

# 3D-Printing of High-Strength and Bioresorbable Ceramics for Dental and Maxillofacial Surgery Applications – the LCM Process

In dentistry and cranio-maxillofacial surgery, various ceramic materials are used. Recent developments in Additive Manufacturing (AM) of ceramic materials finally allow for the use of 3D-printed ceramics as materials for patient-specific surgery.

## Introduction

In dentistry and cranio-maxillofacial surgery, various ceramic materials are used in different clinical situations and in a variety of indications. These indications include the application of ceramics as a bone grafting material, as a dental implant or as a prosthetic part.

While the first mentioned indication of bone grafting uses the ceramics beta-Tricalcium Phosphate ( $\beta$ -TCP), dental implants and prosthetic parts can be made of the high-strength ceramic zirconia.  $\beta$ -TCP is a bioactive and bioresorbable ceramic which is used as a bone graft substitute in the field of oral and maxillofacial surgery, implantology and periodontology [1–2]. While smaller defects can normally be treated using particulate  $\beta$ -TCP [3], the treatment of larger or critically sized defects is still an obstacle for standard alloplastic biomaterials.

Here, the 3D-shaping and mechanical stability of the biomaterial seems to be crucial for successful treatment [4]. Consequently, 3D-printable biomaterials possessing high strength properties bear significant advantages in cases of larger bone defects. 3D-printing allows for the production of interconnected porous scaffolds with defined geometry and pore size,

## Keywords

LCM process, zirconia, tricalcium phosphate, dentistry, cranio-maxillofacial surgery

which therefore facilitates the ingrowth of bone from adjacent tissues [5–6].

Zirconia is commonly used in the field of prosthetic dentistry to restore lost teeth or tooth substance by means of tooth supported crowns, Fixed Dental Prostheses (FDPs) and defect-oriented restorations such as occlusal veneers [7–11].

As early as 1900, the US dentist Charles Henry Lund invented the jacket crown, the first all-ceramic crown restoration. However, the technical application was very complicated and was associated with many problems, meaning that this crown variant was aesthetically pleasing but had little mechanical strength. In order to achieve greater strength, VITA Zahnfabrik/DE made its first attempts in 1958 to burn dental ceramic materials onto a Degussa/DE precious metal alloy. Ultimately, the introduction of the VITA VMK 68 in 1968 led to the great breakthrough of metal ceramics [12]. Crowns and bridges made of metal and ceramics are still the standard form of restoration in the field of ceramic restorations.

In contrast, tooth-colored materials show significant advantages when it comes to fabricating restorations that appear as natural as possible. Due to the increasing aesthetic demands of both patients and dentists, a large number of new metal-free restoration forms and materials have been developed. Due to their excellent biocompatibility and optical properties, all-cer-

amic materials are recommended as the material of choice [13–14]. Especially in the optical imitation of the natural tooth, all-ceramic restorative materials have significant advantages over metal-ceramic materials [15]. Among the large number of all-ceramic framework materials, zirconia demonstrates the best mechanical properties compared to all other all-ceramic materials [16–19] due to its transformation reinforcement. However, clinical setbacks were also reported for all-ceramic restorations based on zirconium oxide frameworks. Of those the most important was

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the chipping of the veneering ceramics. While fractures of the zirconia frameworks were seldomly recorded, chipping in the veneering area was reported numerous times [20–21]. One possible approach to avoid the chipping problem is to fabricate fully anatomical monolithic zirconia crowns and bridges without a veneering layer. The main clinical advantage of monolithic zirconium oxide restorations is the significantly reduced material thicknesses compared to veneered restorations or other monolithic ceramics, such as silicate ceramics [22–23]. The most commonly used zirconia material possesses a content of 3 mol-% yttrium oxide (3Y-TZP = Yttria-Stabilized Tetragonal Zirconia Polycrystal) in order to be stabilized at room temperature in the tetragonal phase. This enables the so-called conversion amplification, which occurs during high mechanical stress and causes a conversion from the tetragonal to the monoclinic phase. The resulting increase in volume (around 4 %) virtually compresses the crack flanks. This special feature gives 3Y-TZP interesting mechanical properties, and makes this oxide ceramic particularly suitable for dental use. However, 3Y-TZP is very opaque, so that an application for monolithic restorations is associated with sub-optimal aesthetic properties. Most dental zirconia manufacturers have found different approaches to meet the increased translucency requirements. On the one hand, light transmission can be increased by either by increasing the concentration of yttrium oxide or by reducing the concentration of alumina, that is also usually present in low amounts for toughening

purposes. Examples include zirconium oxides with 4 or 5 mol-% yttrium oxide content, respectively. With these so-called cubic zirconium oxides (e.g. 5Y-CZP), more than 50 % of the zirconium oxide is in the cubic phase, which does not allow conversion amplification and thus leads to a reduction in crack toughness. Consequently, the material becomes more brittle. The introduction of Computer-Aided Design/Computer-Aided Manufacturing (CAD/CAM) made the processing of this high-strength ceramic possible [24–26]. Zirconia can also be used when it comes to replacing missing teeth by means of dental implants and implant-supported prosthetic parts (as depicted in Fig. 1–3 [27–29]). Nowadays, the CAM procedure for processing zirconia is performed by subtractive techniques, meaning that the zirconia parts in the aforementioned indications are milled from a pre-fabricated zirconia blank in a pre-sintered condition – the so-called white



*Fig. 1*  
Full ceramic crown (3 mol-% Yttria-Stabilized Zirconia – 3Y-TZP) that was manufactured by the LCM process: the fissures of the perfectly shaped occlusal surface can be seen, as well as the support structure on the bottom of the part; the support structure is used as sinter support during thermal postprocessing and removed by tooling after sintering



*Fig. 2 a–b*  
Full ceramic crown (3Y-TZP) with highly pointed fissure geometry at the occlusal surface



*Fig. 3 a–b*  
Ultra-thin occlusal veneers for minimal invasive reconstruction of hampered dentition. The left image shows the support structure of the part, while in the right image it has already been removed; very fine edges down to 100 µm can be achieved with the LCM technology

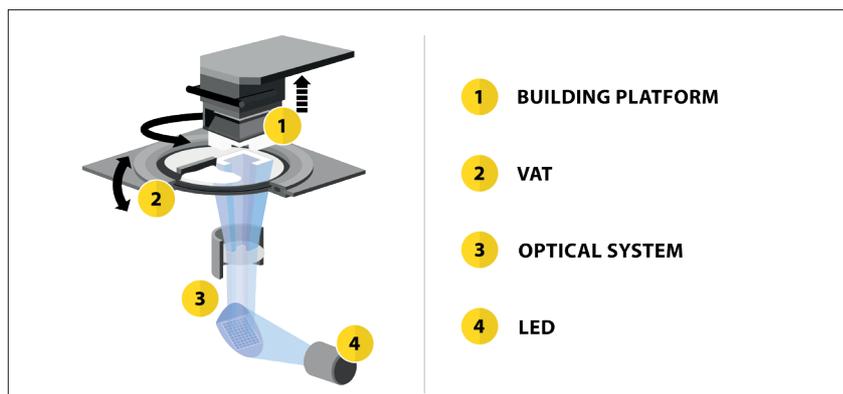


Fig. 4  
Schematic view of the CeraFab's assembly: the arrows indicate the moving directions of building platform and material vat, the raw material (slurry) is depicted as white mass within the material vat

body. In this state, zirconia has a low inherent strength. Due to this fact, during subtractive machining of the material, thin borders can break out and consecutively lead to an evident discrepancy between the design and the fabricated part [8]. For this reason, thin borders and edges often have to be designed overcontoured in these areas to prevent the edges from breaking out during the machining. However, this also results in a considerable amount of post-processing work in these zones. Since the crown margin is, along with the occlusal surface, a very important

area of a crown and bridge restoration, the post-processing must be carried out very carefully and under the stereomicroscope. This post-processing is considerably time consuming and, thus, cost intensive. Furthermore, fissures of the occlusal surfaces also require post-processing, as rotating instruments can only reproduce the classic tapered fissure geometry to a limited extent.

With the development of the Lithography-Based Ceramic Manufacturing (LCM) process, the 3D-printing of these materials is now feasible, and offers some advantages in comparison to standard fabrication procedures. In this context, AM offers significant advantages as these procedures are able to reproduce pointed inner geometries with a high accuracy. Improvements in translucency and colouring are still necessary. However, 3D-printing also offers advantages in this aspect, as, on the one hand, individual colourings can be realised, and on the other hand individual colour gradients are conceivable due to the layered structure.

This article describes the process of 3D-printing high-strength and bioresorbable ceramics. Some of the materials and their material properties which can be fabricated in this manner are described, and potential applications in dentistry and maxillofacial surgery are highlighted.

#### LCM process

Among all different AM techniques for ceramics, vat polymerization based processes stand out in particular due to their high precision, their homogeneous and anisotropic

microstructure, excellent surface quality and, lastly, due to their comparable mechanical properties which provide special benefits for the industry.

The following section focuses on a dedicated methodology for high-performance and bioresorbable ceramic parts – the LCM process. All parts discussed within this contribution were produced by means of LCM technology, using a CeraFab system by Lithoz. As depicted in Fig. 4, the assembly of the CeraFab systems comprises of a rotating vat that is filled with the photocurable suspension. The bottom of the vat is transparent; thus, the light source can illuminate the suspension from below through the vat. The projected image is generated via a Digital Micromirror Device (DMD).

The building platform is positioned above the vat, and moves upwards along the z-axis during the fabrication process. Unlike most AM technologies, LCM builds the part upside down. This method significantly reduces the amount of slurry required. Moreover, almost 100 % of the material that is fed into the process is solidified, which makes this an extremely attractive technique in terms of cost and resource efficiency.

Fig. 5 shows a photograph of the actual CeraFab 7500 system and Fig. 4 gives a schematic overview of the machine. The LCM process relies on the concept of photopolymerization. Ceramic powder is dispersed into a mixture of photocurable monomers to give the photocurable suspension (i.e. slurry) [30]. A thin layer of this slurry is first automatically coated onto the transparent vat, then the building platform approaches the vat, leaving a small gap of a couple of microns which is filled with slurry. Since the slurry has a relatively high viscosity, a recoating system is needed to spread a fresh layer of slurry before each curing sequence. The recoating system consists of a wiper blade in combination with a rotating vat. The photosensitive compounds comprised within this slurry are cured by selective exposure using light of a certain wavelength. In the areas where light hits the ceramic-filled slurry, the monomers photopolymerize into a cross-linked network, which then acts as a cage for the ceramic filler.

After completing the layer, the building platform is elevated and the entire sequence is repeated. After this structuring,



Fig. 5  
CeraFab 7500 system – 3D-printer for high-performance and bioresorbable ceramics

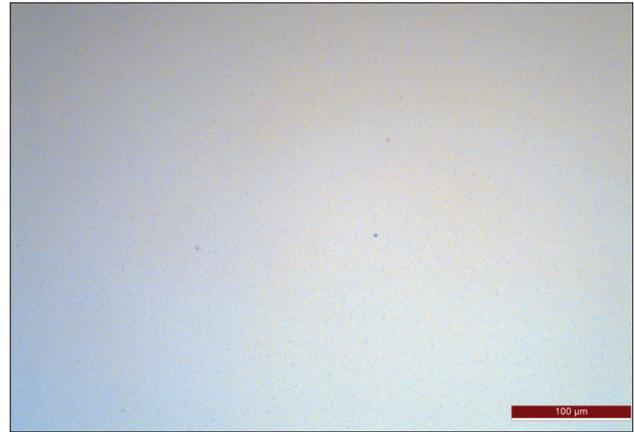
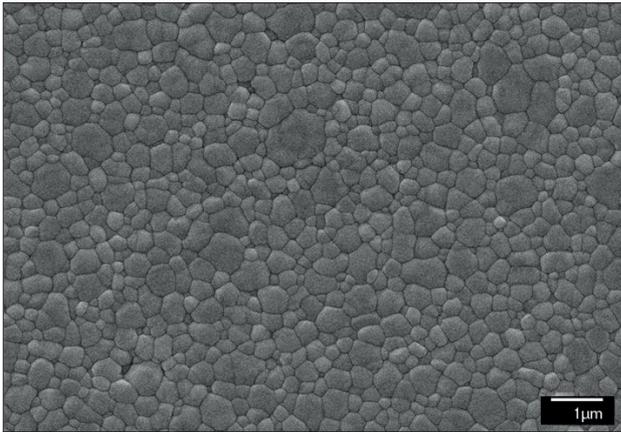


Fig. 6 SEM image of the polished and thermally etched zirconia surface (l.) and light microscopy image of a polished zirconia surface (r.)

the produced parts consist of both ceramic particles and an organic photopolymer network. Surfaces and channels need to have any excessive slurry removed by cleaning the parts using compressed air and appropriate solvents, which are capable of dissolving the slurry without damaging the cured structure. Subsequently, the cleaned green parts need to be debinded and sintered, as with conventional ceramic forming technologies.

This process is well known from traditional ceramic processing, and the material properties are equal or, at least, very similar to conventionally formed parts where the same powder has been used. This treatment at very high temperatures also ensures that no organic residuals are left within the ceramic parts, which is crucial for biocompatibility and mechanical strength, both of which are mandatory properties for technology being used for medical device applications.

### Materials

In order to guarantee full functionality and reliability, the 3D-printed crowns have to possess properties that are in line with those formed using traditional CAD/CAM processes; high density and high mechanical strength are particularly crucial factors. Using LCM, it is possible to obtain highly dense (>99,8 % relative density) zirconia structures. This high density is a requirement achieving high strength, but it is also important in achieving the necessary translucency for applications where aesthetic properties are relevant. Remaining porosity would act as scattering cen-

tres of light, and would render the zirconia parts highly opaque. Fig. 6 shows the typical quality of zirconia samples produced using LCM.

Light microscopy imaging of the polished surfaces shows that there is very little remaining porosity in the sintered samples; the amount of sub- $\mu\text{m}$  pores is comparable to isostatically pressed samples. The corresponding mechanical strength, tested according to DIN EN 843-1, was 935 MPa and consequently fulfils the requirements for the use in dental applications.

Another important bioceramic in the context of dental and CMF surgery is TCP. This ceramic resembles the inorganic content of bone and is hence capable of undergoing resorption and remodeling into the native bone tissue after implantation; therefore, it can be used as temporary bone replacement material to facilitate bone regeneration. By using LCM, it is not only possible to produce customised patient-specific shapes but also to introduce defined porosity in order to tailor degradation rates and to provide efficient scaffolding for the newly formed bone. An exemplary structure from a filling of a mandibular cage is shown in Fig. 7.

For the TCP-based resorbable bone replacement material LithaBone TCP 300, an ASTM F-1088 4a certified beta-tricalciumphosphate powder from ISO 13485 certified suppliers is used.

### Applications

#### Prosthetic applications in dentistry

Zirconia is a frequently used material in prosthetic dentistry. It offers the possibility



Fig. 7 Printed TCP scaffold with customized outer shape and interconnected macropores as used in a mandibular cage

to restore teeth and lost tooth substance by means of tooth supported crowns, FDPs and defect-oriented restorations, such as occlusal veneers [7–11]. In addition, zirconia is used as a restorative material for implant-supported restorations, as an abutment, as a veneered or monolithic crown and as a veneered or monolithic FDP [27–29].

While conventional crowns, FDPs and abutments can be reliably fabricated by conventional subtractive fabrication procedures, this technique is not ideal for ultra-thin reconstructions as these often require ultra-thin border areas. Subtractive fabrication procedures are not able to consistently produce feather edges in these types of reconstructions [8].

In addition, the longevity of restorations can be influenced by the internal adap-



**Fig. 8 a–b**  
Mandibular cage made of zirconia with a filling of a three-dimensional interconnected pore network made of TCP. During the healing of the injury the zirconia shell gives proper support while the bioresorbable TCP, whose geometry was designed following the trabecular bone, eases the ingrowth of new viable bone. The fixation of the shell to the artificial jaw bone model was conducted with titanium screws



**Fig. 9**  
Dental implants made of 3Y-TZP

tation between the restoration and the tooth [31–32], and, particularly in thin reconstructions, this zone is known to be responsible for crack initiation of the restorative material [33]. With conventional subtractive fabrication techniques, the internal fit and thus the internal adaptation of a reconstruction can be insufficient once the diameter of the bur exceeds the size of the inner configuration.

There is currently a study being undertaken in which ultra-thin occlusal veneers produced via the LCM process are compared to milled zirconia and to pressed lithium-disilicate reconstructions. In this investigation, the internal fit and the mechanical strength of the parts after artificial aging will be compared.

The fabrication of ultra-thin occlusal veneers with the LCM process could be advantageous compared to subtractive fabrication for those type of treatments, due to the high accuracy and thus high internal adaptation achievable through additive manufacturing. Furthermore, the production of very thin borders and feather edges can be reliably produced by the LCM technique (Fig. 3).

By using CAD/CAM technology, zirconia for the use of crowns and FDPs can be processed very efficiently and reliably. Compared to manually veneered zirconia crowns and FDPs, monolithic restorations are much cheaper to fabricate. Furthermore, the clinical issue of the chipping rate of manually veneered zirconia reconstructions could be reduced using monolithic zirconia reconstructions [7]. In order to achieve aesthetic results with monolithic reconstructions, the occlusal surface should be designed to be as natural as possible. With subtractive manufacturing, the occlusal surface with the fissures and cusps needs to be post-processed by hand. This is due to the fact that the rotating instruments used for the fabrication of zirconia can only reproduce the classic, tapered fissure geometry to a limited extent. For this purpose, AM with the LCM process can offer significant advantages, as these procedures can produce geometries, which resemble the nature of an occlusal surface (Fig. 1–2).

#### **Mandibular cage**

A slightly different application is within the field of cranio-maxillofacial surgery

and treats bone defects in the mandibulum (lower jaw). Such critically sized bone defects can be the result of severe trauma (e.g. comminuted fracture) of the jaw or to bone resection due to bone tumors. The challenge in treating such large defects is that, without proper measures, the bone itself will not be able to heal the defect.

Thus, a dual approach is presented here, with a shell of high-strength zirconia giving the proper support during the healing phase and the inner volume of the implant being made of bioresorbable beta-Tricalcium Phosphate ( $\beta$ -TCP) as shown in Fig. 8. It has been proven that  $\beta$ -TCP has good osseointegrative properties, and that by choosing suitable pore and strut dimensions the bone ingrowth can be significantly influenced.

The  $\beta$ -TCP will be resorbed by the cells and replaced by newly formed bone and the zirconia cage can be left in place due to its excellent biocompatibility. Thus, harvesting autologous bone (e.g. from iliac crest), which is frequently associated with severe pain and complications at the donor site, is no longer necessary.

#### **Dental implants**

For replacing a missing tooth, endosseous screw-type dental implants offer a suitable treatment option. There are many different materials available on the market for dental implants, including implants made out of zirconia. Using the LCM technology, it is possible to manufacture complexly shaped implants in large numbers, which possess excellent strength and geometric fidelity. Fig. 9 shows dental implants in their “as-fired” state.

#### **Summary**

Recent developments in AM of ceramic materials finally allow for the use of 3D-printed ceramic as materials for patient-specific dentistry. Possible areas of application go beyond classical crowns or bridges and also the use of printed components in applications such as mandibular cages cranio-maxillofacial surgery or dental implants.

The availability of different ceramic materials allows for applications under load (zirconia) as well as for applications where bone regeneration needs to be induced (TCP).

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