ZnO-1-1-0.25 ceramics, sintering temperature at 1150°C (Fig. (a) and (b)) for 2 hours and at 1250°C (Fig. (c) and (d)) for 2 hours in different magnifications

Unlike single dopant systems, the binary and ternary dopant systems in TCP are full of cracks. Figure 67 and Figure 68 depict the microcracks distinctively. The reason of these microcracks can be the addition of metal oxides dopants. However, TCP ceramics with ternary dopants show also no sign about the layer-by-layer manufacturing except microcracks.

Consequently, microstructure is also tool to detect the presence of microcracks, were also

obtained on the some surfaces. As a result, the presence of microcracks lead to weakening of the bending strength of the ceramics.

5.7 Light Microscopy

Besides micropores, the presence of macropores is essential for tissue regeneration. The micropores depend on the densification of ceramics. On the contrary, macropores can be obtained by CAD data. In addition to bioresorbability, Tarafder et al. have also researched the effects of macropores on mechanical strength. For this purpose, they have printed three different macropore sizes that are 500, 750 and 1000 μm , respectively. As a result, maximum compressive strength of 12.01 ± 1.56 MPa was achieved for 500 μm pore size[110].

In order to examine the parts for cracks and to determine the macropore sizes of scaffolds after thermal treatment at different temperatures and different dwelling times, light microscope was used. Two different designs for TCP ceramics with 5 wt% dopants were chosen in term of macroporosity. The following images show exemplary scaffolds in green state (Figure 69 and 71). Each of the specimens, the scaffolds I (with the macroporosity of 47 %) and the scaffolds II (with the macroporosity of 50 %), were thermally treated in two ways. The first ones were sintered at 1150°C for dwelling time 2 hours and the second ones were sintered at 1250°C for dwelling time 2 hours.

In every scaffold structure, the macropore sizes are more or less the same size in comparison to other macropores, which means the reproducibility of this scaffold is quite high and can be seen in Figure 70 and 72, respectively.

In this work, TCP-TiO₂-5 green bodies was used to analyse. According to Manjubala et al., the compressive strength has the highest value with 5 wt.% in TCP[72].

Table 23 is a summary of average macropore sizes at different sintering temperatures for different macropores in green state. As shown in Table 23, the realized macropore size was 288 μm .

Table 23: Pore sizes of the scaffolds after different sintering temperatures

Pore sizes in green state [μm]	Pore sizes after sintering 1150°C [μm]	Pore sizes after sintering 1250°C [μm]	Figure
780	614	555	70
720	509	509	
660	499	436	
600	407	422	
600	520	406	
450	378	288	72

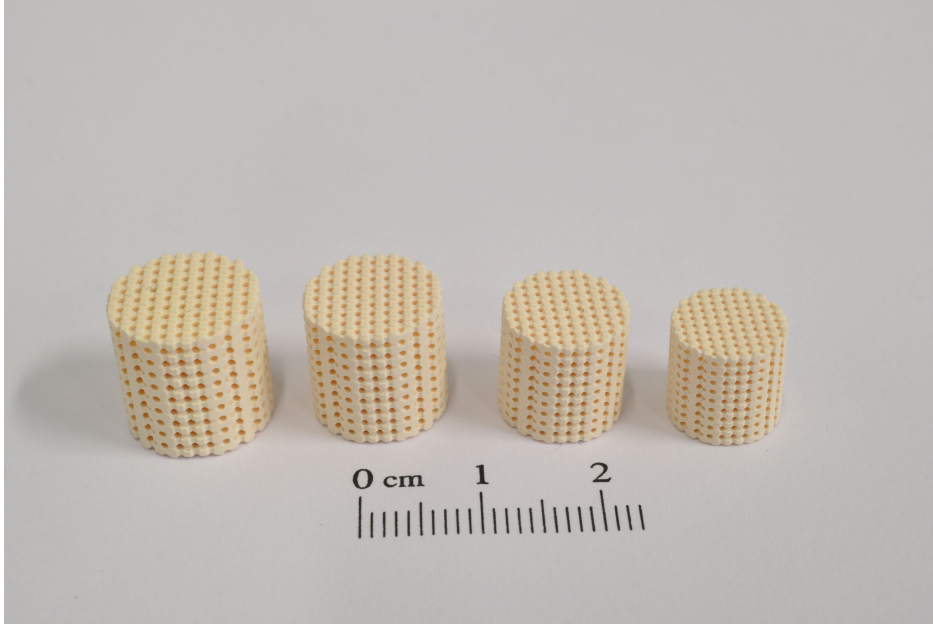


Figure 69: Green bodies of TCP-TiO₂-5: Scaffolds I

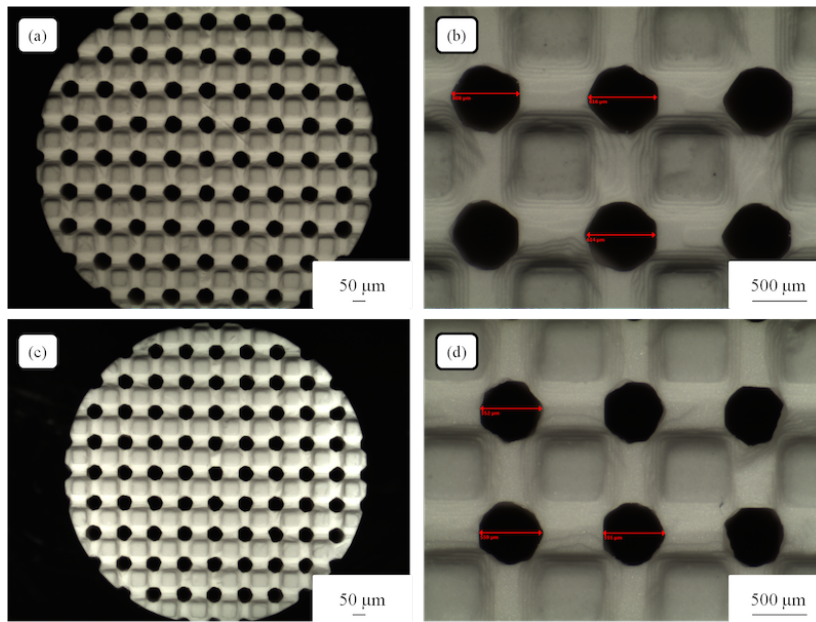


Figure 70: Light microscopy images of TCP-TiO₂-5 ceramics with 780 μm pore sizes, sintering temperature at 1150°C (Fig. (a) and (b)) and 1250°C (Fig. (c) and (d)) for 2 hours in different magnifications

Figure 70 and 72 show exemplary macropores after different sintering temperatures. These microscopy images depict the homogeneous pore structure throughout scaffolds. The sizes of macropores show that there is no over-polymerisation during the printing process. Therefore, these light microscopy images are the confirmation of the macropores uniformity.

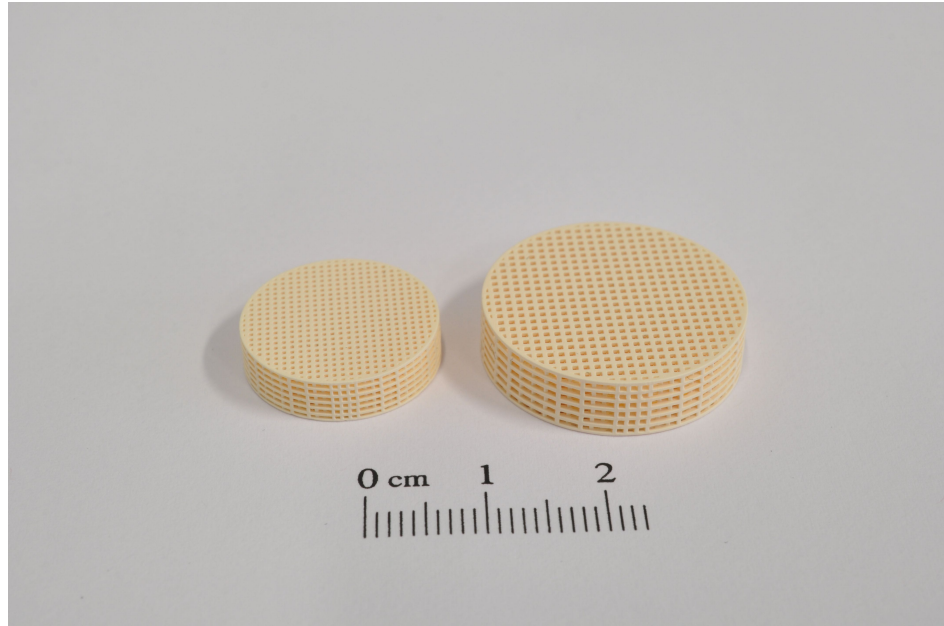


Figure 71: Green bodies of TCP-TiO₂-5: Scaffolds II

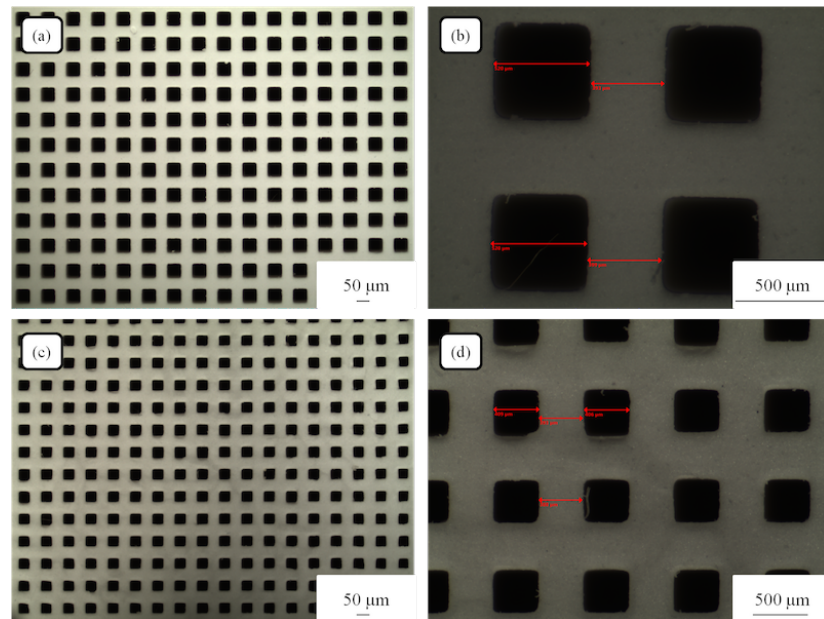


Figure 72: Light microscopy images of TCP-TiO₂-5 ceramics with 600 μm pore sizes, sintering temperature at 1150°C (Fig. (a) and (b)) and 1250°C (Fig. (c) and (d)) for 2 hours in different magnifications

6 Conclusion

The aim of this work was to increase the mechanical strength of tricalcium phosphate ceramics which are already being produced by LCM. For these reason, TCP was doped with metal oxides. Before structuring, light penetration tests were examined to investigate the cure depth. The investigation of slurry viscosities were tested by rheometry. After structuring, green bodies were examined by TMA to obtain crack-free parts. At last, the ceramic specimens were analysed towards their relative densities, microstructures and mechanical strengths.

In this work, it was shown that the processing of TCP-filled photopolymers with lithography based ceramic fabrication is possible. In preparing the green parts, a very good component quality could already be achieved. The optimization of the entire process chain allows crack-free components with defined macroporosity. Highly complex green parts, such as the skeleton, in Figure 73 can be realized.



Figure 73: Further green bodies: Skeleton

An advantage is the complexity of the printed ceramic parts as almost no geometrical limitations have to be considered during part design. This means very fine, well defined cellular or thin walled structures can be produced and the implementation of cavities and undercuts that would not be possible by any other production method can be achieved. Additionally, additive manufacturing does not require any demolding step or finishing treatment.

High porosity is desirable for the scaffolds used for bone tissue engineering due to the absorption by the human body. For these reason, density measurements were performed by using the Archimedes method. With a suitable debinding and sintering profile, a theoretical density of 94 % was achieved. The TCP-MgO-ZnO-1-0.25 ceramic has the highest theoretical density with an optimized temperature profile of 1250°C sintering temperature and a dwelling time of two hours. Unlike technical high performance ceramics, bioceramics such as TCP do not have to be fully dense. Not only microporosity but also macroporosity is the key to integration of cells and absorption by the body. The measured densities, with the respective relative densities and standard deviations can be seen in Table 21 on page 69.

The mechanical properties of ceramics depend on the three basic parameters. These are powder, shaping and sintering process. In this work, mechanical strengths were indicated via three-point bending tests in order to get values for pure tricalcium phosphate ceramics with and without pre-milling process. The modification on grain size changes the mechanical property of tricalcium phosphate ceramics. While decreasing the grain size with pre-milling process, the bending strength of pure TCP ceramics increases. This rising may occur because smaller grain sizes usually bring smaller flaws. As a summary, the pre-milling process has also an positive effect on bending strength. As a result, the difference between with and without pre-milling process is observable. The highest three-point bending strength is 33.4 MPa for pre-milled TCP ceramics with a sintering temperature 1250°C and a dwelling time of two hours.

Besides pure TCP ceramics, TCP ceramics with dopants were also examined via three-point bending test. TCP with 1 % TiO_2 have the highest three-point bending strength of 26.7 MPa with a sintering temperature 1250°C and a dwelling time of two hours. The summary of the mechanical strength of TCP ceramics with various dopant combinations can be seen in Table 22 on page 73.

Consequently, Figure 74 depicts the relationship between bending strength and relative density. It is clear from Figure 74 that the varying TCP samples relative density is not basically proportional to changes in bending strength. For this reason, an important finding of this work was that good densification is not necessary for obtaining better mechanical properties in sintered ceramic structures.

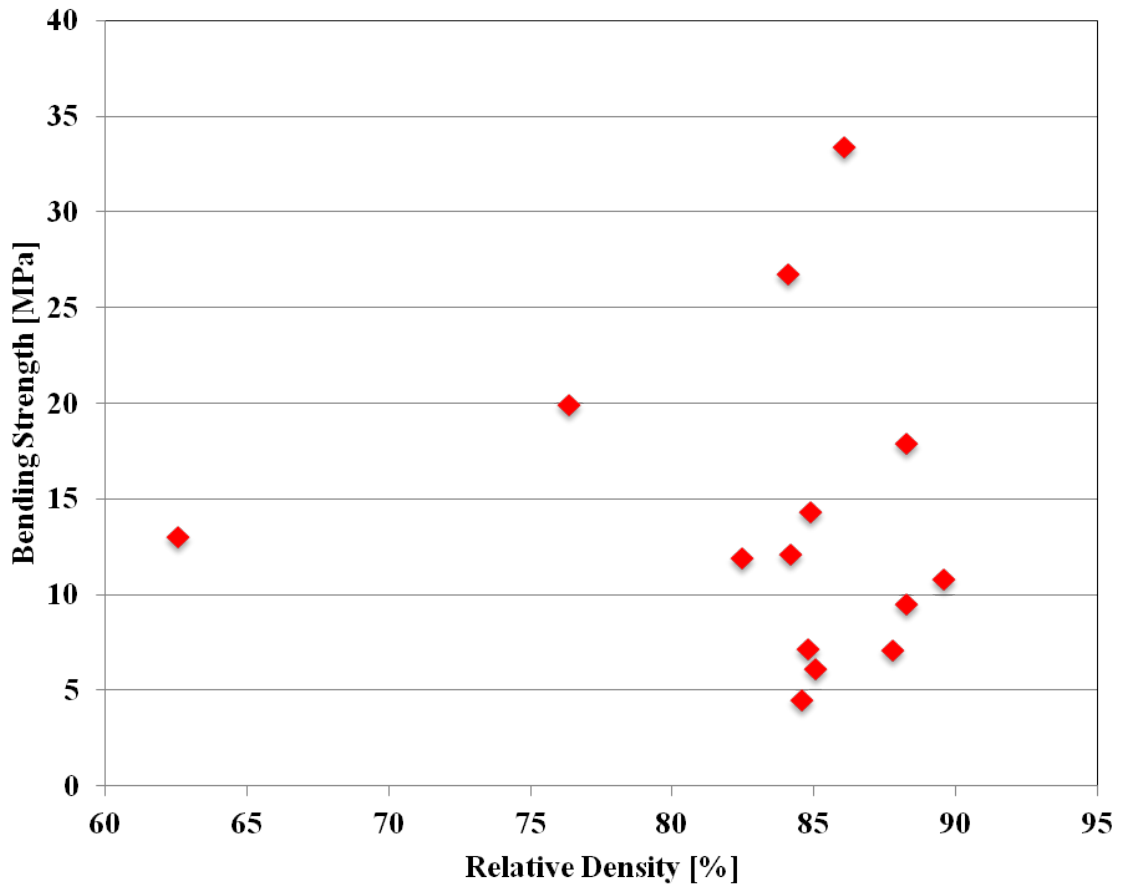


Figure 74: Bending strength vs. Relative density

In LCM process, it is important to have a high solid loading suspension due to the high dense ceramics. However, tricalcium phosphate ceramics do not need to be highly dense. The reason of using highly solid loaded slurry is for a better control of the shrinkage during sintering. Therefore, the solid loading of the TCP slurries were 49 vol% with different dopants. Also, building speed is an important parameter for additive manufacturing methods. Every layer was irradiated for 2.88 seconds. The printing time of one layer was approximately 50 seconds. Therefore, the building speed of the samples was about 2 mm/h in z-direction.

As a future work, the scaffolds which can be obtained from a CT scan, could be structured by LCM process with high reproducibility. Further studies such as in-vivo and in-vitro testing could be done for biological testing and also compressive strength is the other possibility for TCP scaffolds to perform with same dopants.

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