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ADDITIVE MANUFACTURING AND 3D PRINTING IN DENTISTRY

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EXECUTIVE

In recent years, the world of dentistry, as well as that of medicine in general, has begun to entrust a large part of its daily routine to the digital world, both in terms of communication between doctor and patient and in terms of diagnosis and therapy. In the specific case of modern dentistry, in clinical and dental technology, the advent of new technologies and materials has radically changed the approach to the profession.

This change has introduced new working procedures to support clinical and technical expertise. As far as the dental laboratory is concerned, first of all, it began to use, in its daily practice, sophisticated scanners that have evolved over the years to become indispensable tools to deal with the evolution of the market in the use of new materials.

[Goracci *et Al.* 2016; Alikhasi *et Al.* 2017; Abduo *et Al.* 2018; García-Gil *et Al.* 2020; Papaspyridakos *et Al.* 2020]

As far as dentistry is concerned, instead, the approach to the use of digital technologies has developed with the introduction of intraoral scanning systems and the production of the prosthetic piece mainly on the chair side, and then specializing in the increasingly modern technology of digital data collection systems called "digital impression", at the service of which CAD-CAM milling and production centers have been created more recently [Papaspyridakos *et Al.* 2020].

The continuous development in the computer technology and dental processing ensures new opportunities [Schoenbaum *et Al.* 2012], computerized engineering technology is related with consistent precision and reproducible production results in a streamlined work process with reduced manpower [Dawood *et Al.* 2010; Fasbinder *et Al.* 2010].

The establishment of CAD/CAM-technology has been the game changer for the production of tooth-borne and implant-supported monolithic fixed dental prostheses (FDP) by means of digitally on-screen designing with dental software applications, and secondary computer- assisted production with rapid prototyping procedures, such as milling or 3D-printing, in a virtual environment without any physical model situations [Koch *et Al.* 2016].

Several companies offer various computerized software applications and technical devices, and the dental team of clinician and technician has to choose how and when to proceed digitally or stay conventionally [Miyazaki *et Al.* 2011]. The truth in dental business reveals: there is neither the pure classical pathway nor a fully digital workflow

[Weston et Al. 2016]. Single digital working steps infiltrate the proven traditional successful approach [Kapos et Al. 2014]. The result of this evolution is a mixed analog-digital workflow, combining the best of both techniques [Patel et Al. 2010].

Recent studies have shown that more focus and investments on enterprises' sustainable practices not only help them to build up a socially responsible image but also improve their overall sustainable performance in economic and environmental dimensions [Allaoui et Al 2019].

Logistics links different operations and players within a supply chain and is a vital part that largely determines a company's overall effectiveness and resource efficiency [Qaiser et Al. 2017]. Managing a logistics system involves several related activities, i.e., warehousing, inventory handling, information services, and transportation, and any decisions may influence a large number of stakeholders in either positive or negative ways [Murphy et Al. 2003]. The effectiveness and sustainability of a logistics system determine the long-term competitiveness and the success of an enterprise. Therefore, new methods are investigated by both academia and industrial practitioners to improve the economic, environmental, and social sustainability of logistics activities.

The recent technological advancement and innovation of Industry 4.0 have provided new opportunities for enterprises to achieve value creation and proposition through satisfying individualized customer demands responsively and cost-effectively [Wang et Al. 2017].

This has not only led to a shift of the manufacturing paradigm but also drastically affected the way of logistics operations toward a high level of digitalization, connectivity, intelligence, integration, and responsiveness [Winkelhaus et Al. 2020].

To improve the intelligence, agility, and efficiency of logistics activities, recent studies have put predominant emphasis on the adoption of new technologies, e.g., big data analytics [Chalmeta et Al. 2020], blockchain [Reddy et Al. 2021], artificial intelligence (AI) [Tirkolae et Al. 2021], internet of things (IoT) [Tijan et Al. 2019], and additive manufacturing (AM) [Khorram Niaki et Al. 2017]. This trend has led to the new architecture of Logistics 4.0 [Wang et Al. 2016]. Besides, several recent reviews have discussed the connection between Industry 4.0 and general sustainable practices [Roblek et Al. 2020].

The trend of digitalization is an omnipresent phenomenon nowadays – in social life as well as in the dental community [Fasbinder et Al 2010; Weston et Al. 2016]. The overall scientific evidence in the field of complete digital workflows is extremely low, the industrial progress of available digital applications, tools, and devices seems to be faster than the scientific evidence. This issue as well has clinician high interest who has to decide

to invest and implement complete digital workflows in dental routine. Therefore, the advantages of a virtual environment are obvious – even though the scientific validation is still pending.

The appropriate indication is a prerequisite and the correct application is absolutely crucial for the success of the overall therapy, and finally, for a satisfied patient. For digital processing, a teamwork approach is even more important and equally affects the clinician, the dental assistance, and the technician [*van der Zande et Al. 2013*]. The complete digital workflow has the potential to become a game changer in dentistry [*Kapos et Al. 2014*]. Major advantages might arise to reduce production costs [*Joda et Al. 2015*], improve time-efficiency, and to satisfy patients' perceptions [*Joda et Al. 2015*] in a modernized treatment concept.

CHAPTER 1

1.1 - ACTUAL CERAMIC OVERVIEW IN DENTISTRY

Ceramics are defined as inorganic materials, principally formed by non-metals materials, obtained by high temperatures action, and whom final structure is partially or totally crystalline. The majority of dental ceramics are characterized by a mixed structure, i.e., they are composite materials, formed by an amorphous matrix of silicate glass in which are immersed particles of crystalized minerals of different dimensions and that are tidily arranged. [Reza Rezaie et Al. 2021]. According to Gracis et Al. [Int.J.Prost. 2015] the new classification od dental ceramics include: glass-matrix ceramics, polycrystalline ceramics and resin-matrix ceramics, due to the phase/phases present in their chemical composition.

“Glass-matrix ceramics” are nonmetallic inorganic ceramic materials containing a glass phase, while “polycrystalline ceramics” are defined as nonmetallic inorganic ceramic materials that do not contain glass, but only a crystalline phase. In the “resin-matrix ceramics” group are included materials that have a polymer matrix, containing inorganic refractory compounds [Gracis et Al. 2015]. The glass matrix is responsible of the aesthetics of ceramic, while crystals are responsible of the resistance. Therefore, the microstructure of the ceramic has an incredible clinical importance, indeed aesthetical and mechanical behaviours of a system depend directly on the chemical composition.

1.1.1 MOST CERAMICS USED IN DENTAL APPLICATIONS

Feldspathic porcelains

Traditionally in dentistry, dental porcelains had the same chemical composition of ceramics used to produce domestic and artistic utensils. These ceramics exclusively contained three basic elements: felspars, quartz and kaolin.(Fig.1.1) Actually, thanks to development in chemical factory, the composition of feldspathic ceramics has changed: they are made of a feldspar matrix, in which are displaced particles of quartz and little quantities of kaolin.

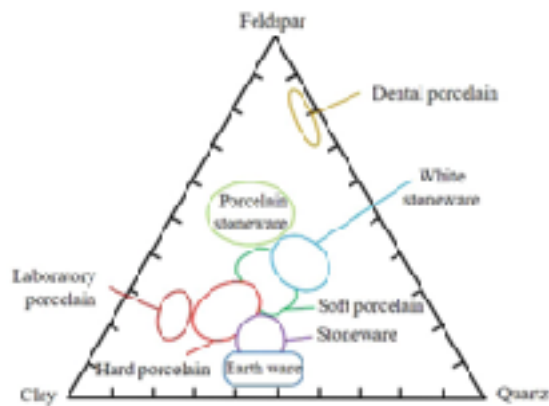


Fig.1.1 Ternary $K_2O-Al_2O_3-SiO_2$ system determining phase fields of important feldspathic dental ceramics. [Reza Rezaie et Al. 2021]

Most ceramics have to different phases:

- the glassy phase
- the crystallin phase.

Feldspar is the major component of the glassy phase, conferring translucency to porcelain. Quartz composes the crystallin phase, that is associated to mechanical strength of porcelain. Kaolin confers plasticity and handleability of ceramics before the firing process. Moreover, some substances, called fluxes, are added to the composition, in order to reduce the sintering temperature of the ceramic. In tandem, some pigments are added, to obtain different shades of colour. Feldspathic porcelain is basically a glassy substance, with excellent optical properties, that allow to reach good aesthetic result. At the same time, feldspathic porcelains are fragile substances, that's why they are used as a covering layer above a core structure, that can be made of metal or zirconium oxide (ZrO_2). Due to the high request for aesthetic outcome of dental restauration, for commercial purpose, the composition of ceramics was additionally changed, in order to discover new materials with adequate tenacity to be used in full-porcelain restorations. In this context, high-resistance feldspathic porcelains were introduced. Those ceramics have a similar composition in comparison with the traditional ones, but with the incorporation of elements that increase the mechanical strength, such as:

- *IPS Empress II* (Ivoclar Vivadent, Schaan, Liechtenstein) (Fig.1.2): this system is made of a feldspathic ceramic, reinforced with lithium disilicate ($Li_2Si_2O_5$) and lithium orthophosphate (Li_3PO_4). The presence of those crystals increases the resistance, but

at the same time increases the opacity of the ceramic as well. This material is therefore used as a core structure, to be covered by a conventional feldspathic porcelain.



Fig. 1.2 : Blocks of Empress CAD, different colors and translucencies (marked by letters and numbers, i.e. C14 A3,5). All the ceramic blocks are connected to a metal pin useful for Milling machine I'm going to describe on next Paragraph

- *IPS e.max Press/CAD (Ivoclar Vivadent, Schaan, Liechtenstein)*(Fig.1.3-1.6): these feldspathic porcelains are reinforced only by the insert of lithium disilicate ($\text{Li}_2\text{Si}_2\text{O}_5$) crystals. Nevertheless, the resistance of these ceramics is higher in comparison with *Empress II*, due to a better homogeneity of the crystallin phase. Equally, a layering with traditional feldspathic ceramics is needed.



Fig.1.3 : Blocks of emax press, identify different colors and translucencies (marked by letters and numbers, i.e. LT A1) and dimensions, to make bridges or multiple crowns.



Fig. 1.4 : Blocks of e.max CAD. The purple color is synonymous with a non-definitive phase which will take place through the crystallization cycle in the appropriate oven.

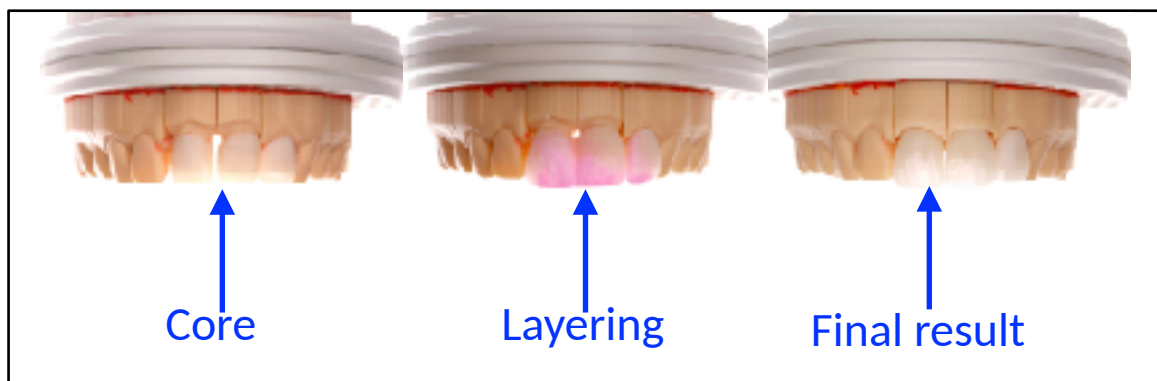


Fig. 1.5 : Lithium disilicate ($\text{Li}_2\text{Si}_2\text{O}_5$), due to its physical properties, is used as a core (on the left) in contact with the prepared tooth, covered by layered feldspathic ceramic (in the center) to achieve with the final restoration (on the right) all the aesthetics details requested for the clinical case

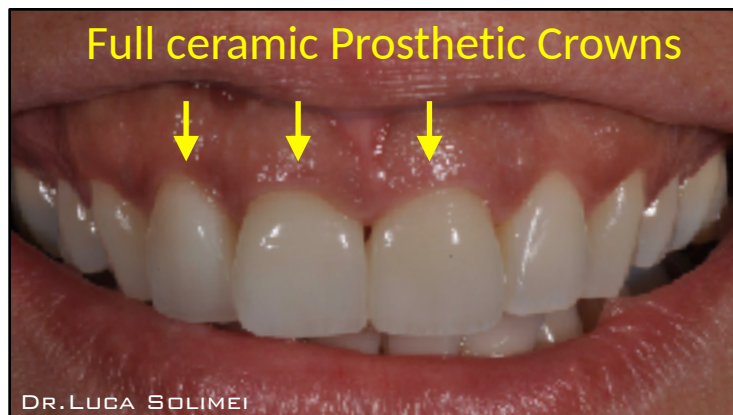


Fig. 1.6 : Due to a proper management of ceramics, the result of Prosthetic crowns is good creating a mimesis that satisfied patient and dentist

Aluminium oxide (Al_2O_3)-reinforced ceramics

In 1965 McLean y Hughes launched a new type of porcelain, adding in the composition relevant quantities of aluminium oxide (Al_2O_3), reducing in proportion the amount of quartz. This material had a mixed micro-structure in which the aluminium oxide (Al_2O_3), having a high melting point, stayed suspended in the matrix. Those crystals extremely improved the mechanical properties of the ceramics, giving the possibility of manufacturing full-ceramic crowns. Nevertheless, the increase of aluminium oxide (Al_2O_3) caused an important reduction of translucency, parameter very important for the passage of light that can create a mimesis between adjacent natural teeth and the prosthetic crown. When the amount higher than 50% in proportion, there is a significant rise of the opacity, requiring a layering of traditional feldspathic ceramic, in order to obtain good aesthetic. Most used commercial type of aluminium oxide (Al_2O_3) reinforced ceramics, in Dental field commonly known as Allumina, are:

- *In-Ceram Alumina* (VITA Zahnfabrik, Germany): it is a ceramic with 99% of aluminium oxide (Al_2O_3), without any crystalline phase, used to produce core structures of crowns and short bridges. Nevertheless, at the end of the sintering process a low-density material is obtained, consequently it is necessary to fill it with a glassy substance, spreading by capillarity through aluminium oxide (Al_2O_3) crystals, in order to eliminate the residual porosity. This process produces a ceramic core, with higher flexural resistance.(Fig.1.7)

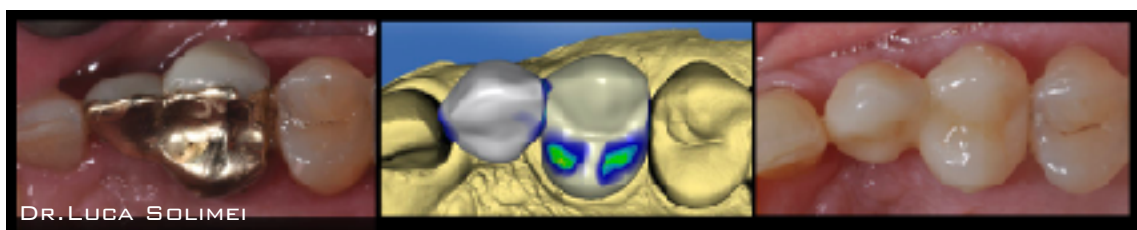


Fig. 1.7 : A clinical case requests for old *Cantilever Bridge* (on the left) removal, its new CAD design (in the center) and replaced with a new *In-Ceram Alumina* (VITA Zahnfabrik, Germany) one (on the right)

Zirconium oxide ZrO_2

Zirconium oxide (ZrO_2) in Dental field is commonly known as Zirconia. Its principal property is great tenacity, due to its totally crystallin microstructure and to its assembly transformation, in response to load. Garvie et Al. in 1975, in fact, discovered that partially stabilized zirconia (PSZ), made of highly sintered zirconium oxide ZrO_2 (95%), partially

stabilized by yttrium oxide Y_2O_3 (5%), under high stresses, undergoes a crystalline phase transformation, from tetragonal to monoclinic, increasing its volume. In such a way, local resistance increases, and fracture propagation is avoided. This property confers to Yttria-Stabilized Zirconia (YSZ)-(ZrO_2/Y_2O_3), also known as Tetragonal Zirconia Polycrystal (TZP), a flexural strength of about 1000-1500MPa, overcoming in strength other porcelains. Similarly, to high strength aluminium oxide-reinforced ceramics, aesthetic properties of zirconia are not optimal, due to the lack of glassy phase and to the high opacity. Therefore, zirconia is used as a core structure material, needing a traditional feldspathic ceramic layering. (Fig.1.8-1.10)

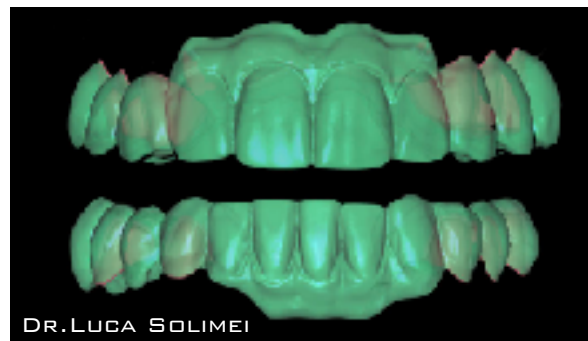


Fig. 1.8 :A Yttria-Stabilized Zirconia (YSZ)-(ZrO_2/Y_2O_3) framework CAD design



Fig. 1.9 : Trough milling CAM, the Yttria-Stabilized Zirconia (YSZ)-(ZrO_2/Y_2O_3) frameworks realized (on the left) and has to be covered, for aesthetic purposes by layering feldspathic ceramic (on the right)



Fig. 1.10 : The Final restoration can be cemented , in this case on posterior natural teeth, achieving good aesthetic and function

1.1.2. PROCESSING TECHNIQUES

Depending on the manufacturing techniques, ceramics for dental applications can be divided in three groups: powder/liquid building, slip-casting and CAD/CAM technology.

- **POWDER/LIQUID BUILDING**

A fire-resistant cast is obtained by duplication of the master-cast. Porcelain is directly applied, after mixing powder and liquid components, on the fire-resistant cast and sintered at high temperatures. Then, the ceramic is removed by the second cast and placed on the master cast for the final corrections.

- **CASTING TECHNIQUE (OR PRESSING TECHNIQUE)**

Traditionally used for metals production. A preliminary wax model is built, then it is covered by refractory material. After wax is eliminated by melting and substituted by fluid porcelain. Cooling will produce solidification of the ceramic reproducing the same shape made with wax. Many scientific researches revealed that this technique increases mechanical resistance of ceramics, due to the porosity reduction and to the uniform crystal distribution inside the matrix.

- **CAD/CAM TECHNOLOGY**

Nowadays, CAD/CAM technology (Computer Aided Design - Computer Aided Manufacturing) allows to produce precise ceramic restorations easily and rapidly. CAD/CAM systems are basically made of three phases: digitalization, design and manufacturing. During digitalization phase the dental preparation is three-dimensional recorded. Those data are transferred to a computer, where the design of the restoration is performed thanks to a specific software. After the design phase, the computer generates the instruction to the milling unit, that automatically starts the manufacturing phase.

Thanks to described technologies it is possible to realize the complete restoration and then to add superficial characterization; or it is possible to produce the core structure, to be completed by a traditional feldspathic ceramic layering. Superficial characterizations are usually applied on posterior or anterior indirect restorations, while layering technique on a core ceramic structure is more often utilized for complete crowns and short bridge manufacturing. (Fig.1.11)



Fig. 1.11 :The layering technique have the possibility to recreate many natural details

1.1.3 MAIN CERAMICS PROPERTIES REQUESTED IN DENTISTRY

In choosing the correct material for a prosthetic restoration, it is important to know the main properties of the ceramics currently available on the market in order to obtain the best possible clinical result. Among the various material properties, the most important in dental applications are fracture strength, marginal precision, aesthetics and clinical survival.

- FRACTURE RESISTANCE

One of principal problems of ceramic restorations is fracture.(Fig.1.12)

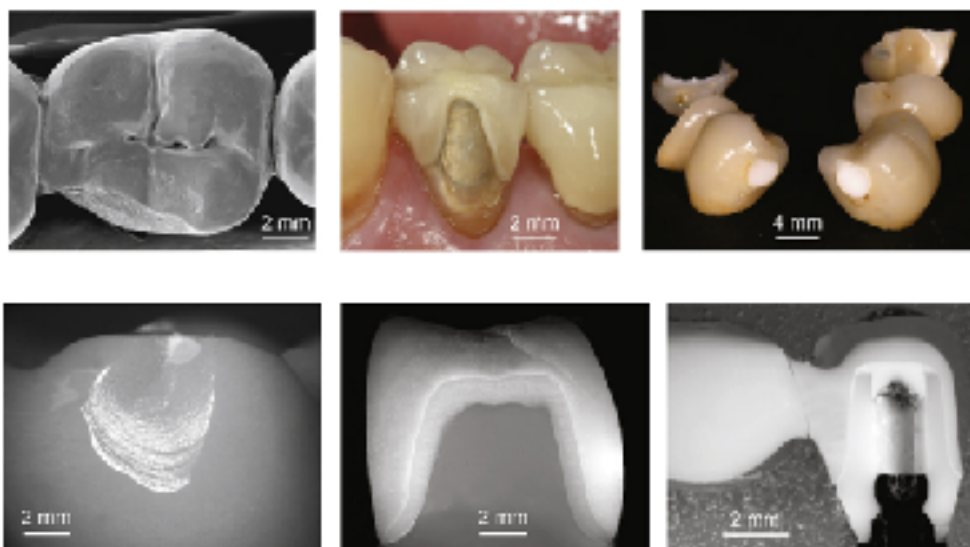


Fig. 1.12 : Different dental ceramic prosthesis fractures in vivo and in in vitro [Zhang et Al. 2013]

All systems now available have values of fracture resistance higher than 100MPa, that is the minimum required by the normative ISO 6872:2015 (*It specifies the requirements and the corresponding test methods for dental ceramic materials for fixed all-ceramic and metal-ceramic restorations and prostheses*). Nevertheless, there are considerable differences between ceramics. Fracture resistance of porcelain fused to metal restorations is comprised between 400 and 600 MPa. These values are considered as the gold standard. All ceramic restorations can be divided in three groups, relating to fracture resistance values.

- Low resistance (100-300MPa): Feldspathic porcelain.
- Moderate resistance (300-700MPa): Aluminium oxide (Al_2O_3)-reinforced ceramics
- High resistance (>700MPa): Zirconium oxide ZrO_2

It is important to keep in mind that values of fracture resistance reported in in-vitro studies don't always correspond to those founded in vivo. Layering ceramics, in fact, strongly influence the behaviour of the core structure material. The weaker is the core structure material, the stronger is the reinforcement action of the layering material. As the tenacity of the core structure increases, the armour-plating effect of the layering porcelain decreases. Moreover, fracture resistance of restorations is influenced by different factors, as dental preparation, structure design and luting technique. If those factors are correctly managed, fracture probability is significantly reduced.

• MARGINAL PRECISION

Success of indirect restorations and prostheses is determined by a good marginal sealing. [Shenke et Al. 2008] Indirect restorations, in fact, are manufactured outside of the mouth of the patient and, for that, a gap can exist in between the restoration and the tooth. The new material and productive technologies work to reduce the marginal sealing guaranteeing a better predictability to the cemented prosthetic crowns. It is interesting to note how the restorations produced through 3D printing showed a lower marginal and internal space than those produced using milling techniques.(Fig.1.13).

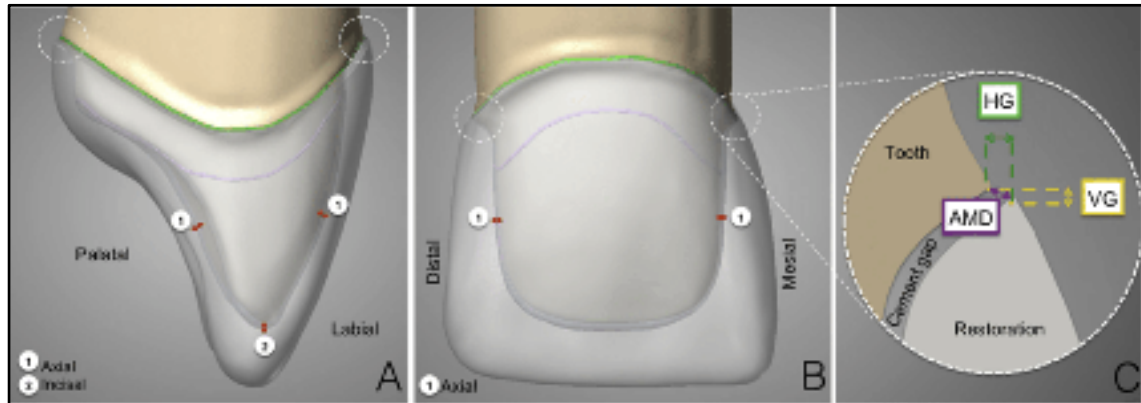


Fig. 1.13 : Internal and marginal fit measurement points on; (A) labio-palatal (LP) sections, (B) mesio-distal (MD) sections, (C) marginal fit measurement points on both (LP) and (MD) sections. Some parameter to evaluate marginal sealing are vertical gap (VG), horizontal gap (HG) and absolute marginal discrepancy (AMD). [Alharbia et Al. 2018]

Objective of the luting agent is to fill this gap, in order to increase the retention. Marginal adaptation has very high clinical importance and imprecisions at this level are often responsible of the failure of treatments, such as secondary caries disease or decementations. Therefore, in order to have a long-lasting restoration, it is fundamental to have a minimum gap at the interphase between preparation and prosthesis. Of course, the ideal situation of no gaps very infrequently, or never, is found, and for this a certain level of discrepancy can be accepted. The level of marginal precision required for a good restoration is not unique and in literature different acceptable values are found, comprised in the range of 5 - 200 μm , with an average value of 120 μm . The value of marginal precision of porcelain fused to metal restorations is of about 40-70 μm and the majority of actual all ceramic systems shows values even lower of this gold standard. [Svanborg et Al. 2020]

- AESTHETICS

Aesthetics is a determinant factor when choosing the correct material for a restoration, especially for a veneer. Traditionally, porcelain fused to metal crowns and bridges were the most common treatment option, having an acceptable aesthetics, even though there was a dark metal core, that deeply reduced the translucency. Nowadays, full ceramic systems have reached excellent results, having much better optical properties than traditional restorations. (Fig.1.14)

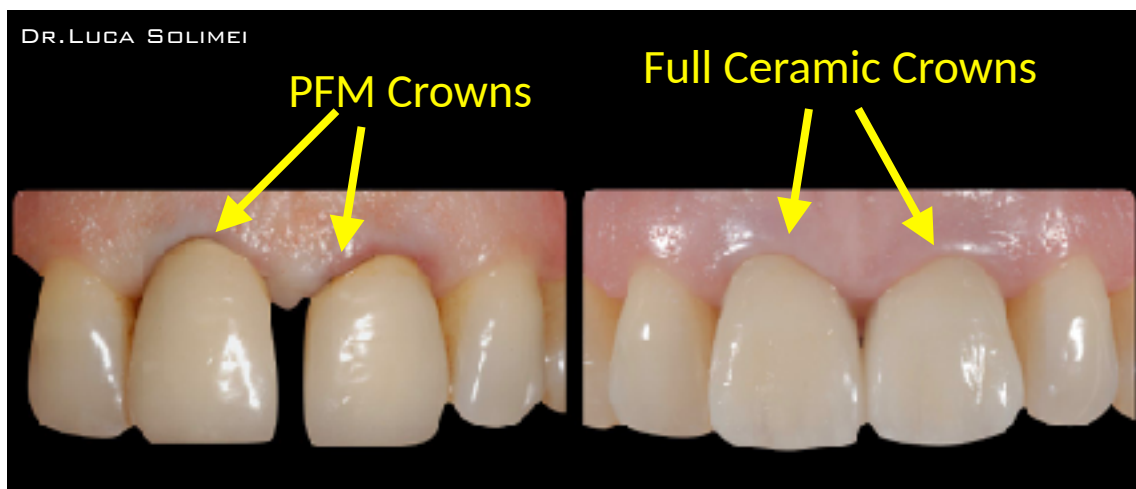


Fig. 1.14 : A clinical case with old Porcelain Fused on Metal (PFM) prosthetic crowns with some grey shadows below the gum due to the metal margin (on the left), replaced with new Full Ceramic Crown (in this case, Zirconium oxide (ZrO_2)-ceramic) on the right

However, differences of aesthetic properties of all ceramic systems still exist, having opaquer and more translucent materials. The glass matrix is responsible of the translucency of ceramics. Therefore, the most translucent materials are those with highest glass percentage, such as feldspathic ceramic. Instead, those materials with little or no glassy phase will be opaquer, as Zirconium oxide (ZrO_2) and aluminium oxide (Al_2O_3) reinforced ceramics. Nevertheless, opacity of materials can be managed by two factors: the thickness (thicker cores will look opaquer) and the colour of the core structure.

Aesthetic outcome of a restoration not only depend on the intrinsic properties of its material, but also natural anatomical shapes, symmetry and proportions will influence the beauty of the manufact.

• CLINICAL SURVIVAL

Clinical assessment is a fundamental step when evaluating ceramic systems. In fact, in the oral environment and inside the mastication system of a patients there are many variables that can't be taken in account during an in vitro study. Those variables can be the presence of parafunctions, hygiene level or occlusal characteristics.

Clinical survival of a ceramic system will depend on the type of restoration in which it is utilized. Some porcelains will better satisfy the requests for anterior and some others for posterior sectors, some for partial and some others for complete restorations. Moreover, adhesive luting technique will require etchable ceramics. Generally, it is possible to state

that highest clinical survival rate on posterior sector will belong to high resistance ceramics, as Zirconium oxide (ZrO_2) and aluminium oxide (Al_2O_3), while on anterior sectors will belong to aesthetic ceramic systems. Actually, ceramics use in dental field is still mainly dedicated to dental prosthetic crowns, while the result of supporting structures for bone regeneration are still not satisfactory, giving even more relevance to this research project.

*

1.2 SUBTRACTIVE MANUFACTURING

Subtractive methods are labeled as traditional methods and various objects are made by cutting or hollowing out material from a larger shape. The most common techniques are CNC (Computerized Numerical Control) mills or laser cutters. [Jaskolsky et Al. 2020.]

The main features that can differentiate milling units are the spindle, wet or dry system, number of axes, milling strategy and tool to create the restoration.

The spindle is the heart of any milling machine and consists of a motor encapsulated inside the machine that turns the cutting tool (cutter). The tool is held in place by a collet. The CAM software inside the milling machine create a milling program that tells the controller the spindle speed. During a project, the spindle speed is adjusted numerous times based on the type of cutting tool used, the size of the tool, the type of material to be milled, and the amount of material to be cut. In fact, the type of material has a great importance determining whether a milling tool should be dry or wet. [Kwon et Al. 2022](Fig.1.15-1.16)

Certain ceramic materials such as lithium disilicate and feldspathic porcelains require wet milling, as do some metals such as cobalt chrome. Other materials, such as zirconia and titanium, can be dry milled or wet milled. In general, wax and acrylic, used for temporaries, for example, are dry milled. [Al Hamad et Al. 2021 ; Mourouzis et Al. 2022] The liquid in a wet milling machine continuously keeps the cutting tool and milling material moist. Some additives may also be included in the liquid to act as a cutting lubricant.

Wet milling machines require both periodic cleaning because material collects inside the machine and eventually must be removed, and replacement of the cutting fluid at regular intervals.



Fig.1.15 : Example of wet milling machine (Roland DWX-4W - Roland, California)

Dry milling does not use liquid to remove waste material from the cutting surface, but rather pressurized air, vacuum, or a combination of both.

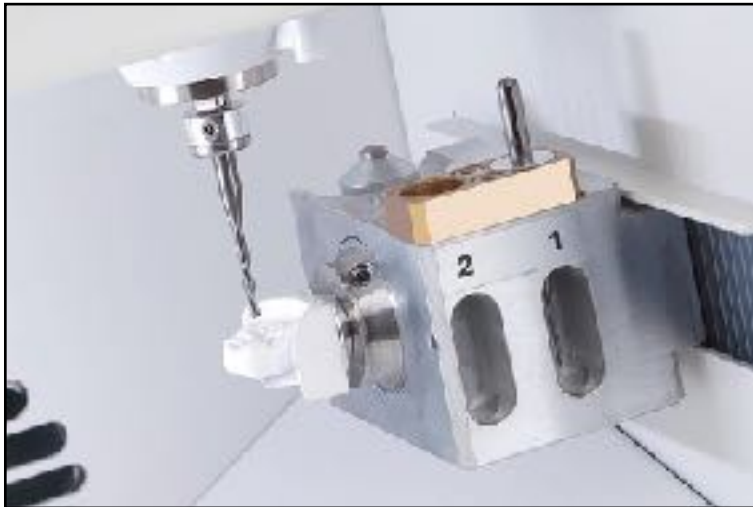


Fig.1.16 : Example of dry milling machine (Roland DWX-52D - Roland, California)

1.2.1 MILLING MACHINES CHARACTERISTICS

An important parameter, that although doesn't effect the milling machine dimensions, is represented by the number of milling axes (Fig.1.17) which instead affect the ability to produce different restorations type and shapes:

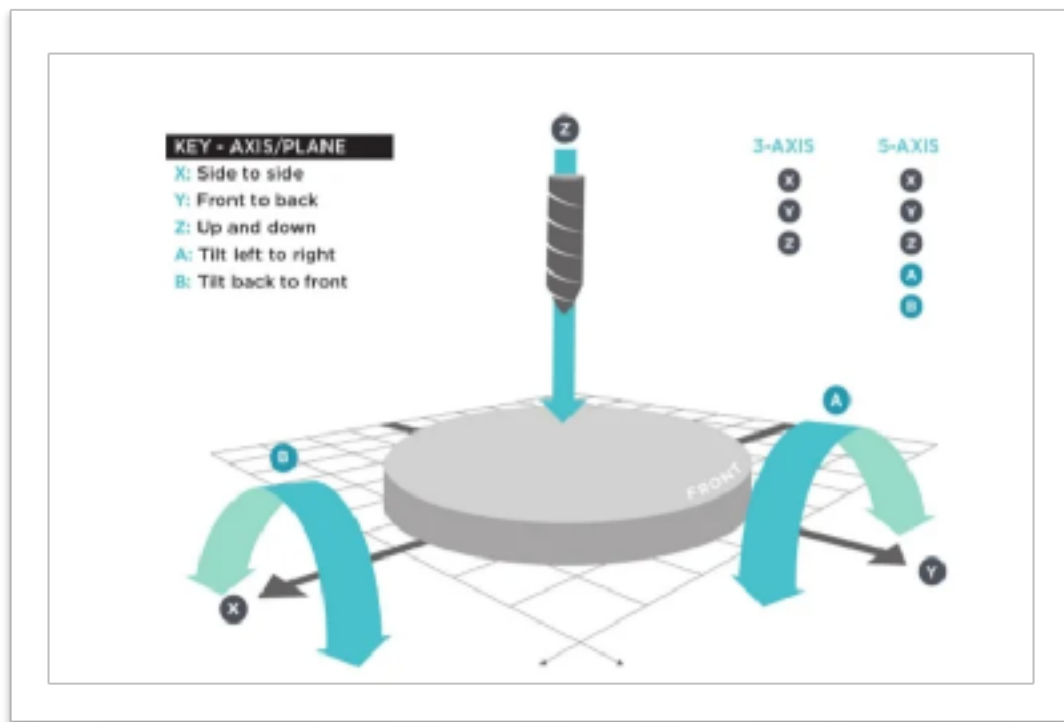


Fig.1.17: Milling machine working Axis/Plane Diagram

- *3-axis devices*

This type of milling machine has degrees of movement in three dimensional directions. Therefore, the points of the path are uniquely defined by X , Y and Z.

All 3-axis devices used in the dental field can also rotate the component by 180° in the course of processing the inside and outside. They are capable of milling from the top or bottom of the stock material, but are unable to mill undercuts, which is adequate for routine crown and bridge work. The advantages of these milling devices are: short milling times and simplified control via the three axes. [IDT Magazine 2013]

Consequently, such milling devices are usually less expensive than those with a larger number of axes.

- *4-axis devices*

A milling machine with 3 linear axes and 1 rotary axis (Fig.1.18), in addition to the three spatial axes, the tension bridge can also be variably rotated infinitely.

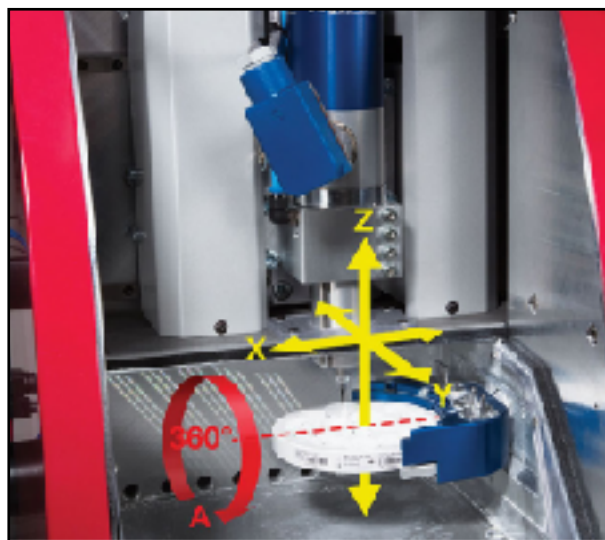


Fig.1.18 : 4-axis : 3 linear axes (X - Y - Z) and 1 rotary axis (A)

The rotary axis can be used :

- To rotate the workpiece 180° and mill each side of the blank
- To rotate the workpiece to an intermediate position where you can actually mill undercuts, angled screw channels or to optimize tool life;
- To activate a simultaneous movement (rotating or continuous 360°) that works primarily in conjunction with the machine's Z axis.

Crowns, single element screw-retained implant parts or small bridge constructions with a high vertical height difference can be adjusted in the usual mold dimensions and thus

save material and milling time. The initial investment is lower, they cost less to service and maintain, and in some cases, the fixture can be supported with more stability. [IDT Magazine 2018]

Typically, mills with four axes can mill undercuts in only one direction, while 5-axis mills can mill undercuts in each direction.

- 5-axis devices
- With a 5-axis milling device, in addition to the three spatial dimensions and the tension bridge (4th axis), it is possible to rotate the milling spindle (5th axis). (Fig.1.19)

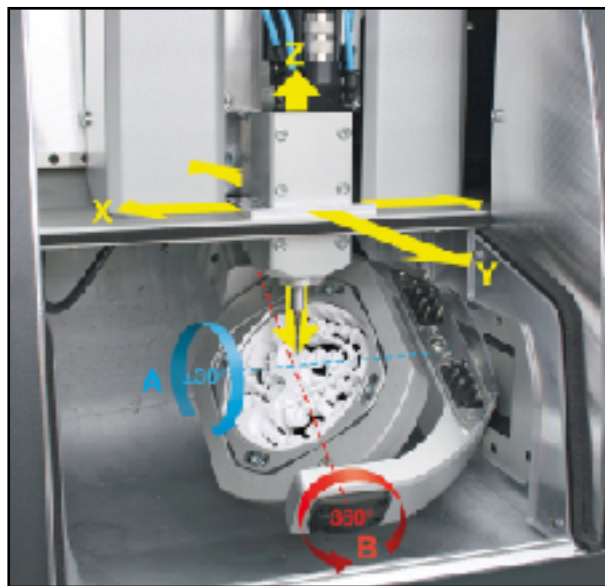


Fig.1.19 : 5-axis : 3 linear axes (X - Y - Z) and 2 rotary axis (A - B)

A 5-axis milling machine uses some of the same techniques (*Toolpath* - route made by the bur to finalize its purpose: roughing stock material, rest-machining leftover material, or finishing part features and surfaces) [IDT Magazine 2018] as a 4-axis machine for many of its milling processes but with the ability to vary the milling methodology in either the 3+2 or 5X simultaneous alternatives as needed.

- 3 + 2: locks both rotary axes at a set angle to mill complex parts, such as an undercut or angled element, effectively.
- 5X simultaneous: activates the movement of all 5 axes to mill complex undercuts or to optimize which surface of the tool should contact the material while having complete freedom of movement.

This type of machine is capable of milling any type of dental restoration. [IDT Magazine 2018]

The CAM software defines the best way to mill a restoration from the original material delivered by the company (blocks or disk)(Fig.1.20) creating a dedicated milling program. The CAM software can be integrated into the CAD software or act as separate programs by receiving the file that drives the manufacturing process. The CAM software must be configured by the Owner Company with all specific information such as the size and shape of the cutting tools, the material to be milled, the spindle controller, and the motors that adjust material and spindle movement.



Fig.1.20 : The same material (Katana Zirconia, Kuraray Noritake Dental Inc., Japan) can be delivered in different forms: on the left a Zirconia Blocks (dimensions cm 1,8 x 2 x h 2) from which can be milled just one tooth, on the right a Zirconia disk (dimensions cm 10 x 1,8 thickness) from which can be milled several teeth due to their dimensions.

1.2.2 MILLING MACHINES IN DENTAL MARKET

On the market there are many different milling machines and each dental laboratory, milling center or dental clinic can choose one due to its own specific needs and device characteristics [Infodent 2016] :

- Axis number (3-axis; 4-axis; 5-axis)
- Type of materials : Disk or blocks
- Number of disk or blocks : from 1 to 8
- Charging : automatic or manual
- Wet or dry milling
- Integrated CAM software

- Milling machine dimensions
- Cost : from 15K to 160K Euro

Due to all these characteristics, the investment for a milling machine and the CAD/CAM workflow can be done by :

- big milling center with the goal to high numbers “items” design, manufacture and sell to different dental Lab that have to finalize, in term of aesthetic details, the restorations and then send to the Dentist [Tapie et Al. 2015]
- Dental Technician that want to make by itself every designing , productive and finalizing step and then sell and send to the Dentist. [Lebon et Al. 2016]
- Dentist that want, due clinical situation and material choice, want to skip the external dental technician collaboration and do by himself (or by an internal dental technician collaboration) with Chair-side strategy [Lebon et Al. 2016]

This last option is mine, having bought several years ago a 4 axis wet milling machine, Cerec MCXL (Dentsply Sirona, Charlotte, USA).(Fig.1.21) The milling machine dimensions cannot be considered as a limitations (700mm X 425mm X 420mm), with a weight of 43Kg and noisiness < 65 Decibel (dB) that allow me to have put it in my clinic without disturbing my daily practice and patients.



Fig.1.21 : Milling Machine CEREC MCXL (Dentsply Sirona, Charlotte, USA) present at Studio Odontoiatrico Solimei, Genova

Using this device, I have the possibility to mill and use different materials (ceramics, polymers, resins) due to different clinical situation needs. The milling ability is for one

block per tooth and, depending on the material choice and the restoration dimensions, the milling procedure can last between 7 (ex.: polymers for an anterior teeth) and 20 minutes (ex.: ceramics for posterior teeth). This milling process can be divided in :

- Initial roughing - the cutting tool movements are very fast removing as much material as possible
- Finishing - it's able to smooth the surface already milled by the previous step with smaller and slower cutting tools movements
- Detail sequence - is the last part of the milling process, used to cut finer occlusal detail and the closure line with slowest movements

Due to the Company strategies and milling machine properties these three step can be separated or follow up each others without cutting tools removal necessity (this last case is mine milling machine one).

1.2.3 CLINICAL STUDY CASE

Here below a clinical case made by me of an old metal restoration on the first upper molar that has been damaged by the aging and has to be replaced (Fig.1.22).

The clinical procedure is to remove the old restoration with a diamond bur mounted on high speed turbinE, with water refreshment to avoid to damage the vital pulp of the tooth, and clean the remaining healthy surface of the tooth to give a proper cavity geometry (Fig.1.23) [*Goujat et Al.* 2019].



Fig.1.22 : Clinical study case - First upper molar - Starting time with the old metal restoration that has to be removed



Fig.1.23 : Clinical study case - First upper molar - Tooth cleaning and cavity design - the tooth is now ready to be impressed/scanned

When this procedure is completed, is necessary to take an impression of the tooth surface prepared and adjacent teeth with an intraoral scanner, CEREC Bluecam (Dentsply Sirona, Charlotte,USA)(Fig.1.24-1.25), which detects through a Blue Light Emitting Diode (LED) camera with automatic capture single images and matches them to generate a digital 3D model characterized by extreme precision. The image is captured only when it is still, ensuring that the images are always in focus. The generated file is processed by the dedicated CAD software Cerec (Dentsply Sirona, Charlotte,USA) to have a restoration CAD proposal automatically generated by the CAD software itself. (Fig.1.26)



Fig.1.24 : The dentist can scan patient's teeth with the live recording on the connected screen, evaluating evaluating to complete the necessary dental surfaces and having an immediate verification of the correctness and completeness of the images obtained through a visual analysis.

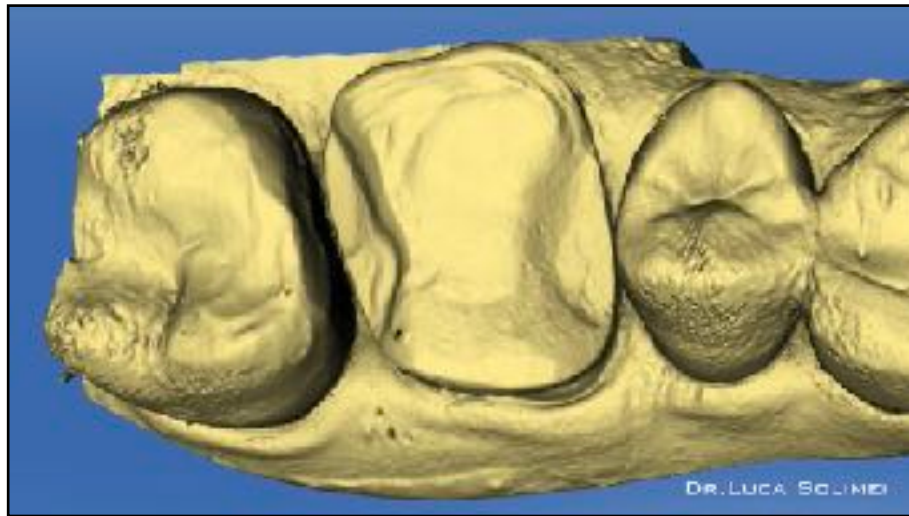


Fig.1.25 : Clinical study case - First upper molar - The tooth (in yellow) has been scanned with Bluecam (Dentsply Sirona, Charlotte,USA)

This procedure can take 1 or 2 minutes for the scanning (it depends on the number of teeth to be scanned) and 5 minute for the full procedure on the CAD software , decreasing with improved knowledges and experience. Once obtained a preliminary proposal depending on adjacent teeth morphology, the dentist or the technician can modify, due to each company software tools, the design proposed changing some morphological details or the position of the CAD restoration.

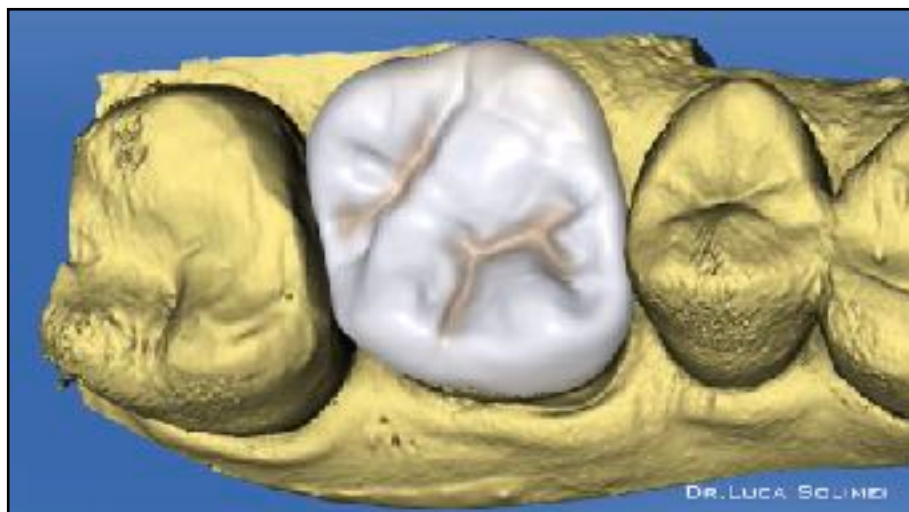


Fig.1.26 : Clinical study case - First upper molar - The CAD (in white) of the restoration - the Dentist can evaluate and eventually make some modifications.

Due to my already mentioned milling machine Cerec MCXL (Dentsply Sirona, Charlotte, USA) is possible to mill in a average time of 7-10 minutes, depending on restoration dimensions, a Lithium Disilicate ceramic block e.Max (Ivoclar Vivadent, Schaan, Liechtenstein). (Fig.1.27).



Fig.1.27 : Clinical study case - Lithium Disilicate ceramic block e.Max (Ivoclar Vivadent, Schaan, Liechtenstein.) before and after the milling procedure

The milled green new restoration need a surface finishing made with dedicated burs (Cod. 94011C, 863104012, 858104014 Komet, Gebr. Brasseler GmbH&Co.KG, Deutschland) just to remove the supporting pin and eventually increase the morphological details and smooth the surface. (Fig.1.28)

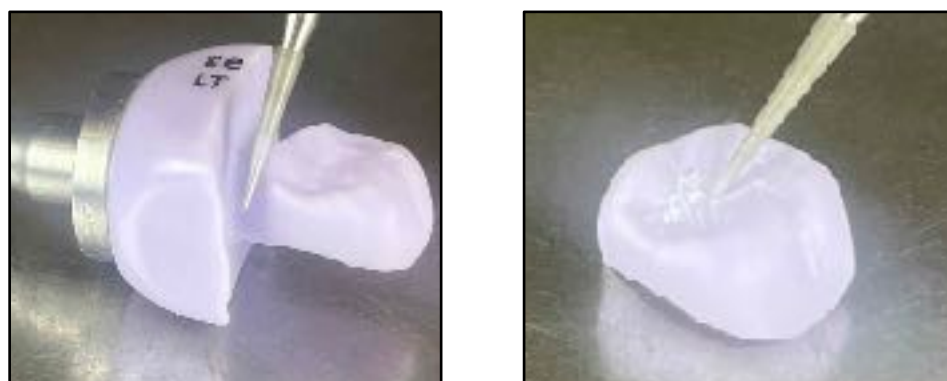


Fig.1.28 : Milled restoration finishing procedures: on the left a diamond bur used to cut the supporting pin, on the right the deepening of morphological details

The last procedure is to characterize the restoration from an aesthetic point of view through painting it with dedicated colors and a superficial glazer that makes the final restoration smooth and shiny.(Fig.1.29)



Fig.1.29 : Step of staining with different shades to give a deeper tridimensionality and glazing procedures to create a glossy smooth surface

This stain and glaze phase precedes the firing of the restoration in a dedicated sintering furnace. The sintering process, in terms of duration and temperature, varies depending on the material.(Fig.1.30)



Fig.1.30 :The oven Programat P300 (Ivoclar Vivadent,Germany) and the firing program

Once this last phase has been completed, I wait the temperature drops to be acceptable for handling the restoration and then we proceed, (Fig.1.31) according to



Fig..1.31 : Clinical study case - First upper molar - The restoration is now cemented on the remaining healthy dental tissues

the adhesive protocols recommended by the company, to its cementation on the healthy tooth surface.

This type of treatment can be possible just when we have a remaining healthy part of the tooth on which we can cement the restoration. In many case, unfortunately, the lack of remaining healthy tissues or some other problems like root fracture, bone crest volume deficiency that can decrease the predictability of the therapies don't let the dentist to use this approach and it become necessary to go on with extraction. (Fig.1.32-1.33)



Fig.1.32 : Clinical study case - First upper premolar - complex situation with a vertical fracture on the dental root that determinate the extraction of the root.



Fig.1.33 : Clinical study case - First upper premolar - complex situation with an extraction of the dental root.

Once extracted the tooth, due to the bone crest situation, it is possible to immediately put an implant in titanium (Fig.1.34) and, if the primary stability is present [Luca Solimei Thesis,2003] it is also possible to make a no functional immediate loading. [Al Sawail et Al. 2016] This procedure means that, after having inserted the titanium implant in the bone crest and evaluated a lack of any movement, it is possible to proceed taking a scanning with intraoral scanner, CEREC Bluecam (Dentsply Sirona, Charlotte,USA) of the titanium implant position, through a titanium reference, called implant abutment, screwed on the implant itself, and its relationship with adjacent teeth.(Fig.1.35)



Fig.1.34 : Clinical study case - First upper premolar - different x-rays made : before the extraction (on the left), after the titanium implant positioning (in the center) and after the screwing of a titanium abutment that will be the base on which is necessary to cement the new crown.



Fig.1.35 : Clinical study case - First upper premolar - It is possible to see the titanium abutment (the metal cylinder that comes out from the gingiva) , screwed on the titanium implant, that the scanner has to record as a reference of the position of the titanium implant itself.

As already described in the previous clinical study case the dedicated CAD software CEREC elaborates a CAD of the new anatomical tooth (Fig.1.36) that has to be manufactured through milling a Lithium Disilicate ceramic block e.Max (Ivoclar Vivadent, Schann, Litchnestein) with previously mentioned CEREC MCXL (Dentsply Sirona, Charlotte, USA) and then, after stain and glaze procedures and the sintering process already described, I could cement it, according to the adhesive protocols recommended by the company, on the implant titanium abutment used for the scanning (Fig.1.37).



Fig.1.36 : Clinical study case - First upper premolar - The scanning procedures of the implant titanium abutment (on the left) and the CAD proposal of the tooth (on the right).



Fig.1.37 : Clinical study case - First upper premolar - The final restoration cemented on the implant titanium abutment (x-Ray and clinical situation)

1.3 ADDITIVE MANUFACTURING

1.3.1 3-D PRINTING IN MEDICINE AND DENTISTRY

Additive Manufacturing (AM) or 3-D printing, is a production process that allows the creation of different objects through the use of various techniques and materials. Although it has only become widespread in recent decades, the beginnings of this technology date back to the 1980s. Subsequently, printing has been improved, both in terms of time and product, and this has ensured its application in various fields such as the dental sector.

In contrast to the classic technologies, such as methods based on melting or softening of the material, or subtractive techniques, 3D printing is based primarily on the deposition of successive layers of material offering.

Restorations manufactured by means of subtractive methods (milling) represents a reliable treatment option in modern dentistry, as demonstrated in several clinical studies [Mazza *et Al.* 2021; Mangano *et Al.* 2018; Kraus *et Al.* 2019; Tabesh *et Al.* 2021; Abdulmajeed *et Al.* 2016]. However, milling has some limitations, such as the considerable amount of raw material that is wasted (the material used for the supports and remnants of milled discs, which cannot be re-used).(Fig.1.38)



Fig.1.38 : Milling process wasting materials in a ceramic disk. The dental technician can obtain different teeth, related to different clients-dentists, from the same disk

During milling, the burs are subject to abrasive wear, particularly when fully sintered ceramic material blocks are milled [Methani *et Al.* 2018]. These blocks are dimensionally stable, but their milling can generate microcracks on the surface of the ceramic, which can

compromise the longevity of the restoration [Methani et Al. 2018; Huang et Al. 2003]. A valid alternative is provided by using pre-sintered blocks or discs. The use of these more workable materials does not damage the burs; however, the restorations are subject to dimensional changes after sintering, which may partially affect the accuracy [Methani et Al. 2018]. Finally, with milling, the reproduction of surface geometry is dictated by the size of the milling burs, and the number of working axes of the computer numerical control (CNC) machine; therefore, in some applications (such as the milling of individual zirconia abutments), milling suffers from a limited ability to access smaller hollow areas and/or bypass undercuts [Methani et Al. 2018]. Another important limitation directly relates to the geometry of the restoration to be milled and the toolpath obstacles. More complex and detailed the restoration geometry is, more complex the toolpath strategy must be to accomplish the restoration. Sometimes the tooth shape to be fabricated has increasingly complex geometries and undercuts, resulting in the inability of the tools to correctly mill the restoration:

- The part cannot be milled resulting in the production process being stopped
- The workpiece cannot be milled and the production process is stopped. Over-milling occurs, resulting in thinner restoration thicknesses or the removal of more material. This situation occurs, for example, when the inner space of a crown is physically smaller than the smallest cutting tool a milling machine can use, potentially creating a reduction in force, less precision, and consequently inadequate product and/or material.

Modern additive manufacturing (AM) or 3D printing techniques promise to solve these problems [Methani et Al. 2018, Alharbi et Al. 2017, Barazanchi et Al. 2017]. AM is now used by prosthodontists worldwide, for the fabrication of parts in resin (such as models) (Fig.1.39)[Rungrajwittayakul et Al. 2020, Mangano et Al. 2020], interim restorations [Martín-Ortega et Al. 2021], denture bases [Anadioti et Al. 2020] and in metal [Revilla-Leon et Al. 2019]. 3D printing allows the manufacture of extremely complex objects, hollow inside or with a gradient of material, without the limitations associated with other tools used for the classic molding, casting, and milling techniques [Methani et Al. 2018, Alharbi et Al. 2017, Barazanchi et Al. 2017, Revilla-Leon et Al. 2019].



Fig.1.39 : 3D printed rain model reproducing the starting clinical situation

Furthermore, 3D printing reduce the waste of material, potentially reducing working time [Methani et Al. 2018, Barazanchi et Al. 2017, Revilla-Leon et Al. 2019]. Some operative time reductions are too small to result in relevant benefits. Although operative time reduction is a major advantage that could contribute to significant financial reduction, the increased time needed for surgical planning is rarely considered. [Mavilli et Al. 2007] Patients can additionally benefit from technology as anatomical models improve patient understanding of the pathology and procedure. This results in improved patient-doctor communication and greater patient satisfaction. Tactile anatomical models can also assist medical and surgical students to improve their knowledge and clarify some details that just seen theoretically can be eventually misunderstood.

The main advantages of additive manufacturing AM are:

- the ability to give rise to extremely complex and detailed shapes without the use of molds or tooling (Fig.1.40)
- the waste of material is minimal, which means less waste and lower production costs
- the materials that can be used are many: from metal, ceramic or polymers
- additive manufacturing is mainly used in rapid prototyping to produce realistic models of the object, in order to imagine what the final product will be

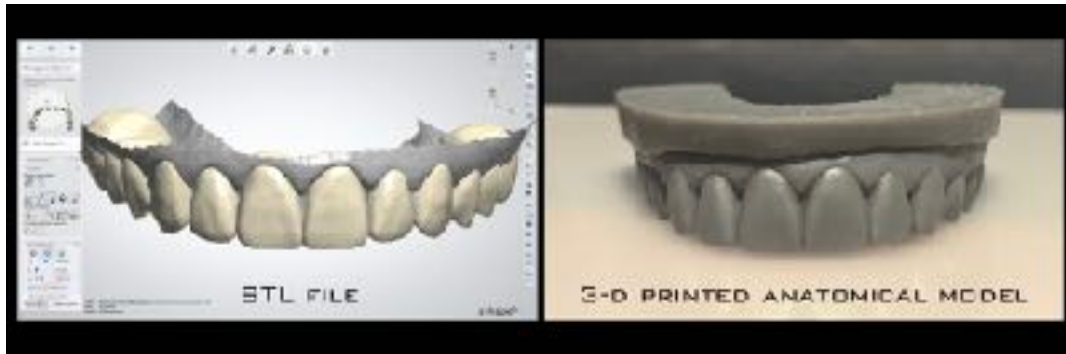


Fig.1.40 : From the STL file to the 3-D printed anatomical model, made by Dr.Luca Solimei with SLA 3D printer Formlabs Form2

Clinical benefits were advocated in literature to justify the main limitations of AM technology: costs, necessity for technical skills and technological availability. Cost-effectiveness was widely debated in literature: the decreased surgical time and employment of self-fabricated 3D-printed models or guides (instead of outsourced manufacturing) appeared to counter balance the price of the starting technological investments and the technical skills required for pre- and post-processing printing activity [Mazzoni et Al. 2013]. Interestingly, in many studies on customized surgical planning, a specific description of the technology adopted is not available due to the choice of externalization of the 3D printing process, as often declared by authors themselves [Martelli et Al. 2016]. To date, the rapid expansion of AM machines and materials has significantly lowered costs, making this technology more accessible. The additive manufacturing methods are several, due to the printing material, as mentioned in the classification of Additive Manufacturing [Appendix A].

New printing technologies make it possible to produce objects based on a digital model developed using dedicated CAD softwares .

The file with the design to be printed contains instructions that the printer must follow and that will be sent by the processor. The models made are produced thanks to the superimposition of layers of condensed polymers of various kinds that aggregate and form a real solid material. The result is an object that has all the characteristics and measurements previously designed on a computer.

The 3D printing process can be divided into three steps:

- Modeling

- Printing Phase
- Refinement

3D Modeling and Fabrication

This is the first stage of the process and consists of two steps.

1. The first passage previews to construct the model through a 3D software (ex.: Ultimaker Cura; Simplify3D; Slic3r) Through CAD type programs, the object to be built is drawn on the computer and any modifications deemed appropriate are implemented.

3D printing software in a professional environment should provide:

- Flexibility for a wide range of workflows
- A reliable process that delivers accurate results with minimal configuration
- An efficient process that optimizes print duration, material use, and part strength
- Support for multi-extrusion printers
- Functional, secure scalability across users and locations

Every CAD model must be prepared for 3D printing using slicing software, which 'slices' the model into thin horizontal layers. Slicing software also performs a complex range of functions to prepare a 3D model for fabrication. (Fig.1.41)

Slicing begins with an STL, OBJ, X3D, or 3MF file easily exported from CAD 3D-modeling software.

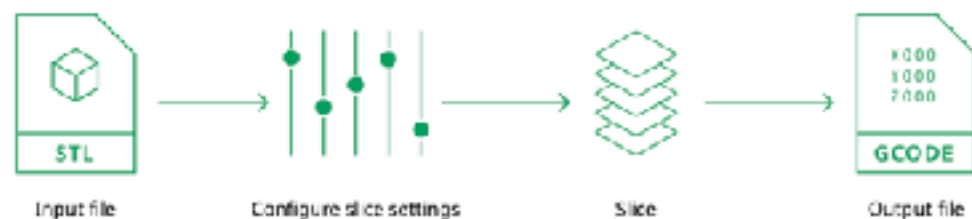


Fig. 1.41: scheme from ©Ultimaker BV 2020 EN 09/2020 v2.02

2. The second step is to transform the .STL, .obj or .stl files of the virtual design into a set of instructions to be communicated to the printer. As the object is built layer by layer, dedicated software "cuts" the virtual model into many two-dimensional horizontal planes.

Printing phase

In the actual object creation stage, the printer reads the ".stl" file and begins to lay down layers of powders, ceramics and eventually binders to create the model through a series of horizontal sections. These sections, which correspond exactly to the virtual layers with which the CAD program has subdivided the designed object, are joined or merged to obtain the final object.

One of the most important advantages of this technique is precisely the possibility of creating any geometric shape or figure without the limitation of undercuts. The thickness of the layers is typically around 100 microns (0.1 mm). 3D points are approximately 50 to 100 microns in diameter. Object dimensions should not be greater than 200x240x150 mm X-Y-Z. The maximum resolution is 0.1 mm in Z and 0.2 mm in XY [Ngo *et Al.* 2018]. Each model must have at least one support plane. Building a model with modern methods can take many hours or even days, depending on the method used and the size and complexity of the model.

Refinement

Although additive manufacturing allows for high quality resolution and output, you may decide to print a slightly larger version of the object at standard resolution and then remove excess material or small imperfections with a high resolution subtractive process. This allows for greater accuracy. Some additive techniques use supports during printing to be able to make and support protrusions in the build phase, and once the process is complete, the supports must be removed.

Printers are now one of the most revolutionary tools serving modern medicine. Of all the sectors in which 3D printing is used, this is certainly the most complex, requiring extreme customization and a great deal of research.

In fact, there are many potential applications of 3D printing in the medical field, mainly in the following areas:

- Surgical Aids;
- Medical Devices;
- Drug Delivery Systems;
- Bone Implants and Tissue Engineering;
- Organ Printing.

In many fields of medicine, such as traumatology, cardiology, neurosurgery, plastic surgery, and craniomaxillofacial surgery, 3D printing is mainly used for digital imaging in surgical planning, personalized surgical devices, and patient education [Aimar *et Al.* 2019]. 3D printed models have been used as surgical aids for a few years now, thanks to their increasingly sustainable cost and speed of production, as they can be delivered within two to three days of request. They can serve as preoperative aids to simulate and plan surgery, and facilitate communication between surgeon and patient. (Fig.1.42)



Fig. 1.42 : a 3D printed prototype of a lower maxilla

Three-dimensional printing, in fact, makes it possible to create prototypes of organs very similar to the original even recreating tumor masses so that doctors can fully analyze how to penetrate the tissues. In addition, with the new scanning techniques it is possible to think about the production of customized medical devices, in particular anatomical braces and prostheses, which patients can customize in aesthetics, functionality and even in therapeutic performance, with the additional implication concerning the doctor-patient relationship. Printers for Drug Delivery Systems are already on the market and can produce over two thousand capsules per hour, and accurately controllable drug delivery systems can also be designed and manufactured.

3D printing has also invaded the dental industry once the wide range of printed products in other areas of application is seen. In fact, printing guarantees the efficiency of digital design in the design phase and precision in the production phase. It brings the efficiencies of digital design to the manufacturing stage by combining oral scanning, CAD/CAM design and 3D printing, enabling dental labs to accurately and quickly produce crowns, bridges and models.

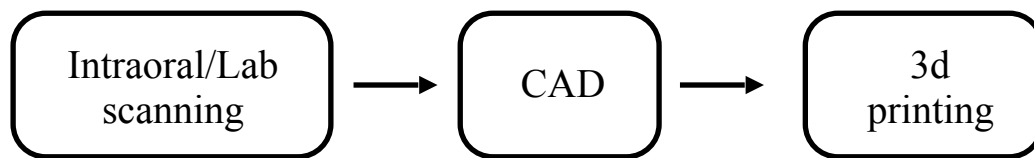


Table 1.1 : the digital workflow from taking information about the mouth of the patients to the final manufacturing

Digital dentistry is enabling more and more labs to speed up production by increasing accuracy and control, making digital dentistry part of their manufacturing strategy.

The main advantages that 3D printing enables are:

1. ability to customize production
 2. reduction of production costs
 3. reduction of production time
 4. high quality of printed products
 5. the ability to easily make changes to the CAD file
 6. greater autonomy for dental offices with the installation of an in-house printer
 7. elimination of physical models of patients' teeth from the warehouse: the models are digitized
- In the field of dentistry, its applications range from prosthodontics, oral and maxillofacial surgery, and oral implantology to orthodontics, endodontics, and periodontics [Oberoi et Al. 2018](Table 1.2)

Oral and maxillofacial surgery	Occlusal splints	Saving time and cost
	Surgical implants	High mechanical strength
	Prostheses	Adjustable porosity
		Convenient and fast
		Accurate
Oral implantology	Working models	Improving the integrity and aesthetics
	Surgical guides	Reducing operative time and risk
		Reducing operation errors
		Simple operation
		High efficiency
Orthodontics	Working models	High accuracy
		Good surface quality
		Light
		High wear resistance

Table 1.2 : 3D printing clinical application classification and main advantages. [Tian et Al. 2021]

Field	Application	Advantage
Prosthodontics	Crown and bridge dentures	Reducing time consumption
		Good fit
		Good detail reproducible
	Complete dentures	Low costs
		Convenient and fast
		Accurate
	Removable partial denture frameworks	Close adaptability
		Uniform contact pressure
		Good mechanical properties

Table 1.2 : 3D printing clinical application classification and main advantages. [Tian et Al. 2021]

- Dental models for restorative dentistry with the trend toward the use of intraoral scanners means that dentists need 3D printing to make a physical model of the scanned jaw. While it is not always strictly necessary to print a master model today, such printing can be used for conventional aspects of fabricating a restoration, such as adding a veneering material.(Fig.: 1.43) Patient model data can be digitally stored and printed only when necessary, easing archival requirements. In orthodontics, treatment can be planned and robotically bent appliances and wires can be created based on a digital workflow using intraoral, laboratory, or even CBCT optical scanning to capture patient data.



Fig. 1.43 : 3-d printed models the technician stratified on with ceramic to achieve the best esthetic result

The Invisalign® system, digitally realigns a patient's teeth to create a series of 3D printed models for the production of "aligners," which progressively reposition teeth over a period of months/years. An example of multi-material printing is in the production of 3D printed bracket splints, printed in rigid and flexible materials for precise bracket placement using orthodontic CAD software. Patient data can be digitally stored and

printed only when needed, resulting in large savings in physical storage space requirements.

- One of the first applications of printing in surgery can be considered as the production of an anatomical "study model". This has been made even more accessible by another important technology that has become indispensable in "modern" dentistry, namely CBCT (Cone Beam Computerized Tomography). This makes it possible to carefully analyze anatomical structures, even that which is particularly complex, unusual or unknown, and to plan or practice a surgical approach prior to surgery.. A wide variety of 3D printers and materials can be used to print medical models, but because it is useful to have such models in the operating room, materials that can be sterilized, such as nylon, are particularly used. Drill and cut guides need to be robust and precise, as well as sterilizable as in a surgical setting, and their use in implantology is becoming common and increasingly an opportunity for the operator. The use of drilling guides and cutting guides allows the creation of a virtual 3D plane, designed on screen by the software and transferred to the operative site. Inaccuracy resulting from the scanning mode, software, and the presence of artifacts can be clinically relevant for subsequent implant procedures or where prostheses are prefabricated and must fit precisely into a pre-programmed postoperative outcome. Precise 3D printers and high-resolution printing materials must be used for surgical guides, and unfortunately some of the best materials that can be used for this purpose are not autoclavable. In addition, with the use of intraoral optical scanners or laboratory scanners, an accurate virtual model of the implant position and dental arch can be developed.(Fig.1.44)



Fig. 1.44: Titanium implant positioning through a 3-D printed resin drilling guide 3D-Pilot (BTK, Italy)

- In fixed and removable prosthetics, treatment can be planned and restorations designed using CAD software. The scan data and design can be used to mill restorations, as also seen in Section 1.2, or print copings, implant abutments, and bridge frameworks. The limitations still relate to the types of materials that can be printed, to date the most popular 3D printing is used to fabricate metal structures indirectly through a lost wax process, or directly into metals or metal alloys. The advantage of printing in resin/wax lies in post-production processing. Printing metals directly requires the use of more expensive technologies that require a great deal of post-processing before the various components can be ready for use. As far as the possibility of printing other materials is concerned, restorations/tooth crowns in resin are feasible, but must be considered as temporary solutions, due to the poor medium-long term performance of the materials themselves. Thanks also to the continuous evolution of technologies and materials, nowadays it is finally possible to make molded ceramic crowns.

1.3.2 AM IN DENTAL MARKET

Research firm Markets and Markets recently released its new report on dental 3D printing [*Market Research Report MD6394, March 2022*], which is expected to generate \$7.9 billion by 2027, growing at an annual rate of 20.2% from this year. Dentists may be more likely to invest in technologies such as CAD/CAM and dental 3D printing to reduce the turnaround time for dental appliances and treatments, and patients may be more likely to opt for these solutions for the same reason. On the basis of application segment, the market is divided into prosthodontics, orthodontics, and implantology, with the latter expected to grow at the highest CAGR (compound annual growth rate) of 21.5% during the forecast period. The negative impact of Covid-19 has certainly slowed down the development of the 3D printing market because, as a result of restrictions from various governments, many clinics and dental labs have had to close, minimizing investment. However, when they reopened, they saw a restart so much so that industry experts believe they can resume in 2021 as pre-Covid levels.

The interest of dentists, as well as patient demand, was increasingly to be able to achieve a fast, independent workflow, and this need, driven by CAD/CAM systems and 3D printers, has made the recovery forecast positive.

The high incidence of dental caries in the population and the fact that a large number of people in adulthood have undergone at least one extraction, makes it increasingly

common to resort to restorative and prosthetic treatments to restore lost dental tissue and it is this need that favors the development of the 3D printing market, aimed precisely at the realization of restorations of aesthetic-conservative type.

The fact that not only in the United States, but also in many populous Asian countries, the elderly population is increasing in percentage, further underscores the need for certain types of dental care that are positively associated with the manufacturing potential of 3D printers. The real advantages of 3D printers are speed and accuracy, making the manufacturing process fast and efficient.

The fact that CAD/CAM systems are increasingly being embraced by the dental industry due to the high precision of restorations suggests that they will be increasingly used in conjunction with dental 3D printers.

An additional interesting aspect of this market sector is the versatility of 3D printing systems as there are industrial-grade, high-productivity 3D printers that have good capacity and quality for dental clinics whose goal remains to have high production numbers and desktop printers, on the other hand, that offer great print quality and are smaller and more versatile, with lower productivity. In the face of increased market demand, price reductions are also occurring, making it easier for small and medium-sized facilities to invest and make the entire dental 3D printer market more accessible.

Lithoz GmbH

Lithoz GmbH was founded in 2011, specializing in the development and production of additive manufacturing materials and systems for 3D printing of high performance ceramics. The 3D printing method that has been developed and adopted by the company for the additive production of high-strength, dense and precise ceramics is Lithography-based Ceramic Manufacturing (LCM). (Fig.1.45)



Fig. 1.45: Lithoz ceramic 3D printing device

This technology is suitable for ceramic applications where high precision and accuracy are required in combination with density and mechanical performance, similar to ceramic injection molded parts. CeraFab machines, developed by the company, allow photocurable ceramic slurry to be automatically dispensed and coated onto a transparent tank.(Fig.1.46)

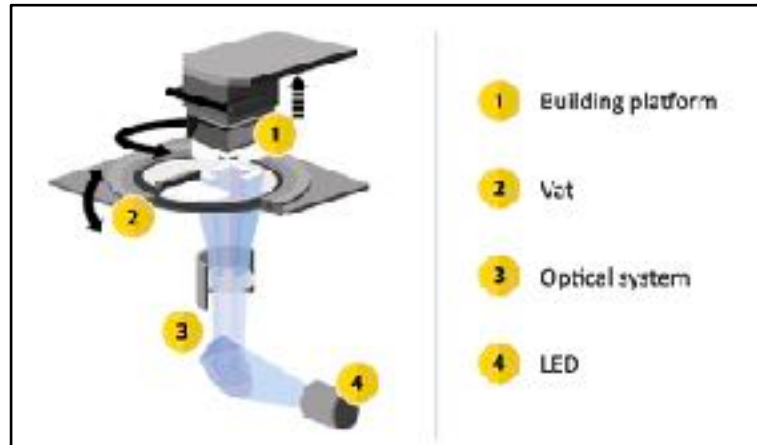


Fig. 1.46: Schematic illustration of the operating principle of CeraFab LCM systems. The arrows indicate the moving directions of the building platform and the vat

LCM meets the challenge of providing fully dense ceramic components with excellent mechanical properties and surface finish in a highly precise and reproducible manner. The layer formation method, typical of LCM, has a number of significant advantages. Unlike other vat light curing methods, parts are not immersed in the slurry, thus minimizing the amount of material required and avoiding the introduction of defects related to interactions between the green parts under construction and the mechanical coater.

In addition, this process reduces the task of cleaning the uncured suspension between the immersed parts, as well as eliminating material recovery operations.

Inert ceramics such as alumina and zirconia offer a mechanically stable metal-free solution for dental implants, crowns and load-bearing bone defects. These materials do not release their components into the human body or generate an antibody response, and therefore the success rate should be higher than that of metal implants.(Fig.1.47)



Fig.1.47 : Dental products 3D printed

Related to the 3D printer device (CeraFab system), from a user point of view is important to evaluate the technical properties (Table 1.3) such as dimensions and weight, that can determinate some limitations for its positioning in the dental Lab/Dental clinic.

Technical Properties	
Lateral resolution	40 µm (635 dpi)
Layer thickness	10-100 µm
Number of pixels (X, Y)	1920 x 1080
Build volume	76 mm x 43 mm x 170 mm (x/y/z)
Data format	.stl (binary)
Number of vats	2
Light source	LED
Build speed	up to 100 slices per hour
Size (L x W x H)	1,8 m x 0,85 m x 1,78 m
Weight	550 kg

Table1.3 :CeraFab 2M30 Technical properties (Source: Lithoz GmbH)

WASP

An Italian company whose vision focuses on 3D printing, *“because a small, fast printer that materializes objects in bio-plastic, clay, silicone, bio-compatible materials, that mills wood and aluminum, allows you to start mini-productions and create what you need yourself.”*

WASP manufactures and sells 3D printers. It works in a research environment defining itself as a machine and material developer.

The proceeds from the sale of 3D printers are invested in research and development of integrated projects in the perspective of a productive revolution that brings widespread well-being. Research that proceeds in parallel in the field of eco-sustainable and functional materials and innovative systems. The projects carried out so far by the group are completely self-financed. A continuous research on materials to extrude, a path that has led them to 3D printing of ceramics and porcelain.

WASP's goal is to build zero-kilometer houses, thus using materials available locally. Such a design requires the machine to be portable and energy-efficient.



Fig. 1.48 : Delta WASP 2040

In 2015 the BigDelta was created, a 12m tall giant printer to build houses, thanks to a complex research path that has involved us in the last three years.

In 2016 the Maker Economy Starter Kit was released, a gigantic architectural scale design and construction system enclosed in a single container, which gives shape to a large mobile technology park dedicated to 3D printing.

In 2018 the Crane WASP was released, a modular collaborative 3D printing system. It reinterprets the classic building construction cranes with a view to digital manufacturing.

WASP Med is a multidisciplinary work team born 4 years ago that brings together doctors, bioengineers, orthopedic technicians, materials producers and WASP for the application of 3D printing in the medical field.

The WASP Med project elaborates 3D printing solutions for the medical sector, proposing a new model of Orthopedic Workshop.

The *Officina Ortopedica Digitale* (ODD) is a network of manufacturing centers that, thanks to shared design, develops customized solutions for the medical field, providing the skills and tools necessary to produce advanced medical devices.

The installation of an ODD requires only the presence of form detection equipment (scanners), a 3D printer (Fig.1.48) , the dedicated material and a technician trained within the project.

DWS

DWS is an Italian company, founded in 2007, producing 3D printers for prototyping and rapid manufacturing, materials for 3D printing, and related management software.

There are many possibilities , due the material and technical properties. (Fig.1.49)

All the devices use 3D stereolithography technology to obtain the extremely high resolution and definition required in the dental sector, is a system designed for large-scale production, ideal for the rapid manufacturing of large quantities of burn-out models, orthodontic models, and gypsum-like models obtained from intraoral scanning.



Fig. 1.49: DWS 3D printers on the market. Different characteristic, different materials manufactured, different technical properties.

3DCERAM

3DCERAM SINTO opened in Limoges in 2001, dedicating its know-how to the production of ceramic parts by additive manufacturing, from 2005 focusing interests and development on biomedical field. 3DCeram has developed its mastery of 3D printing ceramics process, its machines, materials and services as maintenance and trainings. They produce different printers (Fig.1.50) depending on production capacity requirements for biomedical devices or dental. 3DCeram leverages SLA 3D printing technology for more than 10 years to manufacture custom-made or small series of bone substitutes and cranial or jawbone implants.



Fig.1.50 : 3DCeram C-100-EASY

Dimensions 940 x 1060 x 1826 mm (LxPxH) - Weight 750 kg

1.3.3 DENTAL USER PRODUCTS COMMENTS

After reviewing the state of the art on manufacturing processes, both subtractive and additive, and mentioning some of the commercial proposals on the market, it becomes necessary to make some assessments:

- Dentistry deals with individual solutions, each defined by the specifics of the damage and the patient's condition. The optimal solution, unfortunately not always feasible, is when, as from Fig 1.51 to Fig.1.56 it is necessary to perform an intervention on a situation only locally damaged, without apparent interactions with other teeth and in a condition of absence of comorbidity.

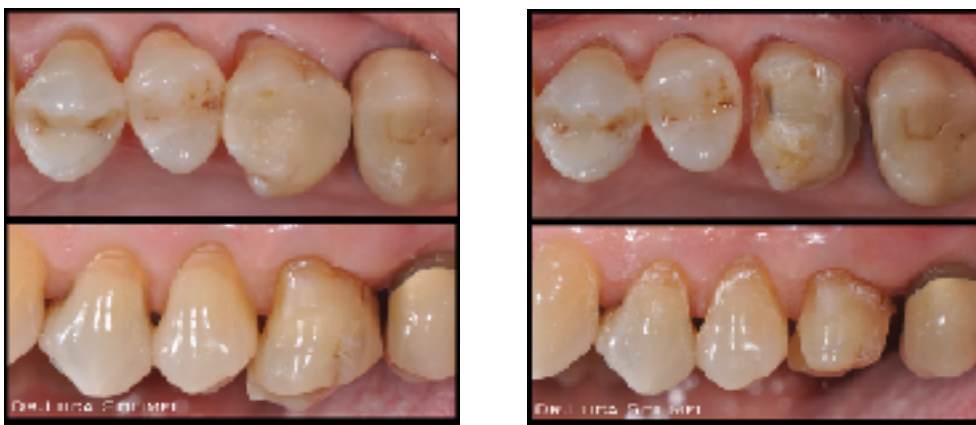


Fig. 1.51-1.52 : from the initial situation (on the left) to the cavity preparation of the tooth (on the right)

Clinical Case Dr.Luca Solimei - First upper left molar

The clinical case is referred to a molar 2.6 (in each picture the second from right) with an old restoration that has to be removed due to a secondary caries disease below it.

In each figure, are visible two different point of view, an occlusal one (on the top of each picture) and a lateral one (on the bottom of each picture).

The procedure requests to remove the old restoration with diamonds burs mounted on a high speed device (500.000 rpm) and clean the tooth from caries disease. It's now necessary to shape the cavity with proper details to create the space for a regular thickness of the new restoration that, trough a scanning and a CAD, can be produced trough a milling machine and then, after dedicated surface treatment due to the material choice, has to be cemented with an adhesive system on the prepared tooth.

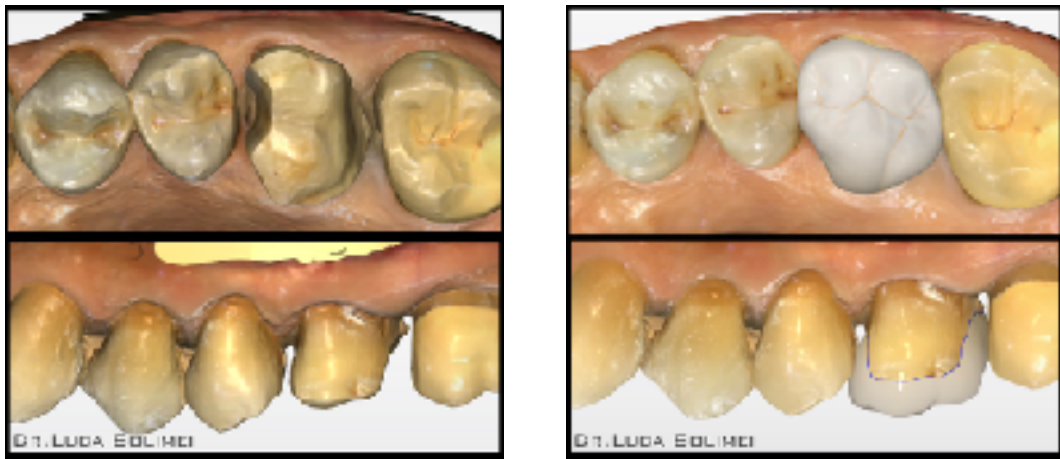


Fig. 1.53-1.54 : occlusal and lateral view of the scanning of the prepared tooth (on the left)
and the CAD proposal (on the right)

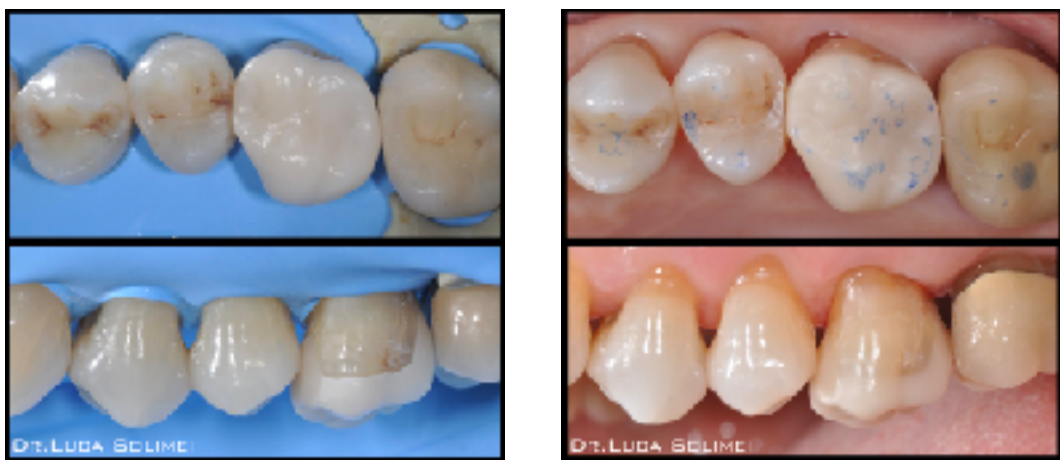


Fig. 1.55-1.56 : evaluating CAM restoration accuracy and contact point with adjacent teeth
(on the left) and the final result after luting procedures (on the right)

In the majority of cases, with the exclusion of cases due to traumas and accidents, the dentist operates instead on:

- Patients not very young, with limited capacity 'regenerative
- Situations deteriorated by previous interventions that further reduce the spectrum of possible technical choices (Fig.1.57-1.58)
- aggravated by long waiting times of the patient who waits until the last moment before asking the professional for help
- Bad habits (smoking, approximate oral hygiene) that contribute to aggravate the problem being treated.(Fig.1.59-1.60)



Fig. 1.57: Previous incongruous treatments



Fig. 1.58: Pink and white ceramic final result on Implants

Clinical Case Dr.Luca Solimei - Fig.20-22 : Prosthetic rehabilitation on implants

The clinical case is referred to a patient that came for an inflammatory situation on the anterior upper area, due to previous treatment with incongruous positioning of implants and as well incongruous metal-ceramic crowns cemented on them. The main mistake was to do not recreate trough surgeries the proper bone and gum volumes and put the implants in a too high position determining gingival retraction, difficulties in oral hygiene mantainance, bad aesthetic results, all accompanied by a low quality of prosthesis (are visible many gaps between crowns and abutments). In this case the ideal Plan of Treatment should be to extract old implants, make a bone regeneration and then, after the healing time, positioning titanium implants and a new prosthesis on them. Unfortunately the patient refused it due to economical reason and I performed, thanks to my dental technician collaboration, a new prosthesis with pink ceramic that could cover the lack of volumes obtaining a better aesthetic result with a more acceptable oral hygiene mantainance.



Fig. 1.59: Bad oral hygiene that determines unhealthy situation



Fig. 1.60: Pink and white ceramic final result on teeth

Clinical Case Dr.Luca Solimei - Fig.22-23 : Prosthetic rehabilitation on teeth

The clinical case is referred to a patient that came with a not acceptable oral hygiene (in Fig 20 are visible tartar blocks) that determined inflammation, bone crest and soft tissues retraction with teeth mobility. In this case the ideal Plan of Treatment should be to extract not stable teeth, make a bone regeneration and then, after the healing time, positioning titanium implants and a new prosthesis on them. But, due to the lack of oral hygiene as well as a bad patient compliance, the proposal, accepted by the patient, was to perform, thanks to my dental technician collaboration, a new prosthesis with pink ceramic that could cover the lack of volumes obtaining a better aesthetic result with a more acceptable oral hygiene maintainance.

In these conditions the problem related to the single tooth, intended as a visible part outside the gum and therefore identifiable in the anatomical crown, is aggravated by the loss of stability of the part immersed in the periodontal tissues (bone, periodontal ligament, gingiva). In these cases it is necessary not only to treat the crown but also to operate on the supporting structures, therefore working on the consolidation of the bone support in order to be able to opt for a radical solution such as that offered by an implant. The dental implant is a medical device of surgical type used to replace one or more missing teeth by rehabilitating functionally and aesthetically the area concerned, allowing the support of a prosthetic substitute, the dental crown, through the direct support of the bone thanks to a biological process known as osseointegration. [Lages et Al. 2018]

The most commonly used type is formed by one or more sections, usually varying in shape between cylindrical and truncated cone, and is often provided in its endosseous

part with coils or other accessory retention elements. The most frequently used material is titanium in its commercially pure form, as it allows for better osteointegration, forming an intimate bond with the bone of the upper and lower jaw. (Fig.1.61)

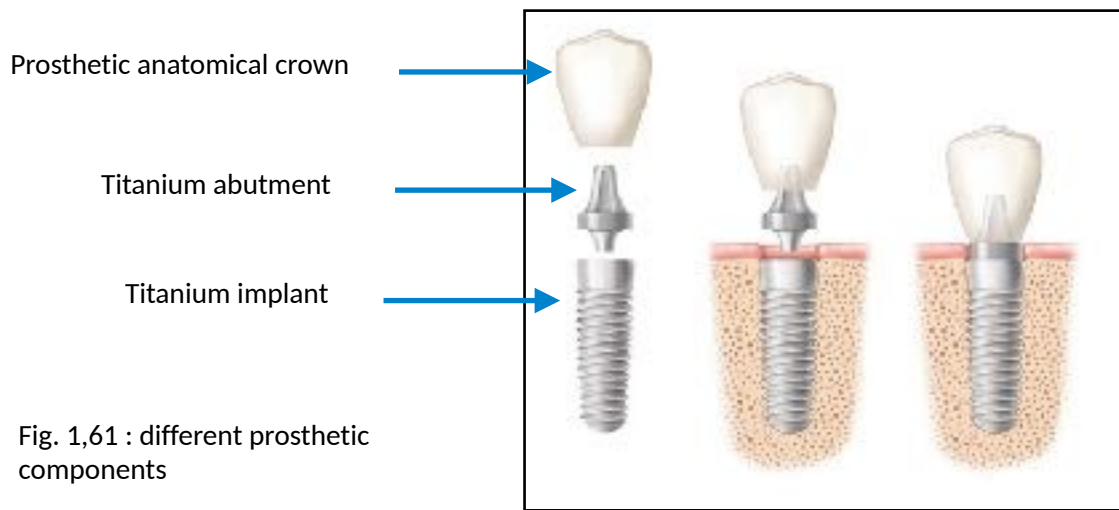


Fig. 1,61 : different prosthetic components

The success or failure of implants depends both on the health status of the patient receiving it and any medications taken that have a possible impact with the osteointegration and the condition of the tissues of the mouth, without of course neglecting the necessary skills of the practitioner performing the therapies. In fact, the prerequisites for the long-term success of osteointegrated dental implants are having healthy bone and gum.(Fig.1.62)

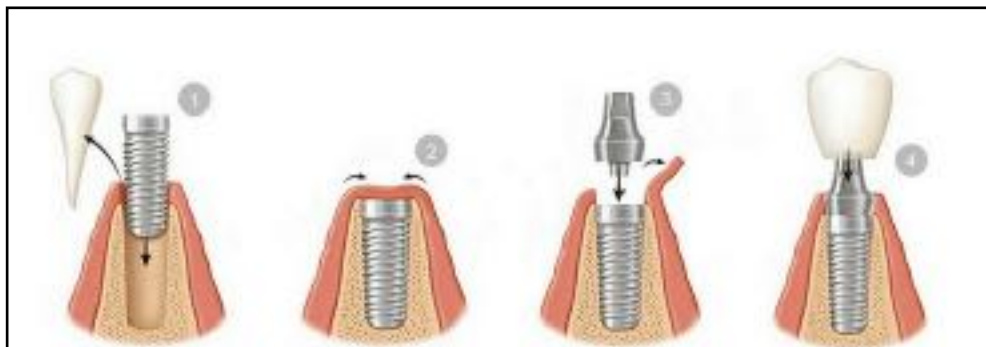


Fig. 1.62 : Different phases: 1- implant insertion; 2- waiting of the osteointegration; 3- fixing on the implant of the prosthetic supporting structure (titanium abutment); 4- Prosthetic anatomical crown positioning

Since both of them can atrophy after a dental extraction procedure, it is sometimes necessary to resort to bone-originating gum grafts in order to recreate ideal bone and gum conditions. The risks and complications related to implant therapy are divided

between those that occur during surgery (such as excessive bleeding or nerve injury), those that occur in the first six months (such as infection and failure of osteointegration resulting in mobility of the implant itself) and those that occur in the long term (such as peri-implantitis and mechanical breakdown).(Fig.1.63)

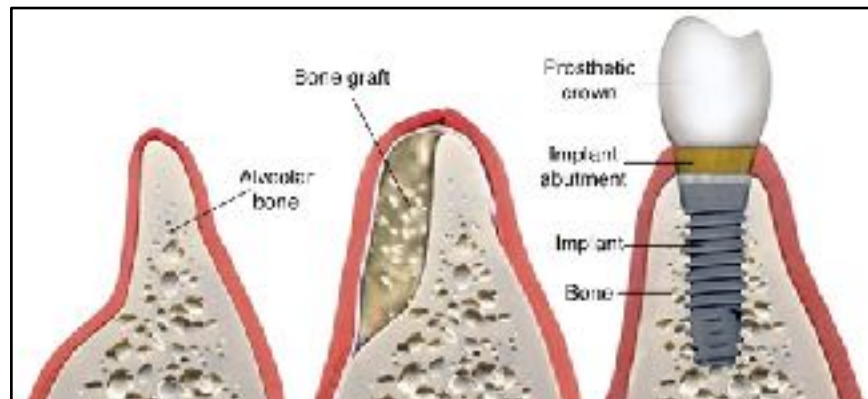


Fig 1.63 : Bone regeneration for implant placement. On the left is visible an atrophic bone crest that, due to a lack of volumes, cannot accept the insertion of an implant. It becomes necessary to increase these volumes (in the center) with different typologies of techniques creating a proper support for the implant and the connected prosthetic components (on the right)

The implant post is inserted into the bone matrix, whose structure is identifiable in a compact component, or lamina dura, and a trabecular part, or alveolar bone. The stabilization of the post within these two types of bone is essential to ensure the proper functioning of the overlying crown.

Many different types of implants have been produced at the moment to optimize, essentially through different geometries of the gripping thread of the post, its stabilization within the bone. (Fig.1.64)



Fig 1.64 : Different implants shapes, dimensions and prosthetic connections

The problem is currently understood and partially solved. In fact, the implant (also called fixture) has to work in complex conditions due essentially to some fundamental aspects:

- Bone is not an isotropic material but a tissue structured in cortical and trabecular with different capacities of resistance and flexibility to the loads applied through the dental elements surrounded by the periodontal ligament
- The loads applied are not only axial but, according to the theory of mastication, also the movement of the two dental arches facing each other (rotational, translational, etc. etc.), generating a complex of stresses to be assessed
- The conditions of the bone are in continuous variation: the progression of age leads to a reduction of the organic component with a subsequent reduced ability to dissipate the stresses and developed there. At the same time the inorganic component can undergo progressive further embrittlement due to the action of drugs that contribute to modify the structure of the material. [Khac-Dung et Al. 2018]
- Even in the absence of co-morbidities, bone is a self-healing material, with the ability to adapt to the direction and intensity of the loads imposed. This implies that a new implant inevitably tends to modify the distribution of stresses not only on the site of application but also in the surrounding areas, involving in the physiological response the adjacent areas. The situation is complicated when working with several implants, perhaps installed at different times, with different materials, which have gradually readjusted their position according to the changes in operating conditions in the patient's mouth.

The evaluation made so far on CAD/CAM techniques applied to dental problem solving shows that there are many solutions available on the market to help the dentist to individually perform the rehabilitation of a dental element to meet the specific need of each patient.

The advent of additive manufacturing techniques has allowed individual dentists to couple a very effective method of creating dental crowns exactly aligned to each patient's condition.

In fact, these manufacturing technologies close a digital workflow, potentially managed entirely by the dentist, which involves taking an impression of the oral cavity and the dental elements present through an intraoral scanner (which has long since replaced traditional silicone impressions) with the generation of a file on which to create the CAD

project and from which to extrapolate the file of the final work to be produced through CAM. (Fig.1.65)

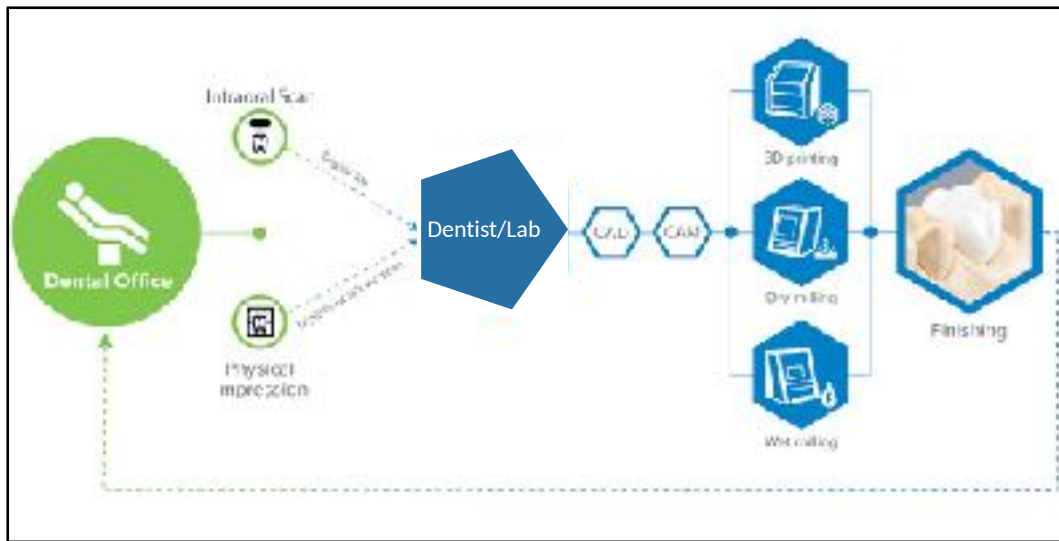


Fig. 1.65 : The digital workflow : after taking an impression (analogical with dedicated silicones or digital with scanners), the CAD/CAM procedures can be done by the dentist himself (chair-side strategy)or the dental technician and then, through already mentioned different devices (wet or dry milling machine, 3-D printers), the prosthetic element can be positioned in the patient mouth

In this way it is possible to make an extremely precise evaluation of the damage to be corrected and it is also possible to realize a substitute at first with extractive techniques (milling machines) but now also with additive (3-D printers) .

These 3D printing techniques allow to work easily with polymeric and ceramic materials, in order to realize dental crowns able to satisfy practically all the needs found in the dental field.

Leaving aside the techniques applied to polymers, not of immediate interest for this PhD and however briefly described in Appendix B, we want to focus attention here on the applications available for ceramic materials.

Brands such as mentioned Lithoz, 3D Ceram etc. are sure references for the demanding dentist who is looking for a crown that can be made with ceramic materials through additive printing. The materials used are Zirconia, Alumina and their blends and the quality is currently close to that obtained with extractive procedures of non-sintered ceramic blocks.

What is available on the market focuses on the obvious, i.e. on dental crowns.

The printers mentioned above are bulky, complex and expensive machines that are not suitable for a dental professional to operate in their office. This aspect can be an

advantage, declining to others, experts in CAD and printing procedures, the realization of artifacts dedicated and ordered by dental professionals. This business model (ex.: Materialise) has numerous advantages:

- relieves the individual dentist from incurring expenses beyond the capabilities of the individual practitioner, in terms of both initial investment and material procurement
- it guarantees the non-obsolescence of the equipment used through the continuous updating of software and hardware maintenance
- it allows to make use of expert and updated technicians in the additive sector - it allows to take advantage often of consulting services on the planning and realization itself.

On the other hand, this system hides some limitations that prevent the dentist from:

- to be able to intervene directly, individualizing each situation in practice
- being able to plan every single treatment according to his own timing and the needs of the patient
- develop hidden-knowledge that is the main technical asset of the dental office and a stimulus for continuous learning
- it does not allow the dentist to deal with issues outside the scope of the general business model.

This Doctoral Thesis moves away from what has been presented, which is already on the market with the advantages and limitations described, to focus on a different topic, less obvious but essential, which is the design, study and realization of ceramic supports specifically dedicated to the stabilization of dental implants. The topic is not currently studied and developed by the manufacturers of the most famous 3D brands and requires a deep knowledge of surgical techniques and problems related to the stabilization of the implant inserted in the patient's bone, i.e. make it functional to the mounting of a dental crown.

The following Chapter 2 describes the problem in detail.

CHAPTER 2

BONE REGENERATIVE METAL FREE STRUCTURES

2.1 IMPLANTOLOGY PRINCIPLES

Implant-prosthetic rehabilitations, in the treatment of edentulous conditions, now represent the best therapeutic choice. [Moraschini et Al. 2015] (Fig.2.1)

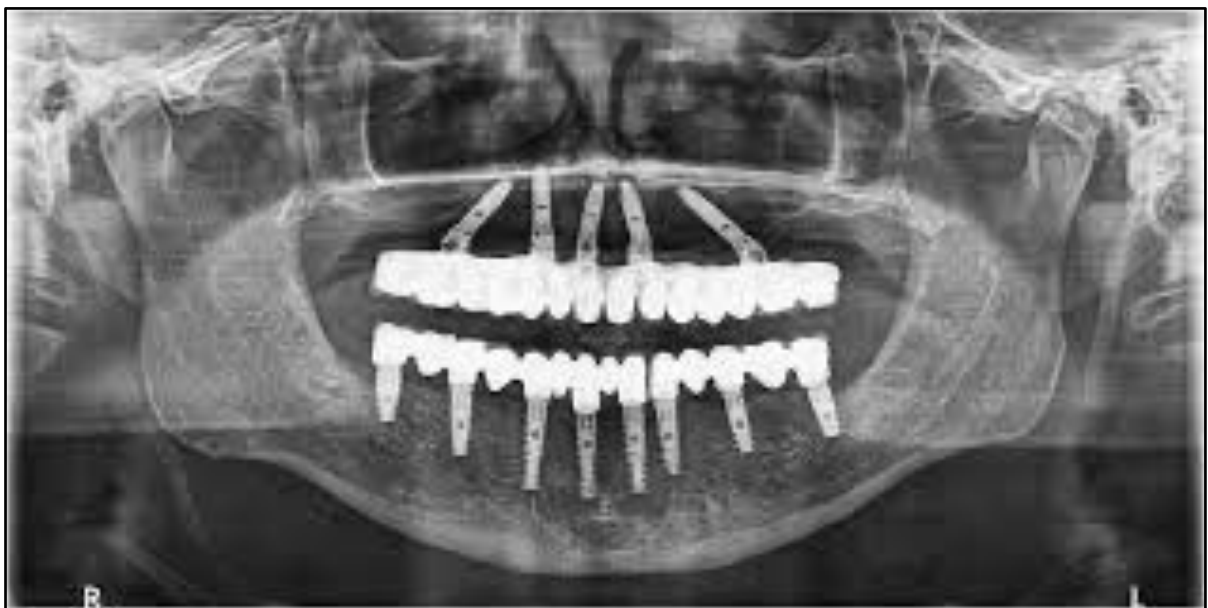


Fig 2.1 : x-Ray evaluation of Full-arch prosthesis implant supported

As known, the implant is inserted into the alveolar bone respecting an optimal primary stability , evaluated with two different methods: insertion torque (IT, expressed in N/cm), [Lemos et Al. 2021] measurable with a manual dynamometric torque wrench, able to measure torques up to 100 N/cm and resonance frequency analysis (RFA) [Andreotti et Al. 2017], used to measure the implant stability quotient (ISQ) (Osstell AB, Göteborg, Sweden) and then undergoes the process of osseointegration, corresponding to secondary stability. [Lages et Al. 2018](Fig.2.2)

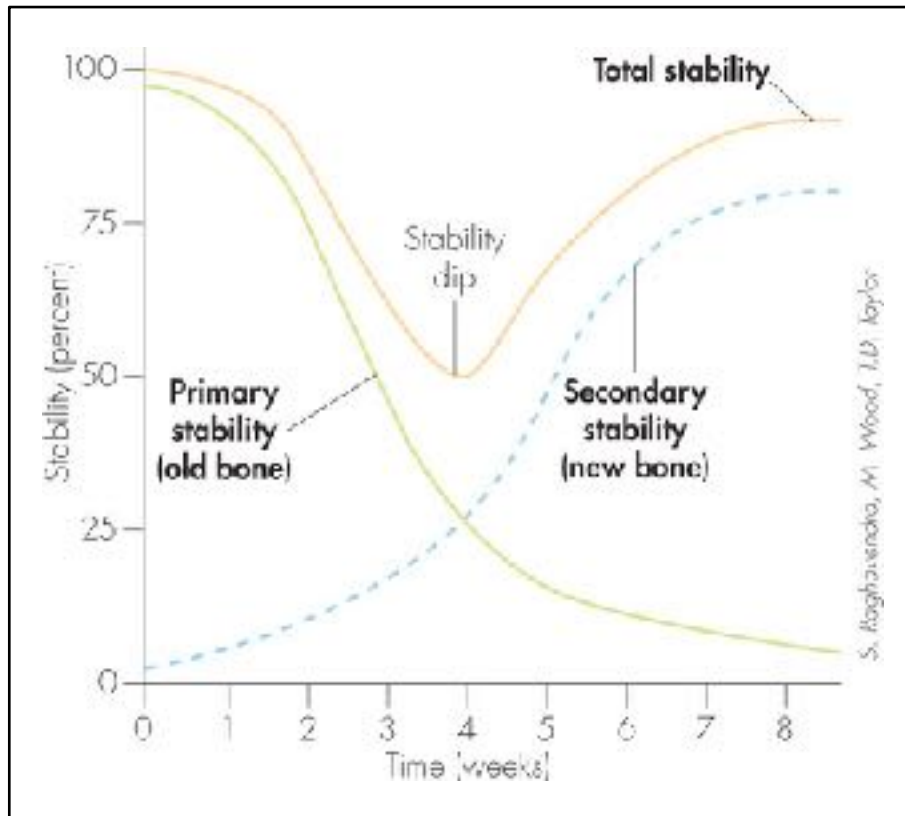


Fig 2.2 : After its positioning, the implant stability is guaranteed by the native bone quality and quantity that determinate primary stability and the new bone generation that surround the implant che determinate the secondary stability. Both give the total stability, important for the long term predicability of the implant

Native bone is always the gold standard for implant placement. However, in order to retrieve for implantation purposes maxillary jaws subject to severe atrophy, the need to implement the present skeletal structure often becomes systematic. In this regard, several bone augmentation techniques based on the insertion of bone grafts have been studied and validated. Autologous tissue is in turn the reference standard, but it is however burdened by operational complexity and morbidity for the patient. A valid compromise can be represented by the addition of bone substitutes: the most widely used in the dental field are xenogenic ones. [Majzoub et Al. 2019]

It is clear that xenograft has different characteristics from autologous graft, which is also different from native bone: it is desirable that these differences are as small as possible. However, it seems logical to expect that the behavior of the implant may vary, in terms of stability, depending on the bone substrate.

Often, however, we are faced with atrophic ridges (Fig.2.3) , with reduced volume in the bucco-lingual/palatal sense, according to class IV of the Cawood and Howell classification, or with an additional vertical component, corresponding to class V. [Cawood and Howell 1988]

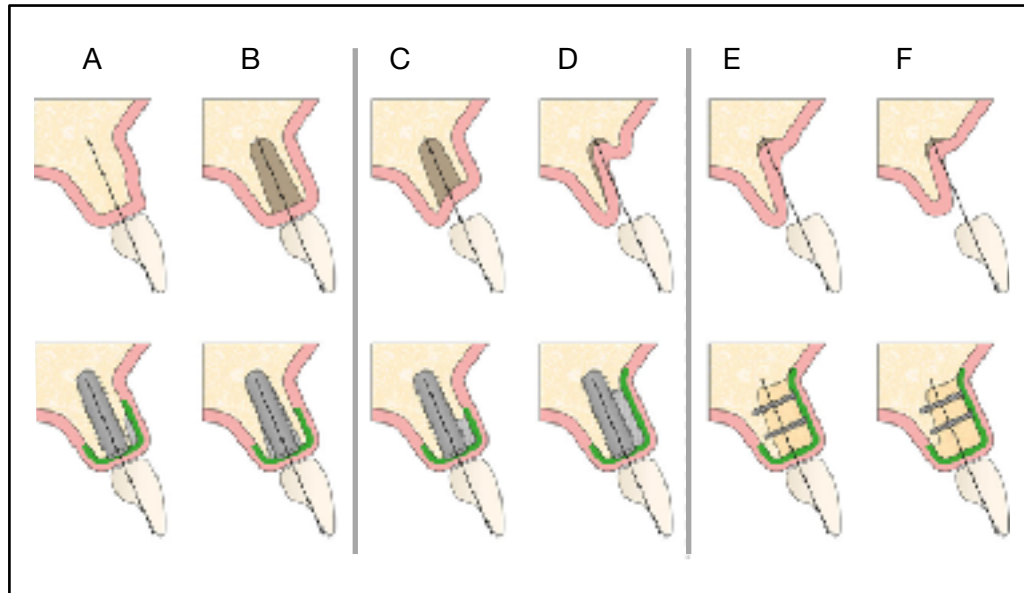


Fig 2.3 : Different clinical situations related to the alveolar bone crest without (on the top) and with the implant simulation (on the bottom). Is quite intuitive that the surgical bone regenerative procedures are strictly related to the remaining bone crest volumes. The implant positioning can be done with just some bone particulate (A-B), with a resorbable membrane (C-D) or a screw stabilized mesh (E-F).

This makes it very difficult to achieve a correct implant rehabilitation that respects the principles of anatomy, periodontal physiology and above all masticatory biomechanics, expressed by the principle of prosthetically guided implantology.[Gowd et Al. 2017] In order to obtain an adequate prosthetic rehabilitation and an optimal intermaxillary relationship, it becomes crucial to have a correct implant positioning in a three-dimensional sense anatomical crown related. As a logical consequence of prosthetically guided implant placement, the final implant position can often face with bone dehiscence or fenestration.[Chiapasco et Al 2009, De Angelis et Al. 2021]

Vertical bone crest augmentation can be achieved with autologous bone grafts in blocks or with surgical distraction and subsequent osteogenesis.[Maiorana et Al 2005, Scipioni et Al 1994] These techniques, however, require high surgical skills and represent, due to the complexity of the therapy and the compliance requested, a psychological and physical demanding procedure for the patient.

Guided bone regeneration (GBR), on the other hand, is a relatively simple procedure from a surgical standpoint and decreases the degree of stress on the patient through the use of biomaterials. This surgical technique is now widely documented and predictable and allows for the neoformation of bone through the use of barrier membranes.[Scipioni et Al 1994]

The protocol of horizontal GBR, in the case of small and medium peri-implant defects, consists of placing autologous bone in frustules (taken either from the same surgical site or from other donor sites depending on the amount needed) in close contact with the exposed implant surface. The autologous bone can also be covered with demineralized and dehydrated bone in granules belonging to the category of xeno-grafts. [Majzoub et Al. 2019]

The whole is then covered with resorbable collagen membranes in case of small and medium defects,(Fig.2.4) while, in case of larger defects or in case of vertical increases, titanium grids (mesh) or PTFE (Polytetrafluoroethylene) membranes reinforced with titanium are used, both belonging to the category of non-resorbable devices.(Fig.2.5)



Fig 2.4 : collagen membranes is adapted on the defect covering the bone graft material stabilizing it and preventing the migration of particles.



Fig 2.5 : PTFE (Polytetrafluoroethylene) membranes reinforced with titanium can be shaped on the defect and maintain on time the same geometry modeled.

2.2 DIGITAL PROCESSING OF 3D-MESH STRUCTURE

A prerequisite for custom titanium mesh using CAD-CAM technology is a CBCT scan (Cone Beam Computerized Tomography) of the affected maxilla with particular regard to the defect area to start the mesh design phase by the dedicated team. The device is designed using CAD modeling software, the morphological and dimensional characteristics of the device, as well as the positioning of the cortical screw holes, are specifically designed to conform to the patient's anatomy while preserving the noble structures present, such as adjacent teeth or nerves and blood vessels. The use of a custom grid, which is pre-modeled and pre-fabricated to the surgery, allows for a morphology that is three-dimensionally adapted to the bone defect, rounded margins, and beveled edges, which simplifies bone regeneration, reducing the operating time and the trauma on soft tissues. [Cucchi et Al. 2019]

Verified and confirmed the geometry, the 3D print is performed through selective laser melting (SLM) and then, after a superficial process of electro-polishing, the product is decontaminated and packaged, ready for sterilization.

2.3 TITANIUM MESH

The titanium mesh (Fig.2.6) must be modeled on the basis of the anatomical characteristics of the bone crest by cutting the margins, with appropriate cutters, extending it about 2 mm beyond the limits of the bone defect. The grid must be controlled directly on the surgical site, carefully avoiding sharp edges that could determine a suffering of the overlying gingiva with risk of dehiscence and exposure of the grid itself. [Chiapasco et Al 2009]

The area under the titanium grid should be filled with autologous bone and the chosen grafting material, and then the grid should be fixed to the bone crest by means of micro screws. [Roccuzzo et Al.2004]

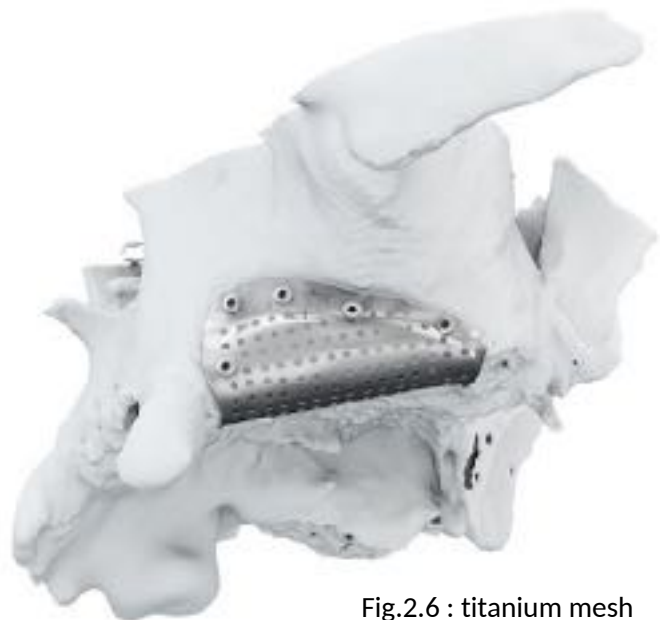


Fig.2.6 : titanium mesh covering a wide bone defect

The use of titanium grids in edentulous maxillary reconstruction has often led to excellent results in terms of bone regeneration and reproducibility. [Boyne et Al. 1969,1985; Von Arx et Al. 1998; Simion et Al 2007,De Angelis et Al. 2021]

Their use is indicated in cases of horizontal and vertical bone defects, in association with an autologous bone substitute.[Von Arx et Al. 1999; Maiorana et Al. 2001] Cases of contextual implant placement associated with the application of grids have been described with satisfactory results. [Malchiodi et Al. 1998] Titanium grids possess several peculiar characteristics that make their use extremely advantageous in numerous cases. [Poli et Al. 2014; Rasia dal Polo et Al. 2014] The rigidity of the metal structure allows it to maintain its shape and prevents its collapse within the defect, unlike collagen membranes. In addition, the rigidity provides greater mechanical resistance to the underlying defect area. The grids can be shaped and molded according to the defect, making their use highly specific and customized. The pins or screws for their attachment are located at the ends of the grid. Finally, the presence of holes in the surface allows for increased blood supply to the defect rich in oxygen, nutrients, and immune cells in the defect, which are critical to ensure successful osteogenesis. Surgical skill requires a learning curve and it is critical to evaluate which variables may affect the final outcome and the occurrence of complications. [Verardi et Al. 2017](Fig.2.7)

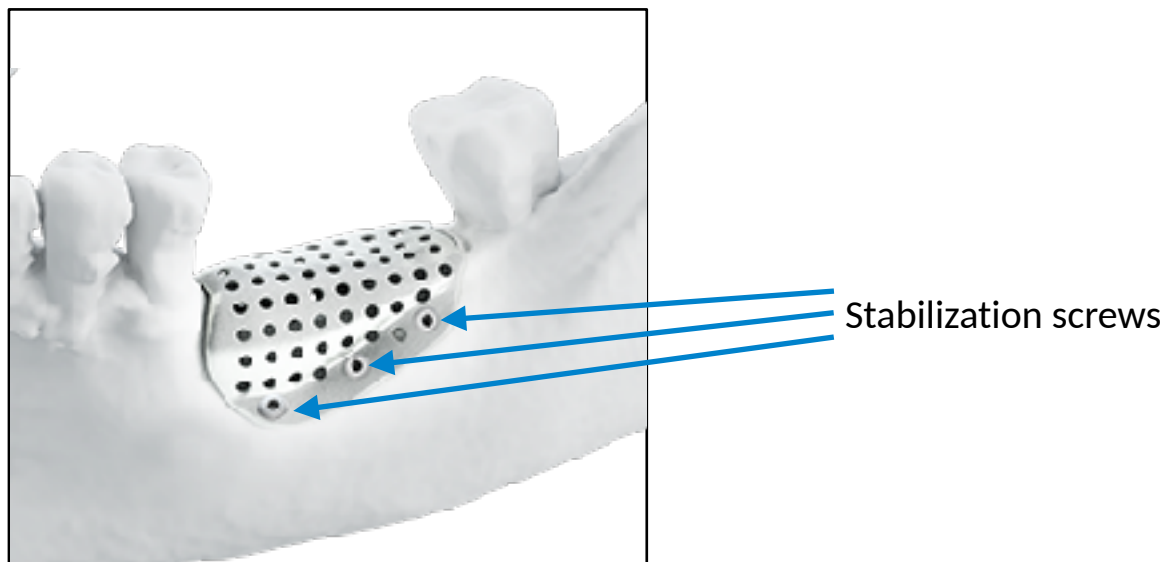


Fig. 2.7 : The stabilization screws are located , after a radiological evaluation to preserve anatomical structures, at the end of the mesh, fixing it to the native bone

Clinical Case - Lower right area

The clinical case is referred to the edentulism of the second lower right premolar and the first two lower right molars.

The need to regenerate the bone crest has the double meaning of preserving the residual volumes by ensuring the stability of the dental elements still present (in this case also an implant on element 4.4) and to prepare the area for the subsequent positioning of implants on which cement a dental prosthesis.(Fig.2.7-2.14)

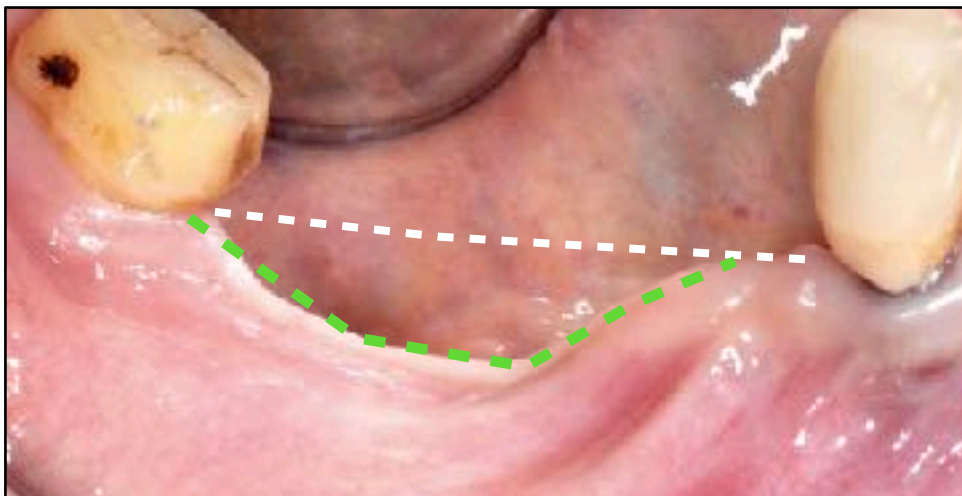


Fig. 2.7-: A large and deep bone crest defect - in white the ideal bone crest level, in green the clinical lack of volumes

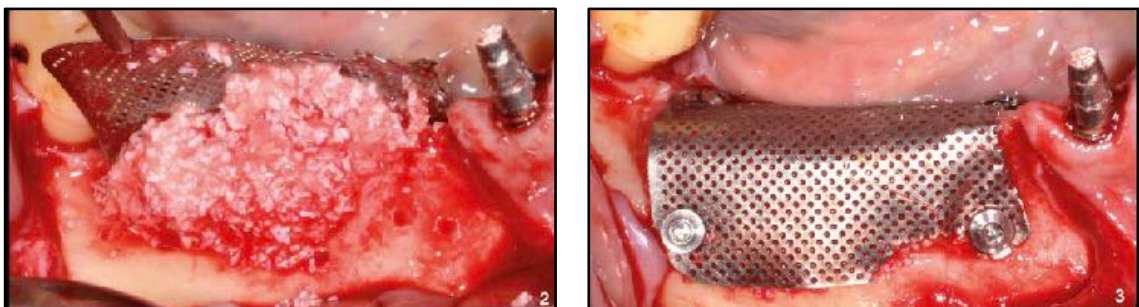


Fig.2.8-2.9 : First surgery with the positioning of particulate bone and the mesh on the lingual surface (on the left) and the cover with the mesh, fixed through screws (on the right)

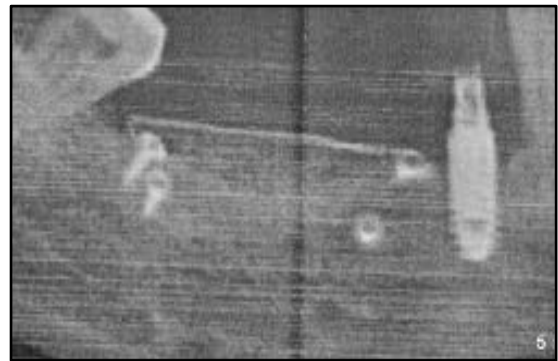
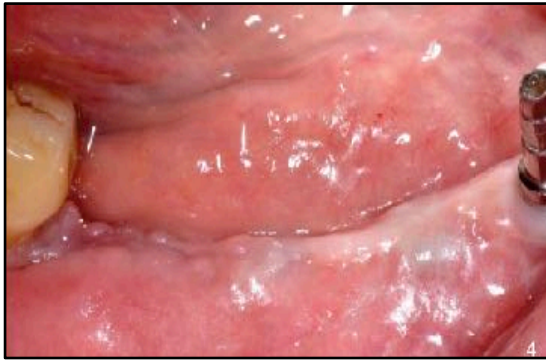


Fig.2.10-2.11 : Evaluation of the clinical healing of soft tissues (on the left) and the radiological one of the bone crest (on the right)



Fig.2.12-2.13 : Second surgery : a flap on the soft tissues is necessary to expose the mesh and evaluate the quality and quantity of new bone regenerated (on the left), due to this is possible proceed positioning a proper number of implant, in this case three, waiting for the healing of soft tissues (on the right)



Fig.2.14 : Prosthetic crowns cemented on implants

2.4 TITANIUM MESH LIMITATIONS

One of the limitations of titanium meshes is the operation of modeling and adaptation of the grid to the bone defect that determines a considerable spent of operating time and creates possible risks related to shape imperfection and margin traumaticity [Cucchi et Al. 2017]. In fact, at the time of suturing, the soft tissue stress resulting from the unsuitable dimensions of the grid or the possible traumatization caused by the sharp edges can cause, in the surgery healing period, dangerous dehiscences of the soft tissues. (Fig.2.15)



Early exposure of Titanium Mesh

Fig.2.15 : Is visible the titanium mesh exposure that can determinate:

- Plaque retention
- Soft tissues damage
- Pain
- Inestetism

As with nonresorbable PTFE membranes, the most frequent complications still consist of device dehiscence and exposure and/or surgical site overinfection. [Roccuzzo et Al. 2004; Lindfords et Al. 2010; Maridati et Al. 2016] While any early exposure of a nonresorbable membrane almost always results in infection that can compromise the outcome of the surgical technique, several authors demonstrate instead that in the case of grid exposure the success of regeneration is not affected and the regenerated bone volume is maintained. [Assenza et Al. 2001] It is always good clinical practice to foresee a possible complication and being able to plan in advance the management of the eventual adverse event can often determine the difference between success and failure of the treatment. Should the morphology and size of the defect necessitate the use of such non-resorbable grids or membranes, additional device removal surgery becomes necessary.

The purpose of using these membranes is to provide stabilization of the grafted materials, provide a space-maker effect, and a barrier effect to cells from the soft tissues.

In general, to try to reduce the frequency of exposure of titanium grids, several studies have proposed the association of grids with resorbable or nonresorbable membranes placed over them. Fewer exposures have been found with the use of PTFE membranes covering the titanium meshes.[Degidi et Al. 2003] (Fig.2.16)

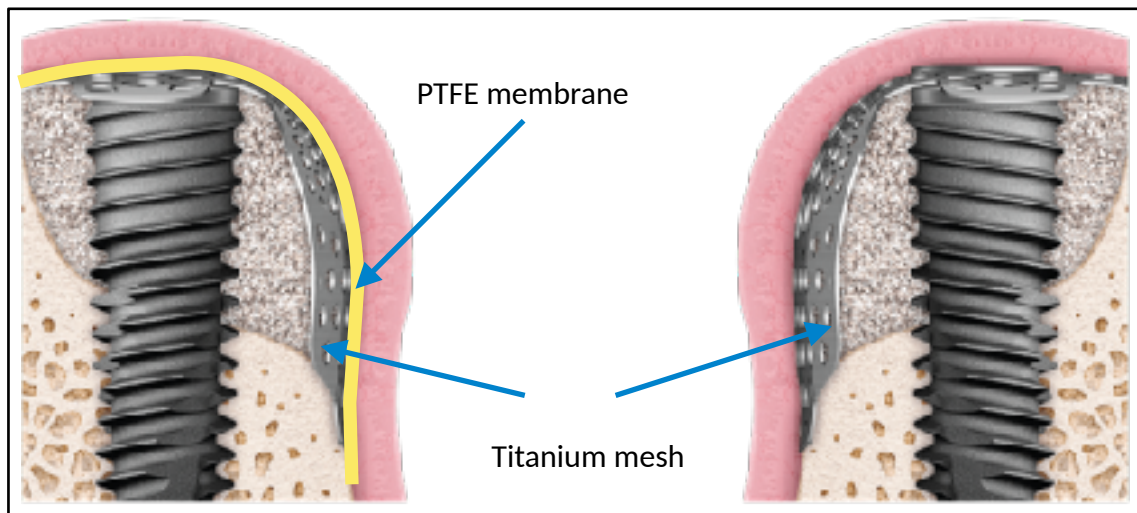


Fig.2.16 :Due to some Authors, covering the titanium mesh with a PTFE membrane can reduce the exposure risk

In case of soft tissue dehiscence, the protocol was to remove the PTFE membrane while leaving the titanium mesh in place without compromising bone regeneration. This procedure is still considered to be highly technique-sensitive and not free of complications that can affect the amount of newly formed bone and the success rate of the treatment.

To date, there have been many reports regarding complication rates, vertical bone gain (VBG), and success rates after bone augmentation with PTFE membranes and Ti mesh. [Simion et Al. 2004; Merli et Al. 2013]

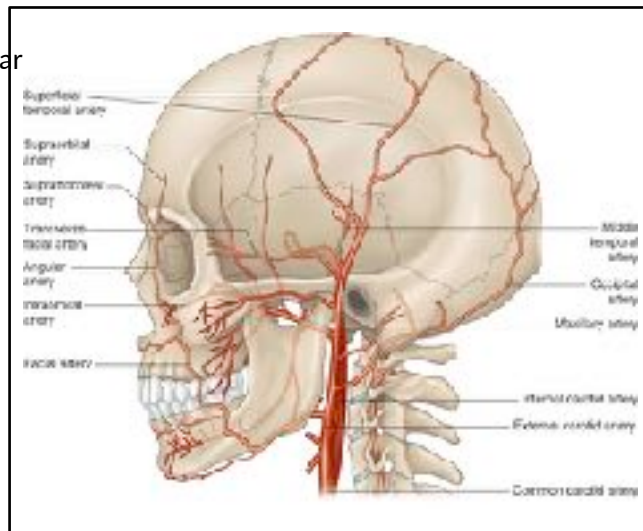
If a membrane or mesh remains submerged completely for at least 6–9 months of uneventful healing, it is possible to achieve complete bone formation under the barrier device. However, if the membrane or mesh suffers early or late exposure, the amount of newly formed bone under the barrier could be affected negatively. Consequences of barrier exposure range from incomplete bone growth to failure of the entire regenerative surgery. [Fontana et Al. 2011]

The main cause of GBR failure is related to early or late exposure of the barrier device, leading to contamination and infection of the biomaterials, irreversibly compromising bone regeneration. [Corinaldesi et Al. 2009]

The significance of membrane exposure for the successful outcome of GBR procedures has been much debated. Several studies have shown that the onset of exposure is important for the success of the procedure. In fact, some authors have demonstrated that “premature” exposure (during the first 4 postoperative weeks) of the barrier device can

- Class C, including vascular damage (hemorrhage) (Fig.2.19)

Fig.2.19: the maxillary vascular system is well known by the surgeon but as well at risk to be damaged



The latter (healing ones) complications are divided into four classes, according to the presence and extent of exposure, as well as the presence of a purulent exudate, also divided into major or minor, depending on the influence on newly formed bone [Merli et Al. 2007] :

- Class I: membrane exposure ≤ 3 mm, no purulent exudate.
- Class II: membrane exposure ≥ 3 mm, no purulent exudate.
- Class III: membrane exposure, with purulent exudate.
- Class IV: abscess, without membrane exposure.

As last the association between mesh and resorbable membrane for the treatment of peri-implant defects was also studied.[Rakhmatia et Al. 2013] With this expedient, the authors observed a reduction in the risk of grid exposure, thus highlighting how covering the grid with resorbable membranes is a reliable and advantageous technique. The mean reentry time for grid removal ranges from 6 to 9 months. Several authors have confirmed the efficacy of grids in bone regeneration. [Leghissa et Al. 1999; Corinaldesi et Al. 2009; Her et Al. 2012; Briguglio et Al. 2019]

2.5 METAL-FREE MESH

With the advent of new high-performance metal-free materials and increased public attention, as well as greater patient awareness, scientific research is continually working to determine the short- and medium-term local and systemic effects caused by metal particles, metal ions, and other contaminants, medium and long term systemic effects caused by metal particles, metal ions and metal-organic compounds arising from the implanted medical device and, if possible provide guidance on threshold values for metals in any form. This issue has been evaluated and reported by Scientific Committee on Emerging and Newly Identified Health Risks (SCENIHR, 7th plenary of 24-25 September 2014), reiterating once again how the importance of human health must always be emphasized. It has been shown that interventions involving the placement of metal implants that, in daily use, result in dynamic contact with other equally metallic surfaces (MoM, Metal-on-Metal) lead to a release of metal products (e.g. particles and ions) that can also form metal-organic compounds in the body, being deposited in draining lymph nodes and internal organs with the risk of causing local and systemic adverse health effects. However, it is not possible to determine whether these are due to metal particles, ions, or metal-organic compounds released by the implants because the timing of their occurrence and the multifactorial nature of the possible causes make it difficult to correlate the cause-effect sequence. However, it is interesting to note that this report concludes that the application of a MoM implant should be carefully considered on a case-by-case basis, because of the potential adverse effects of the released metal, especially in some subgroups of Patients such as, for example, women of childbearing age and patients allergic to relevant metals.

Due to the mentioned limitation of titanium mesh and trend towards new metal-free materials, due to the increasing demand of users (dentists/dental technicians) of being independent with the ability to manage different clinical case, from the easier to the most challenging one , with chairs-side strategies the intention of the research project was to go and verify that niche market still unexplored to date. In Chapter 1 I considered the current state of the art of the clinical problem of a bone deficiency that does not allow the placement of titanium implants to support prosthetic crowns. Although there are clinical operative strategies that allow to solve this deficiency, the ratio between advantages and disadvantages is such to consider still highly necessary the search for new alternatives.

If i consider the discomfort for the patient of having to undergo numerous surgical interventions and the clinical difficulties of removing a titanium grid adhered to the newly

formed bone crest, and the increasingly necessary attention to metal-free by choosing more biocompatible materials that reduce the risk of adverse reactions, is well visible how this market sector is still not fully explored.

The development of new technologies has always gone hand in hand with the development of materials.

I have described how the development and introduction of milling systems has made the dentist able to realize, in an autonomous way without the strict necessity of a dental technician, effective and performing prosthetic elements.

This ability to independently handle a variety of clinical situations is still undeveloped in Additive Manufacturing where limitations are still present:

- Ability to print materials for temporary restorations
- Ability to print metallic or polymeric materials
- Ability to print ceramic materials (only through high-performance but highly expensive printers able to fit with the need of professional printer center - i.e. *Materialise*)

If I give a look at the market proposal, can be found market leader companies such as Lithoz (Lithoz GmbH, Wien), DWS, 3D Ceram that has developed a highly effective and precise ceramic printing system but at costs that are absolutely not sustainable for the end user such as the dentist.

The knowledge for aerospace printed ceramic devices is surely interesting but cannot be considered affordable for the dental market customers.

The company's strategic choice would therefore be to produce the single restoration and then sell it to the end user or to sell the printers to large production centers.

The market trend, however, would be more and more oriented towards making the individual dentist autonomous, as he is already able to be on a daily basis with subtractive systems, which, however, have disadvantages already described in Chapter 1.

In this regard, the PhD has been officially followed by a leading company in the industry as *BTK (Biotec srl Via Industria, 53 36031 Povolaro di Dueville (VI), Italy)*, whose experience and production sector are dedicated to bone regeneration and the application of support structures for this purpose. BTK's mission, combining cutting-edge technology and biology, is to offer an affordable and personalized choice for every implant solution, providing reliable products to ensure oral health and sustainably improve patients' daily lives.

The need to combine the independence of the end user (the dentist) with the new highly efficient systems of additive manufacturing has prompted a market leader in additive manufacturing as WASP (*WASP S.r.l Via Castelletto104, 48024 Massa Lombarda, Ravenna - Italy*) to collaborate in the research project by providing a prototype useful for the development of a new 3-d printer in parallel to that of new ceramic materials thanks to the DIME department in which this PhD was developed.

*

CHAPTER 3

MATERIAL AND METHODS

After of Chapter 2, I agreed with BTK to develop the 3D printing process of metal free material.

Considering the many different 3D printers on the market and the different production techniques, the choice was made with the intent to approach the end user (the dentist) with the same approach seen with the milling machine to allow precisely speed and independence in the realization of the artifacts.

The attention has been turned towards filament printers, as they can be considered among the most convenient to have at home, and consequently suitable for the development project of my PhD that does not want to compete with the 3Dprinters of the big commercial chains but rather to challenge a niche still unexplored in the medical field. FDM printers use polymeric plastic filaments that are melted and extruded and then transferred to the working plate by progressively raising the z-axis of the printer and continuing to position a new one until the complete object is realized. The design process takes place through dedicated slicer software that develops the 3D .stl drawing file converting it into a .gcode file. Some of the FDM printers advantages are:

- Reduced cost for the beginner investment
- Ease of use
- Low costs of basic material
- Excellent printing quality

All factors that seemed very useful for my project.

By conducting market research on companies and 3D printers, I identified WASP as the ideal choice: Italian Company, recognized worldwide as a leading company in the industry, with a big and longterm experience in AM field.

From a meeting at WASP industry , I reached an agreement to work on a prototype (that from now I mention as *Prototype #1*), built by them, of which some external, mechanical and electronic features were inspired by one of their products already present on the market (the Delta WASP 2040 Industrial-X 3D printer) but from which they actually wanted to change the entire production process but without carrying out the development (TRL 2-3) for the dynamics of the Company.

I would like to underline how *Prototype #1* was considered by WASP as a very interesting project from a commercial point of view but with still many elements to be developed, in order to make it work regularly and, with the appropriate modifications, to make it attractive in commercial terms.

Due to this agreement *Prototype #1* would have been sent at DICCA Department of University of Genoa, with the intent to develop it as part of my PhD.

It has been then defined the Research & Development Team that will be involved:

WASP R&D

- Mr. Flavio Gioia

BTK Dental R&D

- Ing. Marco Zotto
- Ing. Andrea Trentin
- Ing. Matteo Marsetti

Università di Genova

- Prof. Fabrizio Barberis
- Prof. Alberto Lagazzo
- Dr. Luca Solimei

3.1 DELTA WASP 2040 INDUSTRIAL-X

As first thing I consider important to understand how some commands of Delta WASP 2040 Industrial-X printer have been reported in the production phase on the *Prototype #1*, taking advantage by the knowhow and the previous experience developed by the Company, and then, going to take the official details from the data sheet, I will be able to avoid to explain them again in the part dedicated to the laboratory activity for the development of the *Prototype #1* itself.

According to the company's description in datasheet:

The printer comprises a heated extruder mounted on a delta robot type structure, a platen and a spool assembly. The material is unwound from the spool, pushed towards the heated nozzle where it is melted and poured through a hole that deposits very small quantities of material on the work top. The material is deposited by the head layer on layer according to "layers" defined by the file created by a slicing software. It is therefore possible to realize any shape and any type of object within the limits of this technology.

(Fig.3.1)

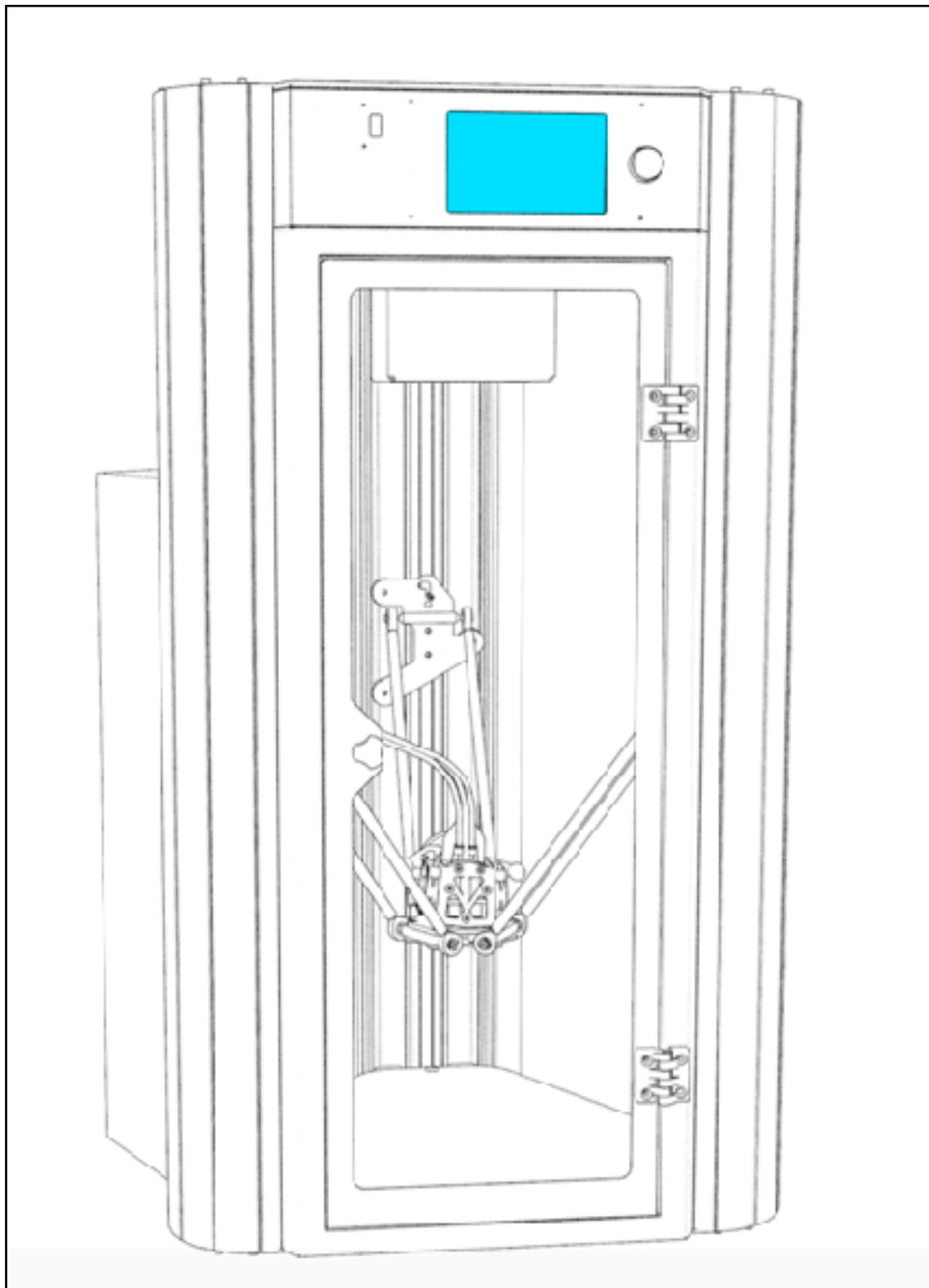


Fig.3.1 : Illustration of Delta WASP 2040 Industrial X from its datasheet

On the top there is the command panel (Fig.3.2) :

1. Ethernet cable port (on the side)
2. USB port (to upload files)
3. Operator display
4. Display control knob (rotates left/right and is clickable)

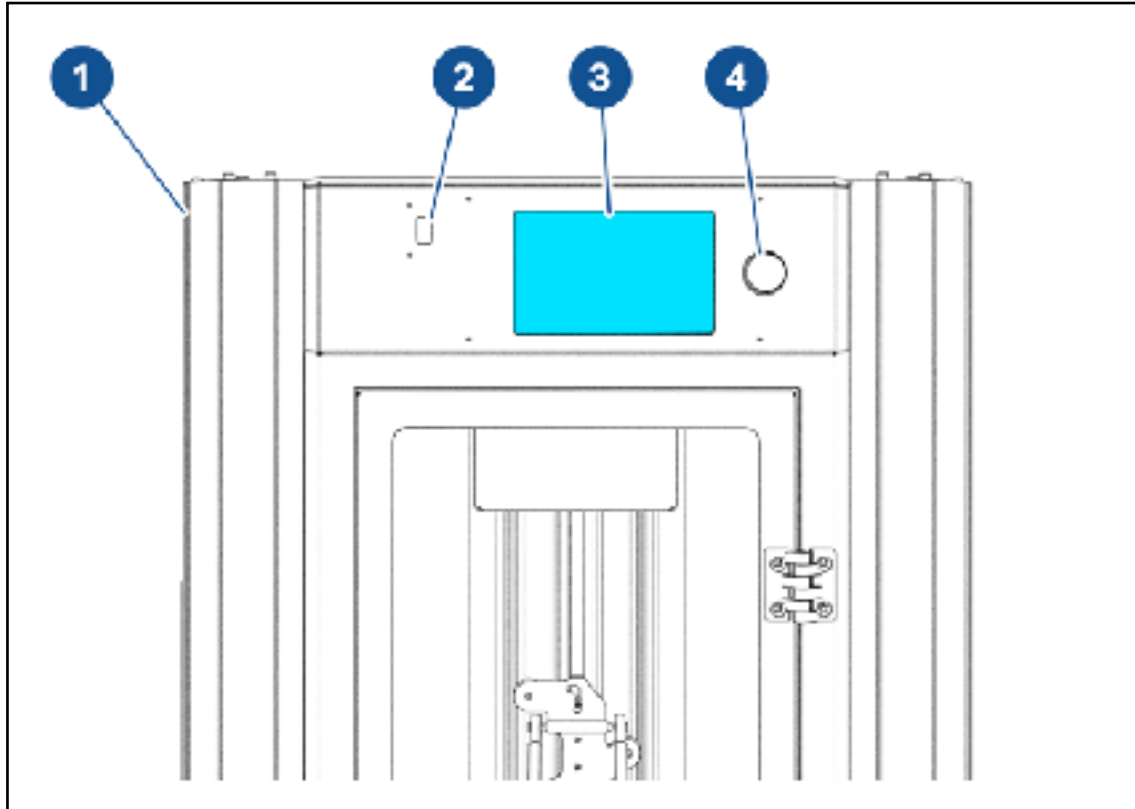


Fig.3.2 : Illustration of command panel from its datasheet

In the working area (Fig.3.3) is well detectable:

1. Heater - to manage the internal temperature
2. Aluminum cart - for extruder movement
3. Extruder
4. PTFE tube - to protect the material filament
5. Support arms

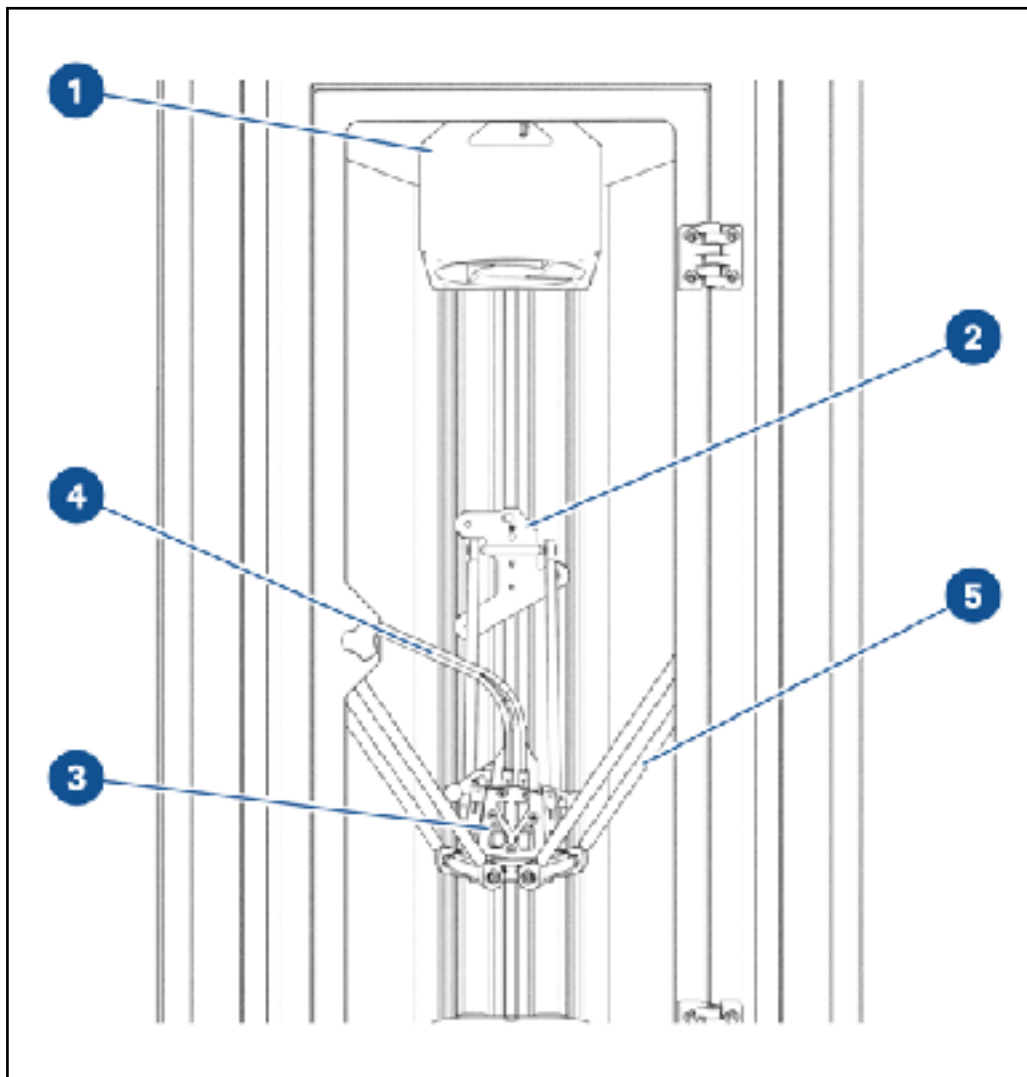


Fig.3.3 : Illustration of working area from its datasheet

On the external area, on the posterior part of the 3D printer, (Fig.3.4) can be found:

1. CE license plate
2. Power cable connection

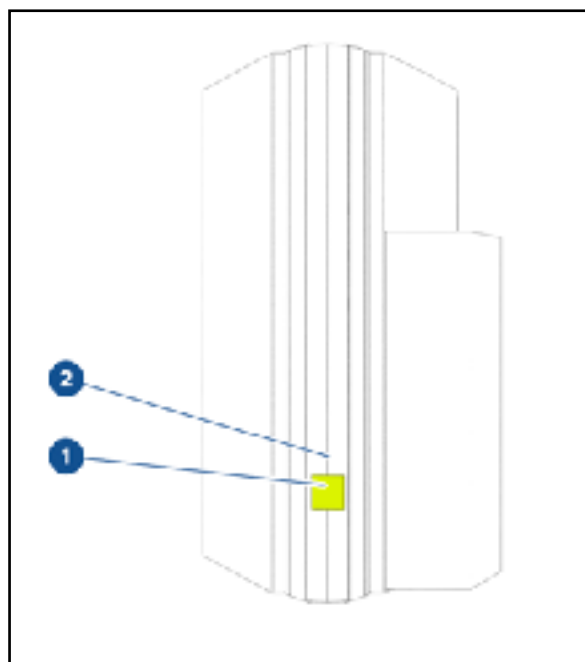


Fig.3.4 : Illustration of external area from its datasheet

GENERAL FEATURES	
Lenght	44 cm
Width	49 cm
Height	87 cm
Aproximatively weight	38 Kg
Noise	< 50 db (A)

Table 3.1 : Delta WASP 2040 Industrial X General Features from its datasheet

ELECTRIC FEATURES	
Input	220/240 V - 50/60 Hz
Power consumption	Extruder : 120W Heated Plane : max 500W Heated chamber : max 750W

Table 3.2 : Delta WASP 2040 Industrial X Electric Features from its datasheet

USAGE FEATURES	
Usage environment	20-30 °C
Warehouse	0-30 °C
Noozle	max 300 °C
Heated plane	max 120 °C
Heated chamber	max 80 °C

Table 3.3 : Delta WASP 2040 Industrial X Usage Features from its datasheet

Having presented the visible parts, I am interested in describing the features of the operator display, appearing when the device is switched on, from which you can set programs, change settings and have a live update of the printing process.

Legend of Delta WASP 2040 Industrial X Operator Display (Fig.3.5):

1. Extruder temperature (by clicking you can change it)
2. Wifi information
3. Operating information: position, feed, flow, status, auto-calibration on/off
4. Plate temperature (click you can change)
5. Toolbar
6. Chamber temperature and door open/closed

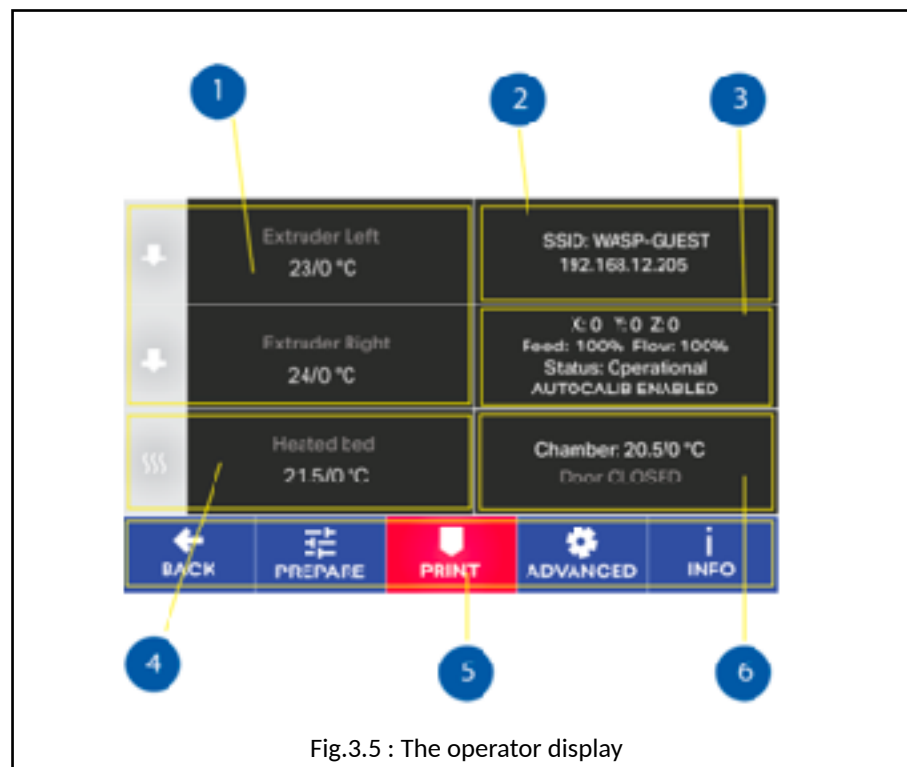
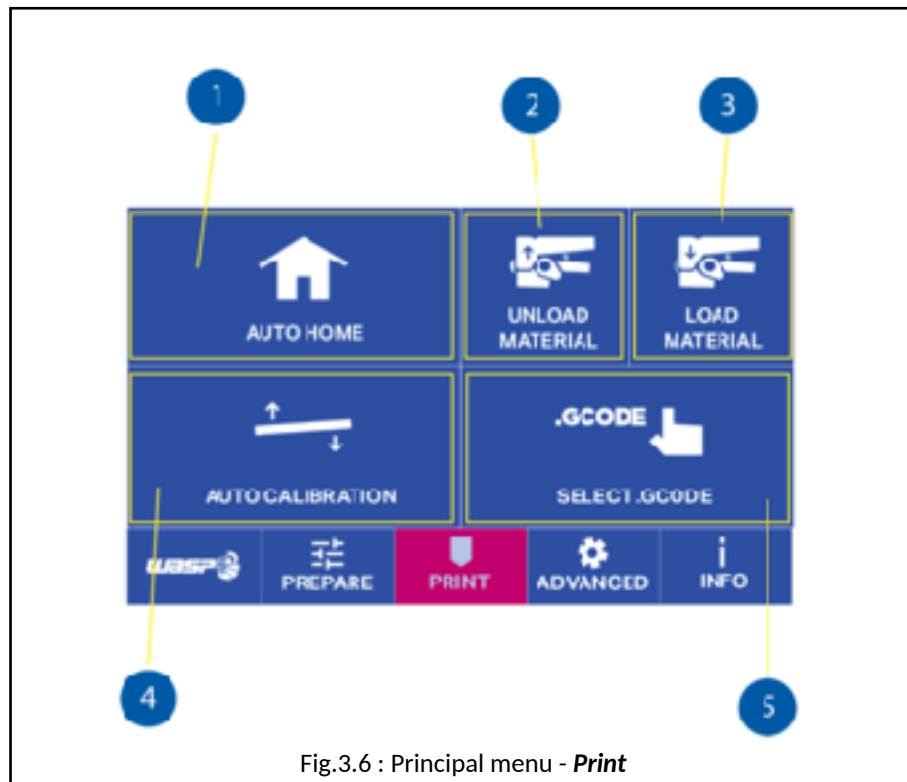


Fig.3.5 : The operator display

The PRINT menu contains the useful commands to prepare and launch the print, from the *Auto Home* button that repositions the extruder to the starting point, through the material management, to the choice of the file to print.

Legend of Delta WASP 2040 Industrial X Print menu (Fig.3.6):

1. Auto home: brings the printer to the axis reset position.
2. Unload material: heats up the extruder and removes the loaded material
3. Load material: heats the extruder and loads the material
4. Autocalibration: heats the extruder and launches autocalibration
5. Gcode: gives access to the gcode menu to proceed with the printing.



If we click "PRINT-GCODE" it is possible to choose the gcodes to launch and save them from the USB pendrive to the internal memory.

Legend of Delta WASP 2040 Industrial X gcode screen (Fig.3.7):

1. Choose USB memory/ Printer memory
2. List of codes, those on the USB memory have the icon next to them.
3. Arrows and sliders for navigation
4. GO: launch the selected print



INTERFACE AND SOFTWARE	
Operating system	Windows, Mac, Linux
Software slicing	Simplify3D, Cura, Slic3R
Interface software	Repetier Host, Pronter Face
File type	.stl, .obj, gcode
Interface	Pendrive USDB,TFT touch display,Wi-fi

Table 3.4 : Delta WASP 2040 Industrial X Electric Features from its datasheet

Returning to the main menu, there's the possibility, in addition to the *INFO* page that provides the specifications of 3d printer and software in use, to open two further pages: *ADVANCED* and *PREPARE*.(Fig.3.8)

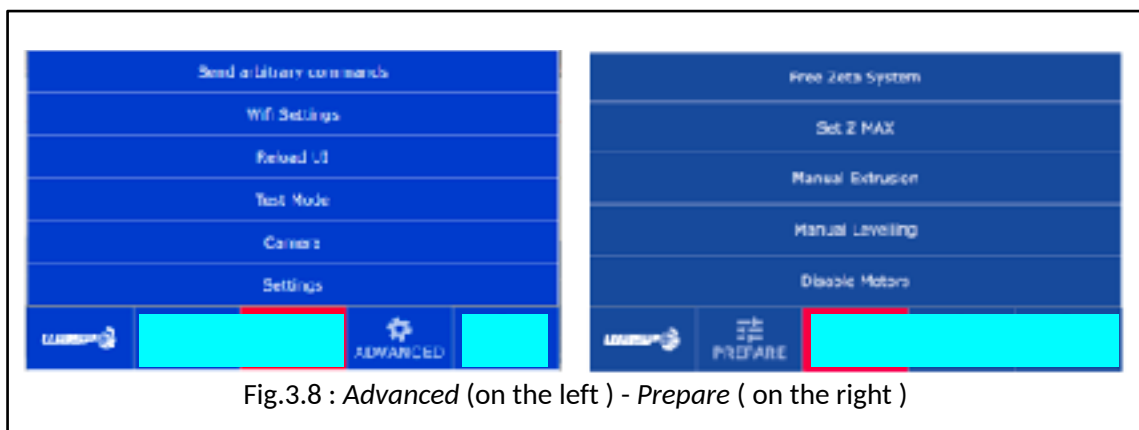


Fig.3.8 : *Advanced* (on the left) - *Prepare* (on the right)

Accessing the page *ADVANCED* are visible several useful commands of extraordinary use:

- *Send arbitrary command*: contains a keyboard that allows you to launch commands directly to the board
- *Wifi settings*: is used to connect the machine to a wifi network
- *Reload UI*: reloads the graphic interface of the machine
- *Test mode*: autocheck of the printer functionality
- *Camera*: shows what the camera sees and allows QR code reading
- *Settings*: allows you to set various advanced parameters

While accessing the page *PREPARE* are visible several useful commands that are not frequently used:

- *Free Zeta system*: enters the Free Zeta System
- *Set Z max*: allows you to set a machine height value

- *Manual extrusion*: enters the Manual Extrusion environment
- *Manual leveling*: manual leveling environment
- *Disable motors*: disables the stepper motors

3.2 PROTOTYPE #1

After having evaluated all the technical and physical characteristics of the Delta WASP 2040 Industrial-X which it is important to remember that it was used by WASP exclusively as a reference for some components without having any proximity to the printing production process, the attention must turn to the development of *Prototype #1* , viewed at WASP headquarters on 19th October 2020. (Fig.3.9)



Fig 3.9 : Meeting at WASP headquarter with WASP, BTK , University of Genova

This meeting at WASP headquarters was attended by:

- Mr. Massimo Moretti , WASP CEO
- Mr. Flavio Gioia, WASP project manager
- Prof. Fabrizio Barberis, University of Genova
- Prof. Alberto Lagazzo, University of Genova
- Dr. Luca Solimei, University of Genova
- Mr. Andrea Peloso, CEO BTK Dental
- Ing. Marco Zotto, BTK Dental

During this meeting it is explained to us how the WASP company had undertaken the development of a prototype printer but due to numerous commitments and company dynamics had to temporarily suspend its development.

The prototype belongs to the “Delta Wasp 2040 Industrial” series, originally conceived for the printing of polymeric material, but has been adapted also to the printing of ceramic materials through some physical modifications. This 3D printer was based on FDM technique but it was modified as a prototype to implement also the CIM technique and the use of material in pellet form. This model was originally equipped with the “Wasp Spitfire Red” extruder (Fig.3.10 a,b)which supported nozzle's diameter of 0.4, 0.7 and 1.2 mm and allowed the printing of filaments with a diameter of 1.75 mm but, due to the new target given, then it has been switched with the totally different “LDM Wasp” extruder, specific for this material.(Fig.3.11)

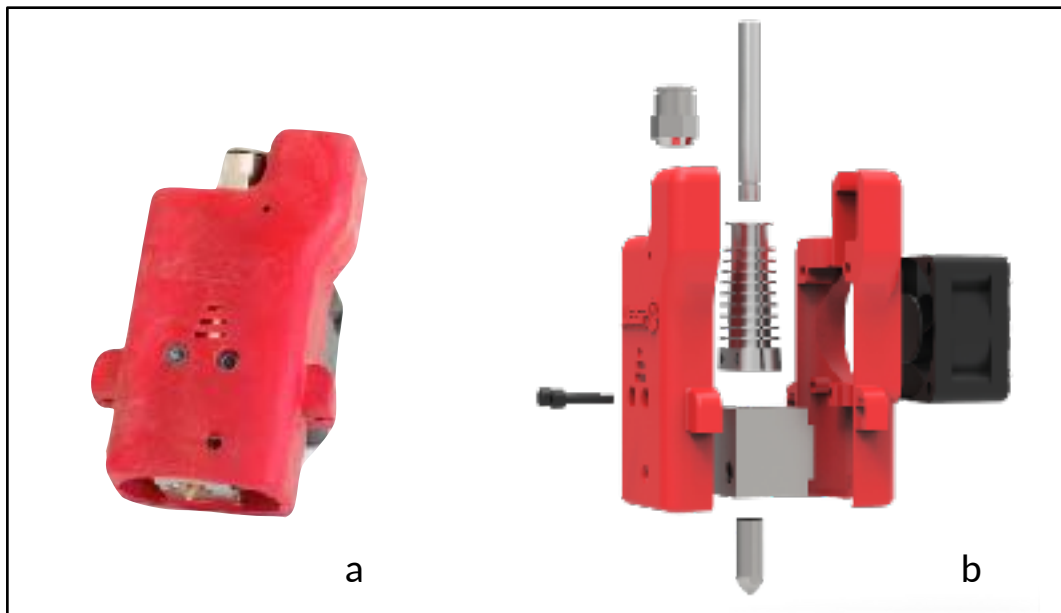


Fig 3.10 : Wasp spitfire Red extruder external view (a) and internal view (b)



Fig 3.11 : LDM Wasp extruder

The temperature dissipation system consisted of two cooling fans placed on the sides of the motor,(Fig.3.14) but in this case there weren't insulating panels on the walls.

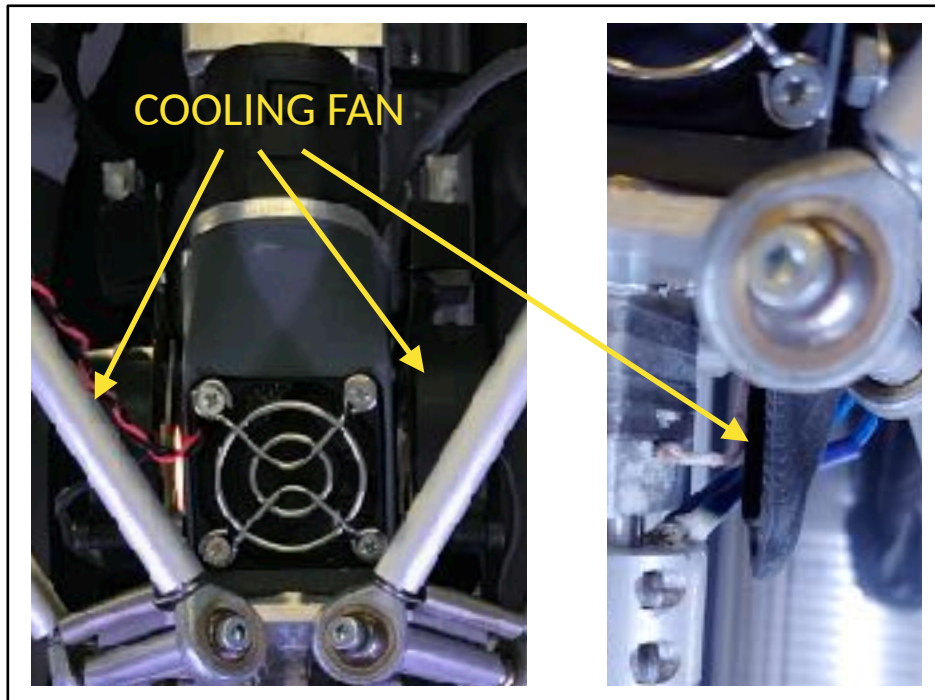


Fig 3.14 : Cooling fans, due to the setting, can regulate temperatures

Regarding the software, the device was compatible with the same slicing programs and could read the same type of file's extension, that could be imported with an USB pen drive or directly from a computer connecting both to the same Wi-Fi network.

The *Prototype #1* has been delivered to DICCA Department of University of Genoa, in December 2020.(Fig.3.15)



Fig 3.15 : *Prototype #1* , delivered and placed at DICCA in December 2020

The starting phase of experimental session aimed at evaluating the functioning of *Prototype #1*, due to this evaluations and the following tests I could set the necessary modifications and development.

The prototype was partially disassembled to have the operating structure clearly in front of it.

The system can therefore be divided into three macro-areas in which to highlight the different components(Fig.3.16):

- Upper Area
 - A plastic loading hopper
 - The two already mentioned cooling fans
- Lower Area
 - The extruder heatsink
 - The extruder nozzle
 - The thermocouples acting on the two previous elements
- Internal Area
 - The screw (coclea)

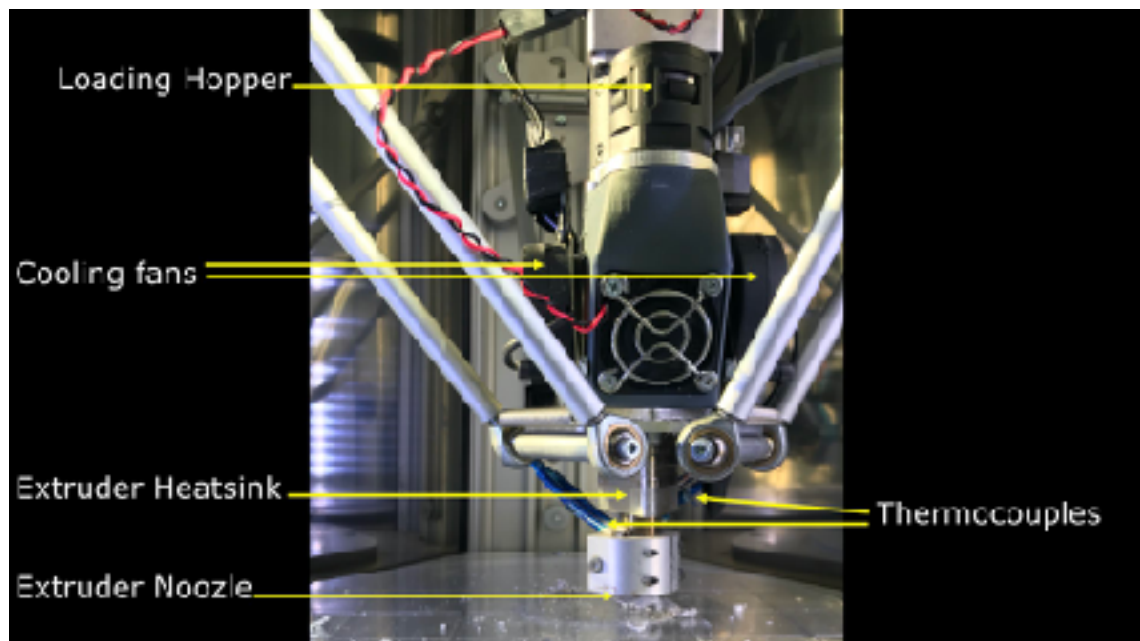


Fig 3.16 : The extruder with all of its features. Some components are visible, some other are internal and will be evaluated just after dismounting the extruder itself

3.2.1 THE SCREW

The first efforts to print provided discontinuous results. I evaluated the separate influence of all the working parameters, then I pointed my attention to the device hardware, in

order to get any useful info on possible actions on specific parts of the the printer. The first analysis was applied to the screw device.(Fig. 3.17):

- Length - 95 mm working area + 10 mm portion connected to the motor
- Diameter - 12 mm on the top, tapered to 10 mm on the bottom
- Proportion between the different section and consequent space for material

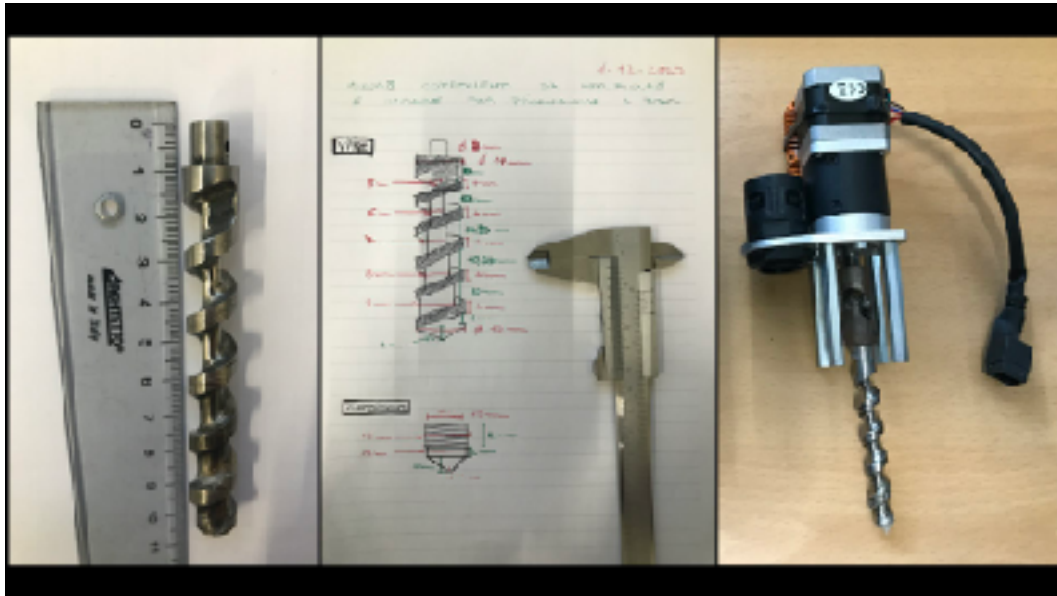


Fig 3.17 : Different pictures of the screw analysis that can show its dimensions and design.

One of the main evaluation done was about the ability of the ceramic material to flow through the metallic cylindric camera and be extruded through the nozzle.

3.2.2 THE HEATSINK AND THE NOOZLE

The *Extruder Heatsink* had been realized with 5 metal plates of 3mm thickness each with a triangular shape, with each side 25mm long (choice dictated by the availability of material from the WASP company), which were stacked one on top of the other and stabilized through 3 passing screws that, crossing at the top 3 holes present on the motor support plate with the purpose of stabilizing the portion below, were to be tightened on a sixth lower plate of 9mm thickness, also triangular in shape, with an internal thread on which to tighten the metal cylinder, covering the lower part of the screw and wrapped by the metal jaw heating, in turn screwed to the *Extruder Nozzle*. The internal section of the *Extruder Heatsink* had a "flower" shape to ensure space for the material and facilitate its passage. The thermocouples were inserted in a cavity between the last two metal plates (one 9mm and one 3mm) forming the *Extruder Heatsink* and in two dedicated holes on

the aluminum jaw positioned around the lower portion of the cylinder, connected to the *Extruder Nozzle*. (Fig. 3.18-3.19)

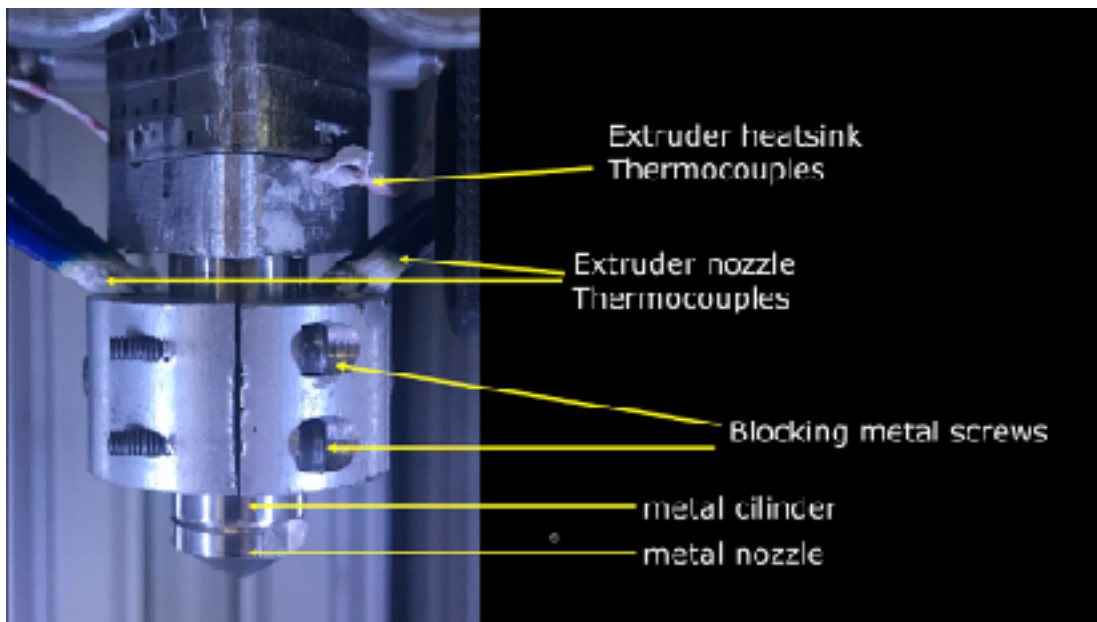


Fig.3.18 :The lower portion of the extruder includes the aluminum *Extruder Heatsink* which is positioned around the screw and the *Extruder Nozzle* in the lower portion, wrapped in an aluminum jaw that is held in place by tightening two locking screws. On both components have been positioned the thermocouples through which the regulation of the temperatures is determined

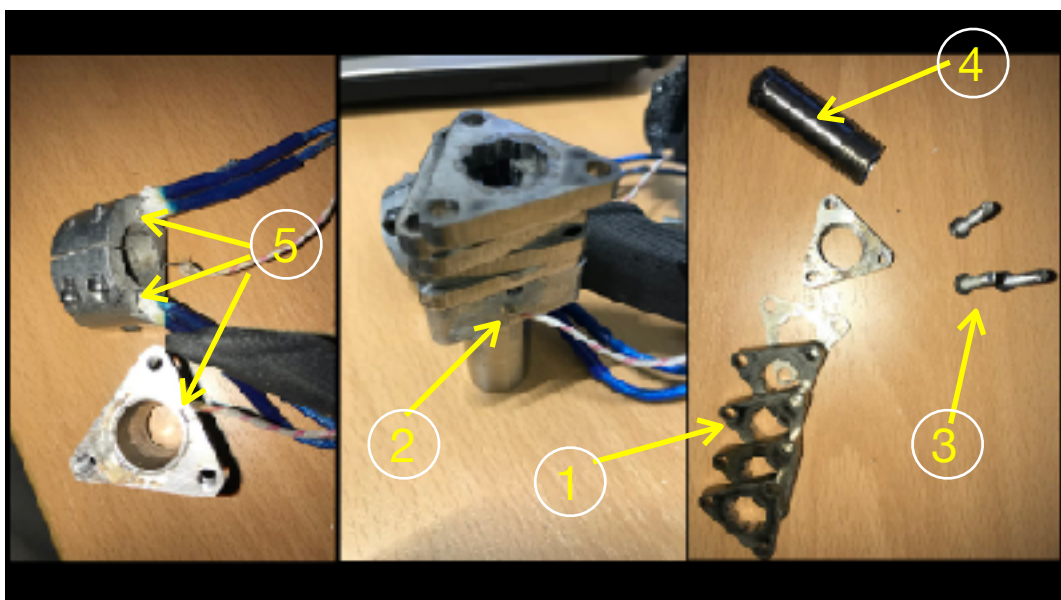


Fig.3.19 :The lower Area : 1) Triangular metallic plaques; 2) Lower 9mm metallic plaque; 3) Screws; 4) Metallic Cilinder + Nozzle; 5) Thermocouples

3.2.3 OPERATING PROCEDURES

The operating principles of *Prototype #1* include the following phases:

- 1) Loading the material into the hopper in the form of pellets (Fig.3.20). I will explain soon, speaking about the material, CIM production process



Fig.3.20 : The variable geometry of pellets

- 2) Transfer of the material through the auger from the Loading Hopper to the Extruder. (Fig.3.21)

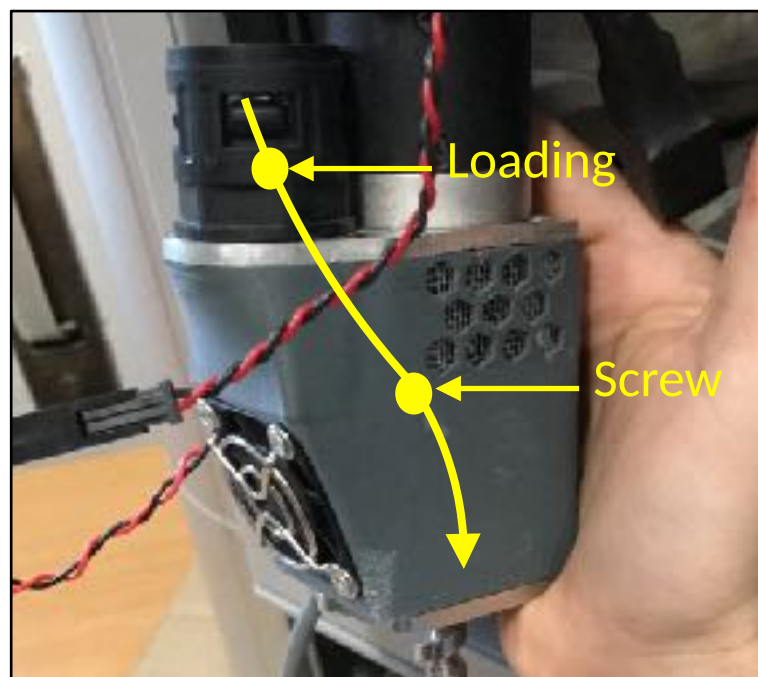


Fig.3.21 : The material follow arrow direction from the Loading Hopper surrounds the screw being brought downwards inside the Heatsink

3) In this transfer phase, the material is progressively crushed and reduced to a powder of unequal granulometry

4) Passing through the heatsink the material is subjected to a heating process which leads to the melting of the polymeric phase, creating the material in a fluid state destined to come out from the underlying nozzle.

The system works with a heating element along the path of the auger flanked by a forced cooling system with fan supported by a feedback circuit that allows to precisely control the thermal working regime.

In this phase I have carefully studied the structure of the process at DICCA. In simplified form it can be said that the material is simultaneously crushed and heated, leading to both physical and chemical transformations. This determines a transitory regime, starting from the loading hopper up to the nozzle in which the material is progressively compacted, removing the air between the pellets and the products physisorbed on the surface by heating.

I noticed (Fig.3.22) some evident signs of wear on the surface of the cochlea and this made me notice a point of possible study on the evaluation of the possible results.



Fig.3.22 : The screw is scratched and this is an information very important for future developments

3.2.4 MATERIAL

The choice of material was for Aluminium oxide (Al_2O_3 , 99.8%) in pellet commercially known as INMAFEED-K1013 (INMATEC Technologies GmbH, Germany)(Fig.3.23-3.24, datasheet available in APPENDIX C) provided by the company WASP, which had used it in the initial tests during the realization of *Prototype #1*.

	Ceramic Powder	Colour	Particle Size d_{50}	Theoret. Density	Sintering Temperature	Atmosphere
INMAFEED K1013	Al_2O_3 99.8 %	Ivory	0.5 μm	3.94 g/cm ³	1.600 - 1.650 °C	In air

Fig.3.23 : INMAFEED K1013 datasheet

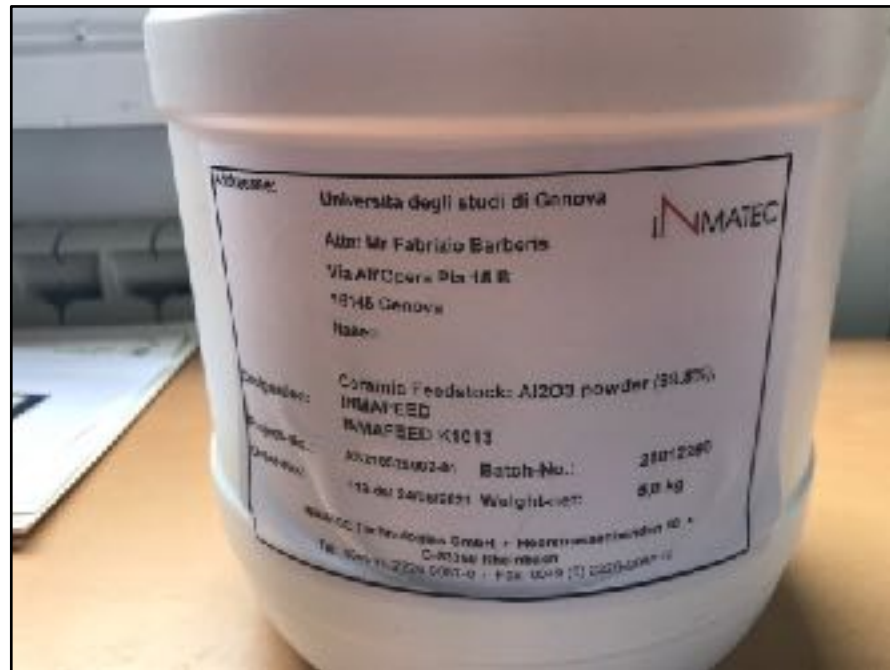


Fig.3.24 : INMAFEED K1013 5Kg box with which I could start testing *Prototype #1*

This material is produced through CIM (Ceramic Injection Molding), a technology of injection molding of ceramic materials.

The CIM technology consists in mixing the ceramic powder with suitable binders and additives with the aim of increasing the fluidity of the mixture itself. At this point, the mixture obtained is injected into a mold using machinery very similar to those used for the traditional molding of plastic materials. Most of the binder is then removed by thermal decomposition and evaporation. The products thus obtained are placed in a sintering furnace where any residual binder is removed and the objects themselves are sintered into the final shape.

In order to verify the polymeric quantity of the available material, I requested a Thermogravimetric analysis (TGA).

From Prof. Peter Dubrueel of University of Ghent, Belgium, I received the result (Fig.3.25) which describe a ceramic component of 85% and consequently the polymer one of 15%.

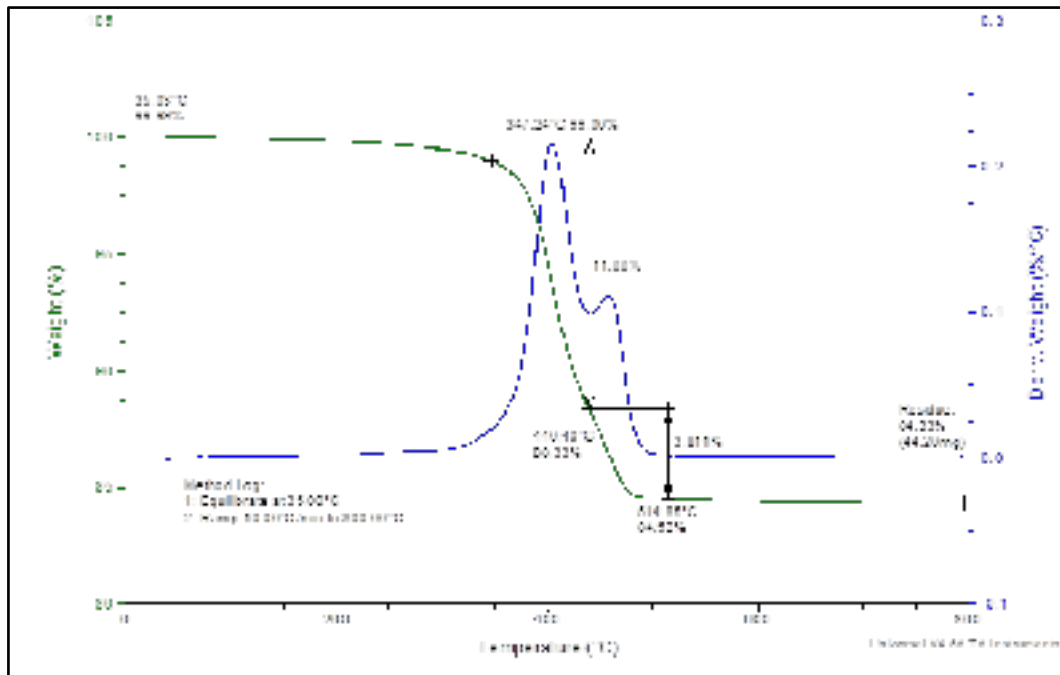


Fig.3.25 : Thermogravimetric analysis (TGA) diagram shows 85% residual ceramic amount

The same results are provided to me through subsequent graphs (Fig. 3.26) also by DCCI Department (University of Genova) to confirm that the percentage of ceramic material is 85%.

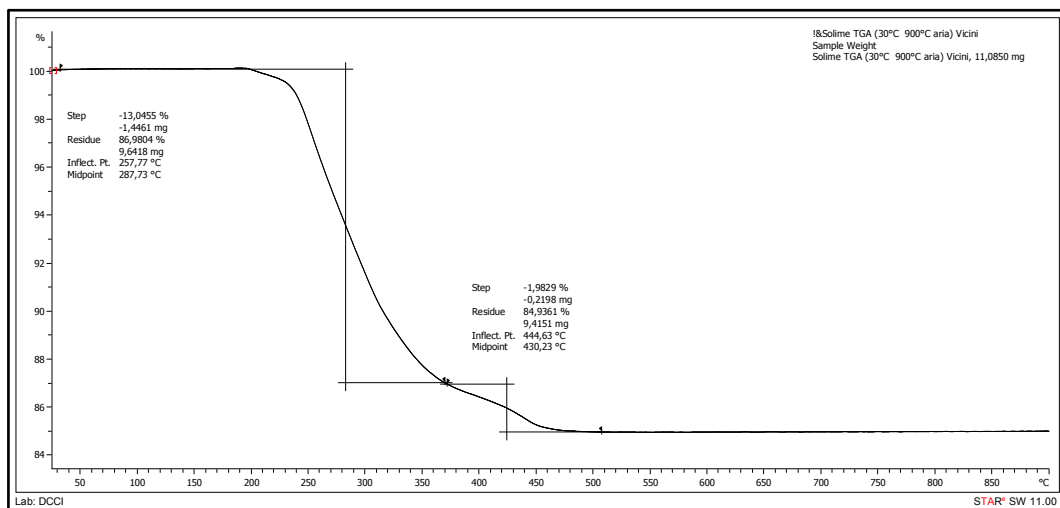


Fig.3.26 : Also TGA test from DCCI (University of Genova) confirm 85% residual ceramic amount

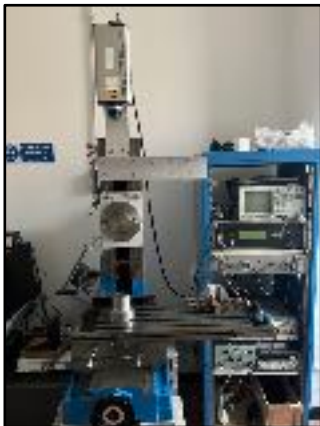
3.2.5 INSTRUMENTS

- At DICCA DEPARTMENT

- Microscope NIKON ECLIPSE VL100



- Internal Friction device inHouse at DICCA



- ZwickRoell AllroundLine universal testing machine Z050



- Oven Sirio InSINT 1600



- Memmert UM500 Lab oven



- Gambetti Low pressure Plasma Colibri



- Grinder Platorello Struers



- FOME Miller



- Airbrush double action system My Olimpos HP-23 BC



- At DISTAV DEPARTMENT

- Powder Diffractometer PW 3710 with software Philips X'pert High Score
- Scanning electron microscope SEM Vega3 – TESCAN type LMU, equipped with detector EDS APOLLO XSDD (EDAX) with type analyzer DPP3, with software TEAM EDS (Texture and Elemental Analytical Microscopy)

- PRIVATE OUTSOURCES

- Stereolithographic (SLA) 3Dprinter Formlabs Form 2
- 5-axis milling machine Imes Icore 250i
- Dental furnaces Shenpaz Sintra Pro

CHAPTER 4 - RESULTS

4.1. PROTOTYPE #1 TESTS

The test session started with some printing processes, simply with the manual extrusion command without loading any .gcode file, to evaluate which features are working and what deserves a closer look.

The attention was given first of all to the basic features of the 3D printer working: correct ignition, correct internal lighting, correct closure of the door, absence of unsuitable noises. Confirmed all these elements, I started the analysis of different factors such as the fluidity of movement of the extruder, the correct air cooling through the cooler fans, the appropriate supporting arms sliding.

4.1.1 PRELIMINARY LABORATORY TESTS RESULTS

The first results have confirmed that the whole system works from a mechanical point of view without showing evident problems or defects, but evidently there are and I will go to analyze, but still not allowing to extrude material (Fig.4.1), probably due to an incompatibility between the chosen material, of which i will explain the details later, and the 3D printer, still adapted from a different production method.

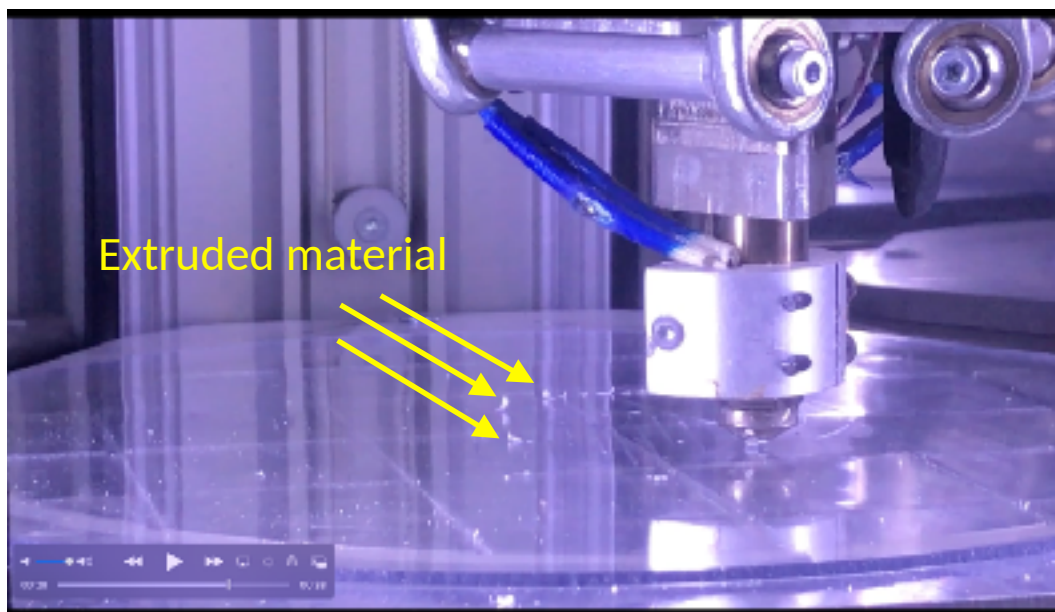


Fig 4.1 : With some video I have evaluated the 3D printing process, making a check list of what had to be more deeply analyzed. On first 3d printing session it has been noticed a lack of material extrusion

The *Prototype #1* was on and running but no material was coming out.

This situation led me to hypothesize and try all the alternatives to make the system work, changing the various settings on the operator display of which, just for the sake of brevity, I do not report all the combinations performed, both in terms of temperatures and extrusion speed.

I have assumed a blockage of ceramic material in the chamber and due to this I disassembled the extruder (Fig.4.2).

After cleaning (Fig.4.3) I noticed that the material polymerizes in the path of the cochlea and the ceramic part causes an abrasion, visible with streaks on the internal surfaces of the chamber and external of the cochlea.



Fig.4.2 : the material, polymerized, is stocked around the cochlea



Fig.4.3 : Cochlea cleaning, is quite evident the presence of streak

The problem is serious for two reasons:

- 1) the printer does not work, in fact what comes out is not of acceptable quality to be printed
- 2) the motor is subjected to excessive stress due to the friction of the material and therefore the failure of the motor has been considered as a certain evolution.

Regarding this last point:

- the replacement of the engine with a more powerful one was considered useless because any engine would have failed equally
- a heavier engine would have increased inertia and led to the imbalance of the delta system.

Evaluating the situation, with BTK Dental and WASP companies I decided, as a quicker and easier thing to do, to buy more material to test (Fig.4.4)

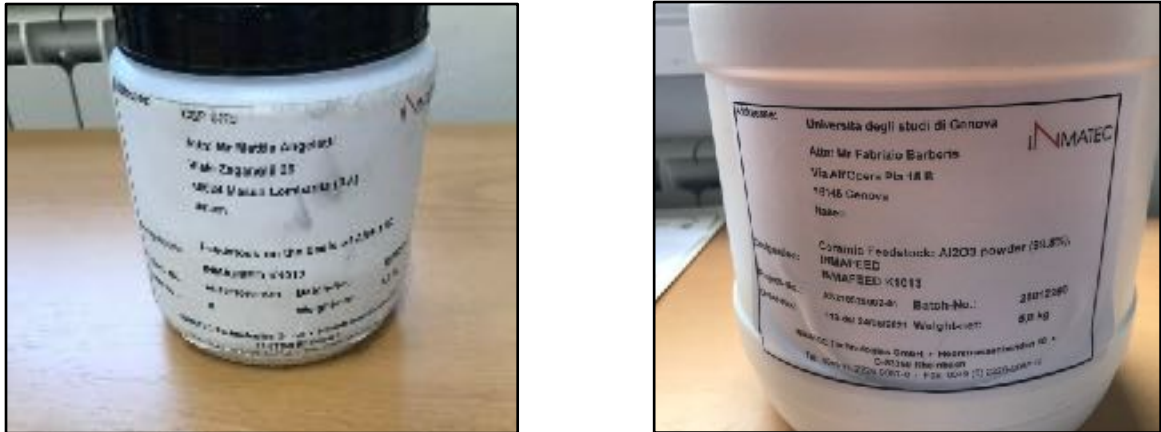


Fig 4.4 :INMAFEED K1013 provided by WASP (on the left) and a new supply ordered by University of Genova

Even after testing the new material order, I did not obtain any results other than those obtained with the previous checks, consequently it means I had to think about hardware modifications that, in agreement with the BTK Dental and WASP companies, was regarding cochlea at first.

The experimental phase is then started with the study and the possible necessary development of each of these components.

4.1.2 SCREW DEVELOPMENT

The R&D team performed a market analysis by evaluating the screws already used in other systems to figure out some features(Fig.4.5)



Fig 4.5 : Different screws found on the market

The visual analysis already described of the auger highlighted how there were streaks attributable to a possible internal contact with the barrel and to friction with the ceramic material.

I hypothesized to replace it with a ceramic auger, but it would have been too difficult to find it, as well as a ceramic barrel, even in this regard considering the validity of the hypothesis of coating the internal surface of the barrel to facilitate the sliding of the material, but also this solution would have been difficult to implement in a short time.

It was then realized that it would have been appropriate to modify the dimensions (Hypothesis *Prototype #2*) by opting for a longer screw that would allow for greater storage of the material inside the cylindrical metal chamber and evaluate whether this modification could be useful to favor the condensation necessary for extrusion, even if with the disadvantage of storing greater quantities of material and keeping it at high temperatures, of which later I will explain the tests made and the relative conclusions, an element that should not be underestimated but which at this stage I have considered of lesser importance and therefore acceptable.

Later, hypotheses were also formulated regarding the cause of the black/silver metallic streaks on the ceramic material, finding two possible answers:

- Due to friction with the internal surface of the metallic cylinder.
- Due to a process of excessive polymerization of the polymeric component of the material due to prolonged exposure to high temperatures set especially in the extruder heatsink, but in general throughout its extension.

As part of the evaluation of these possible modifications, the redesign of the auger led me to reevaluate other components, such as the cardan but also the lower portion of the cylinder, near the nozzle and in fact not only does the polymer block us around the auger but also at its level

4.1.3 HEATSINK AND NOOZLE DEVELOPMENT

A subsequent analysis phase considered the lower and outer portions of the extruder in terms of both operation and maintenance.

In the first attempts at extrusion, the blockage of the material resulted in the need to disassemble the entire extruder to clean it and remove the trapped ceramic material.

This procedure therefore required : (Fig.4.6)

- Disassembly of the loading hopper

- Loosening screws around the jaw to allow its removal from the cylinder to prevent the thermocouples attached to it from tearing or even detaching, with difficulty to be repositioned, because they would be pulled.
- Unscrewing of the screws that we have seen passing through the metal plates of the *Extruder Heatsink*
- Remove the Extruder Heatsink and the connected cylinder

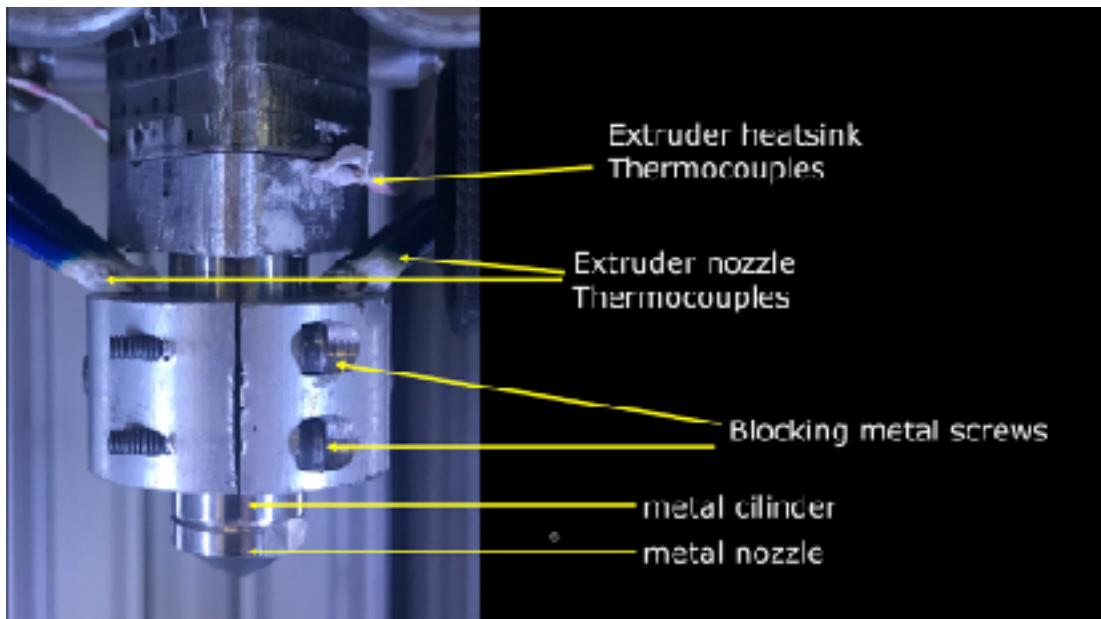


Fig 4.6: The initial test phases required the disassembly and consequent reassembly of all the components of the lower portion of the Extruder.

Regarding the *Extruder Nozzle*, the internal problems in the distribution were essentially:

- 1) The angle of the bottom is too open and this causes a stop to material flow
- 2) Early polymerization in the cochlea path and in the bottom.

I have tackled the most immediate problem and BTK redesigned the nozzles modifying the internal taper which, being 140°, immediately suggested it could be an important cause of material clogging, while the diameter of the cylindrical portion of 12 mm and of the nozzle of 1.2 mm were considered sufficiently large for material extrusion and therefore not initially modified. Two proposals were drawn, similar to each other except for the free space between the auger tip and the exit hole useful for material accumulation. (Fig.4.7)

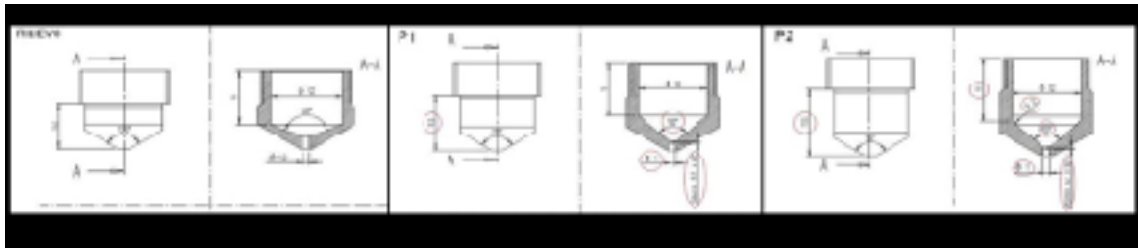


Fig.4.7 : The relief of the pre-existing situation (on the left), in the center and on the right of the image the two different preliminary projects

Based on these evaluations and proposals, two different groups of nozzles were then manufactured by BTK for testing (Fig.4.8):

- Nozzle P1 :Height 9 mm and 100 ° internal angle, with 1mm diameter cylindric hole
- Nozzle P2 :Height 11 mm and 100 ° internal angle, with 1mm diameter cylindric hole

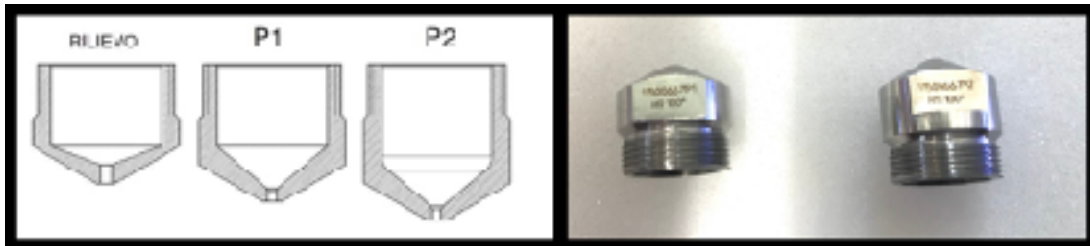


Fig.4.8 The different designs (on the left) and the nozzles P1 and P2 realized

The experimental campaign of this, albeit promising solution, was not completed due to the out-of-tolerance induced by the continuous need to disassemble and clean the auger at each printing cycle which led to subsequent critical issues.

4.1.4 MATERIAL DEVELOPMENT PRELIMINARY EVALUATIONS

Up to now my considerations have been focused on the mechanical components, but this should not confuse that the R&D Team has not paid attention also to the material to be used. This topic would open to an infinite possibility of options available on the market, or even better of development at the collaboration of the various departments of the University of Genoa, but was voluntarily left momentarily in abeyance because the first objective was to be able to extrude first and then print, with consistency and repeatability. The preliminary evaluations already described underlined some criticalities of project type, independently from the used material, that had to be resolved and, only after having developed in such sense the *Prototype #1*, the attention would be turned to

the study and development of the material. The fact that the material was commercially available also supports the practical sense of this PhD as i wanted to focus initially on the 3D printer giving for granted the availability of the material, in this sense, however, should not exclude the attention that, once perfected the printing processes, was given to the material itself for a further step of future development.

4.1.5 CRITICALITY

The main criticality of the development phase of *Prototype #1*, in addition to the lack of material extrusion, involved its own maintenance, as going to disassemble repeatedly the extruder to clean it from clogged material occurred a series of mechanical problems:

- The jaw locking screws around the *Extruder Nozzle* started to wear out creating problems in screwing and unscrewing and eventually having to resort to a metal clamp to tighten the jaw itself (Fig.4.9)
- The metal plates of the *Extruder Heatsink*, as a result of repeated disassembly have lost their internal precision (as each disassembly / reassembly created the risk of even a slight misalignment) going to create even small steps that our opinion could amplify the friction on the ceramic material hindering the escape.(Fig 4.10)



Fig. 4.9 : it became necessary to screw a metal clamp around the *Extruder Nozzle*

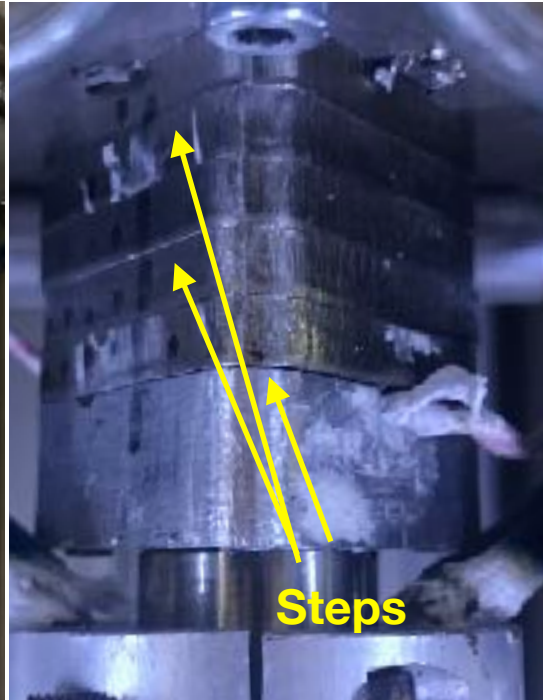


Fig. 4.10 : the lack of accuracy that occurred also in the internal surface of the *Extruder Heatsink*

- During the unscrewing of the nozzle, also the cylinder screwed to it has undergone a rotation and, given the poor grip with pliers to keep it still because of its smooth and circular shape, it was increasingly difficult to tighten it properly. This phenomenon has been seen in the last days of this phase a rotation caused by internal friction with the material rotated by the screw, making the system difficult to use.(Fig.4.11-4.12)

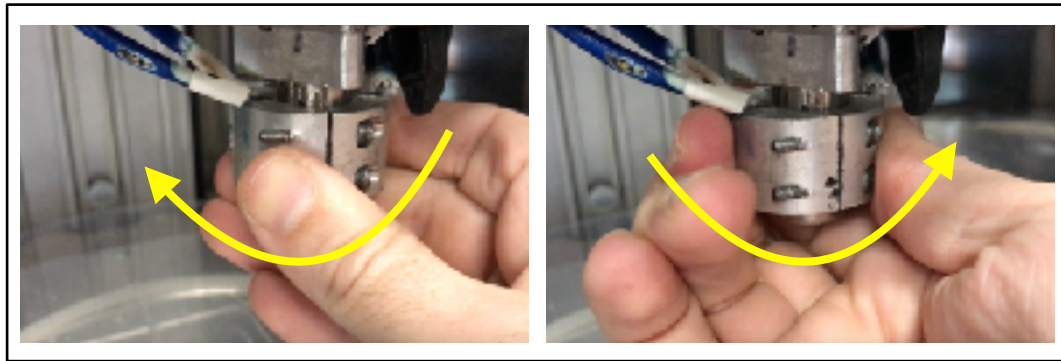


Fig. 4.11-4.12 : the *Extruder Nozzle* and the cylinder move

- The thermocouples, due to the rotational movement of the jaw around the *Extruder Nozzle* started being difficult to fix, these movements have also damaged them due to the torsion exposing the wires and causing a spark and burning smell that has immediately determined the suspension of laboratory tests (Fig.4.13)



Fig.4.13 : the movement of *Extruder Nozzle* determined the rotation and damaging of thermocouples

This first experimental phase could be seen as unsuccessful but in reality it allowed me to understand which were the major critical issues, which should have the priority of resolution in order to be able to eventually intervene on those that in my opinion would not have helped me to obtain an immediate satisfactory extrusion. I then proceeded with the disassembly of the motor, disconnecting it from the electrical connections, of the various components of the extruder to send it to the WASP headquarters for the appropriate modifications that would have involved(Fig.4.14):

- Material loading system
- Cooling fans

- Screw design
- New heating system of *Extruder Heatsink* and *Extruder Nozzle*
- Nozzle

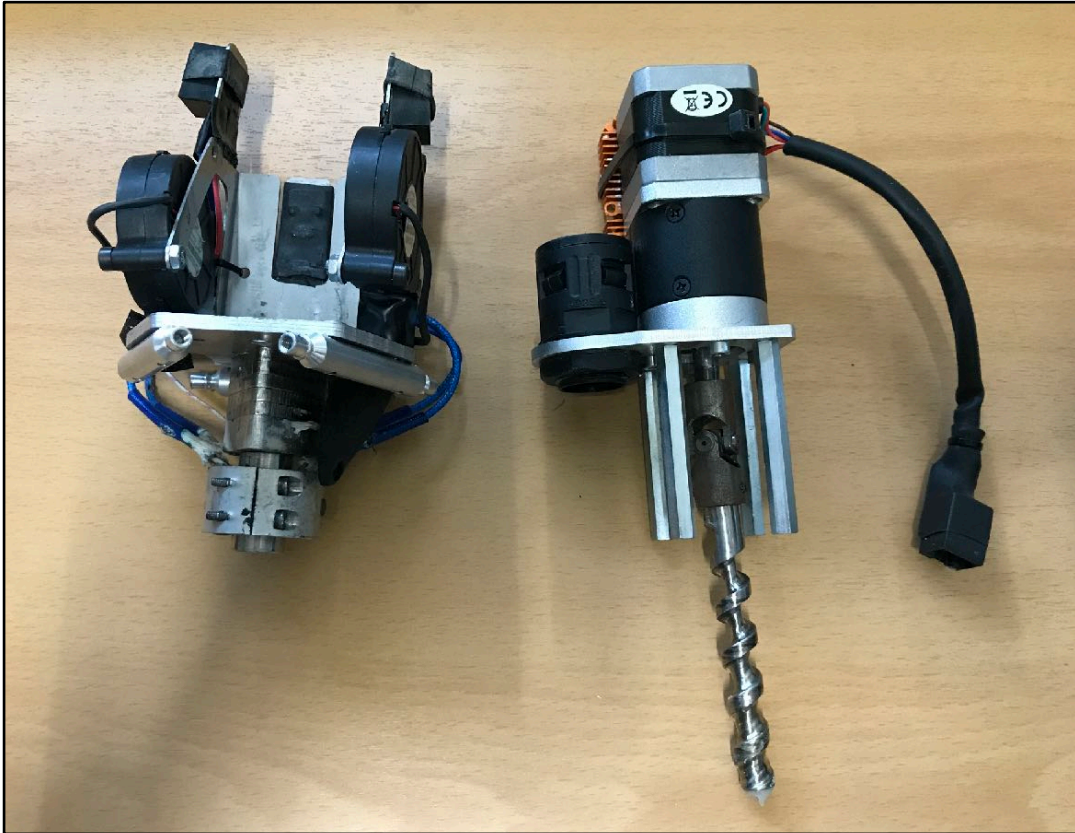


Fig.4.14 : all components disassembled and sent to WASP headquarter
for planned modifications.

*

4.2 PROTOTYPE #2

4.2.1 HARDWARE NEW FEATURES

The development process has seen R&D team evaluate all the appropriate changes studied and the *Prototype #2* has been delivered at DICCA in June 2021. (Fig.4.15-4.16)

The new device has been mounted and set at WASP headquarter in order to guarantee the perfect setting by the producer.

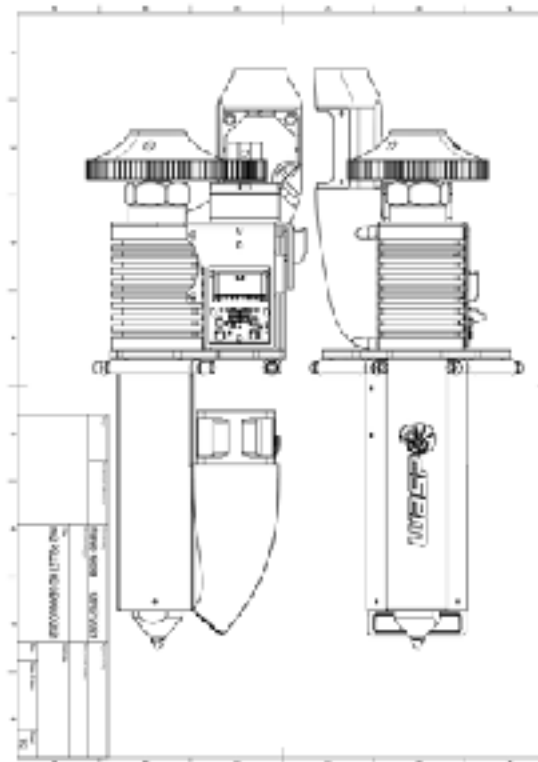


Fig.4.15 : the technical sheet

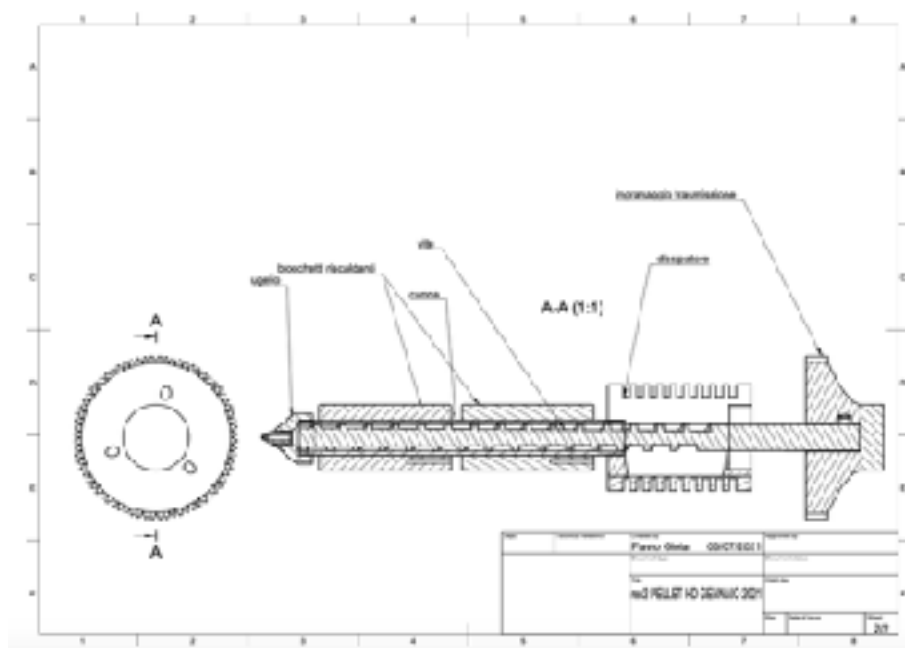


Fig.4.16 : in datasheet, a section of the extruder

Compared to *Prototype #1*, there are some substantial differences (Fig.4.17):

- the loading hopper has been reduced in size, previously considered exaggeratedly large, and inclined to facilitate the slide of the material in the chamber
- the *Extruder Nozzle* has been totally redesigned for a better maintenance, reducing the risk of the rotation of the entire zone (as in *Prototype # 1* had been highlighted)
- the *Extruder Heatsink* has been redesigned creating a single cylinder covering the chamber
- the screw has been directly connected to the motor and its dimensions are greater in length
- a transmission gear has been connected to the motor that directly determines the movement of the screw
- the system of assembly and disassembly has been simplified with a bolt on the head of the screw, connected to the transmission gear, which, although still not easy to manage, makes it less complicated to remove the screw for cleaning procedures.
- The cooling system has been modified mounting just one single cooler fan, positioned on the opposite side from the loading hopper.

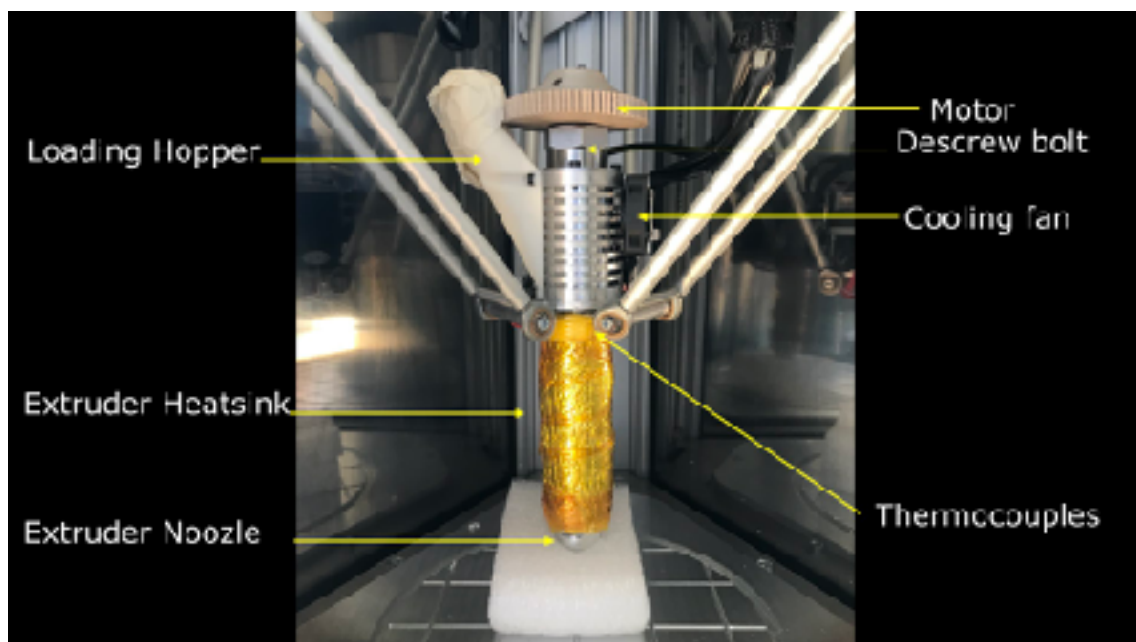


Fig.4.17 : *Prototype #2*

4.2.2 NEW PROCEDURES IN WORKING FLOW

One of the problems noted in *Prototype #1* was related to the ease of disassemble and removal of the extruder in case of blocked material and need for maintenance. Because it is a prototype development phase, certain modifications may not have completely solved the difficulties, but it is also must acknowledge that my attention, and the R&D Team all, focused in this stage on the capacity of the system to be able to print the material although obtaining in this *Prototype #2* very important advances in the maintenance process I will following describe (Fig. 4.18-4.20):

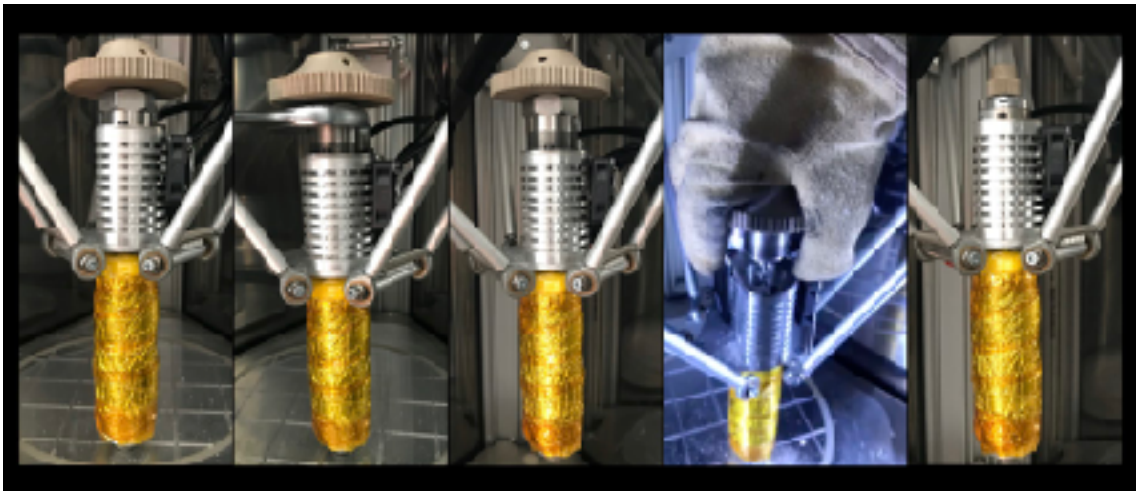
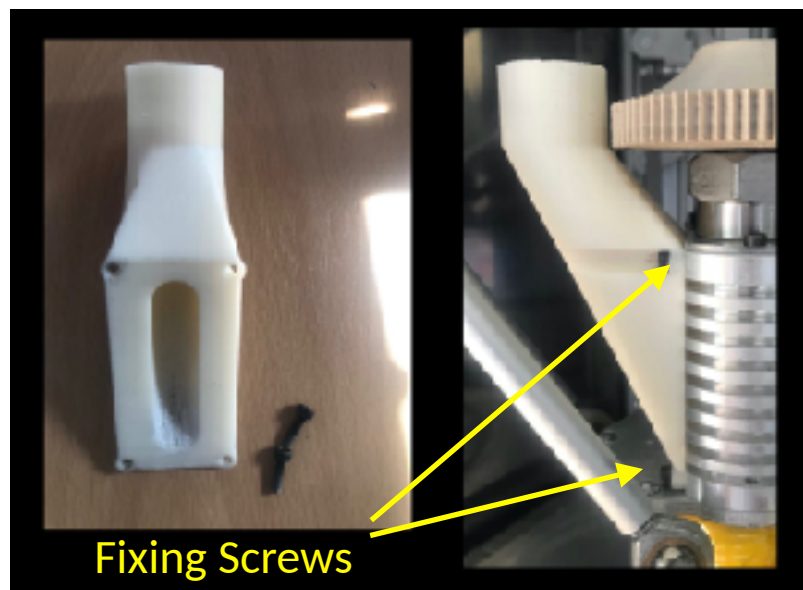


Fig 4.18 : Any need to remove the screw requires unscrewing the bolt attached to it at the top using a #30 wrench. This procedure should be performed at high temperature (150° Extruder Heatsink and Extruder Nozzle) to prevent the material inside the chamber from hardening making it impossible to remove the screw.

Fig 4.19 : The loading hopper, produced by WASP through 3D printing, has an opening on the top and an internal inclination useful to slide down the pellets inside the chamber. It is screwed to the heatsink through 4 screws with 2mm pitch.



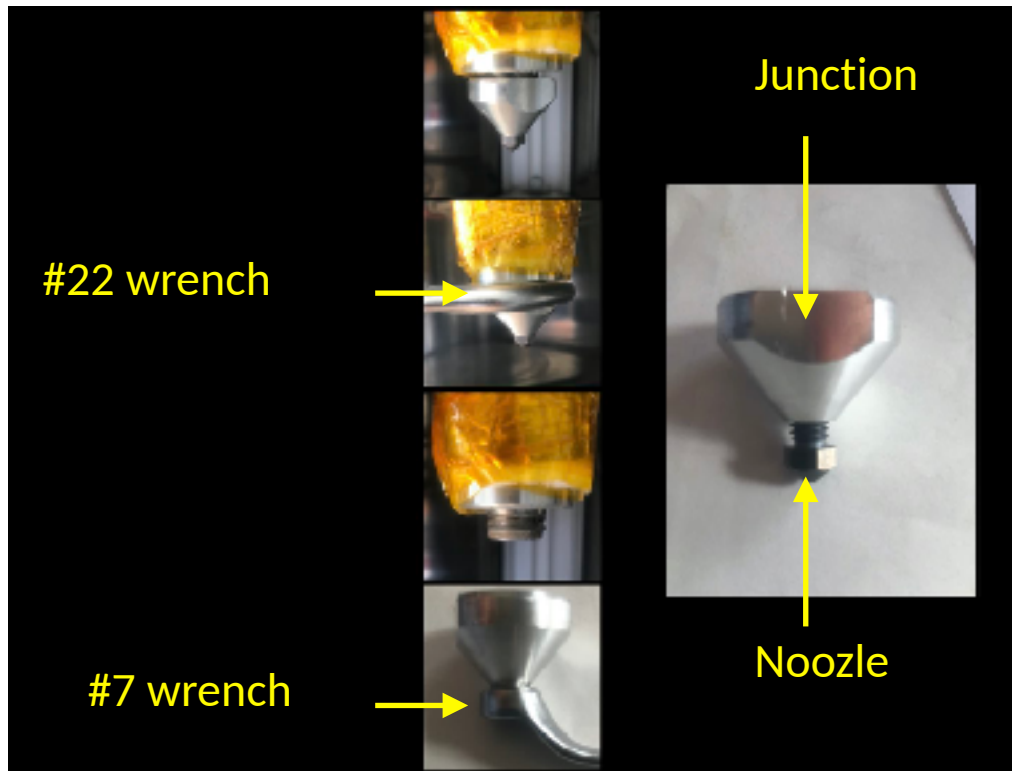


Fig 4.20 : The nozzle consists of a metal conic junction to the metal cylinder that can be unscrewed with #22 wrench and the actual nozzle to be disassembled with #7 wrench. This choice was made to be able to more easily change only the bottom part, preserving the cylinder so as to avoid the problems occurred on *Prototype #1*.

4.2.3 TEMPERATURE TEST

Having described the structural changes transferred to *Prototype # 2*, with a first positive evolution, as evidence of how the changes had already improved the prototype, as just explained have also had positive consequences on the maintenance processes, I started the laboratory tests again.

Before delivery to the DICCA, some checking tests had already been carried out at the WASP headquarters and the feedback was positive, this means that the extruder had demonstrated the ability to release material from the nozzle, in the modalities still to be studied and to described.

The first hypothesis formulated was that, having ascertained how effective the modifications made, by changing the *Extruder Heatsink* (EHT) and *Extruder Nozzle* (ENT) temperatures, it was possible to determine a change in the ability of the material around the screw inside the chamber to slide in a constant and continuous way through the nozzle.

The extrusion commands were carried out in manual mode in order to intervene, stopping the process, in case of problems and the first temperature setting were the

processing temperatures injection molding suggested by the INMATEC Company (150°C-165°C). The first response was the expected one with material extrusion .(Fig 4.21)

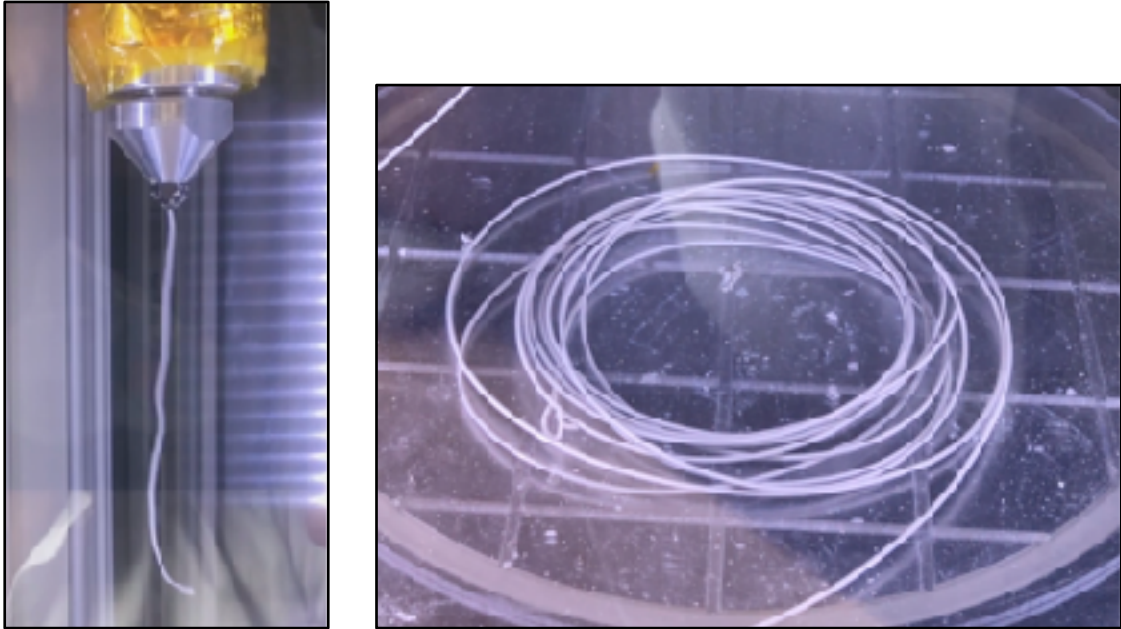


Fig.4.21 : Prototype #2 ,immediately delivered, starts extruding material

Immediately from the beginning I noticed an evident improvement in the functioning as already witnessed and I started the new experimental campaign.(Fig.4.22)



Fig.4.22 : Some specimens of extruder ceramic

An evident sensitivity of the machine is evident to the variation of the imposed parameters convincing me that the direction was correct , continuing to modify some temperatures (EHt and ENt) and analyzing the results both in terms of consistency and roughness (Tab 4.5-4.7), and through a visual analysis performed under the microscope.

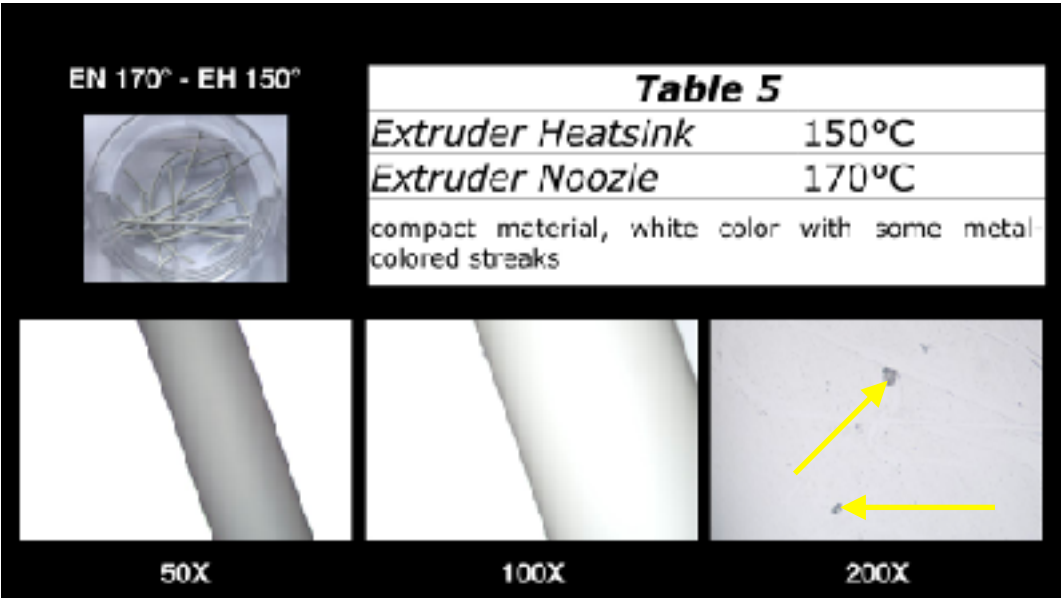


Table 4.5: EHt 150°C - ENt 170°C - some metal colored spots are visible

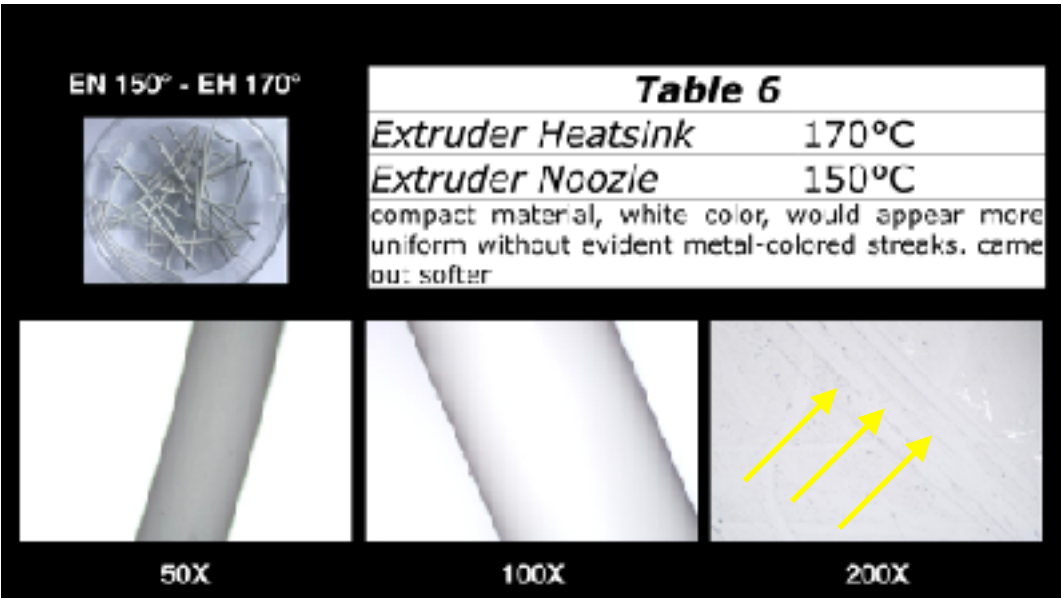


Table 4.6: EHt 170°C - ENt 150°C - some streks are visible on the surface

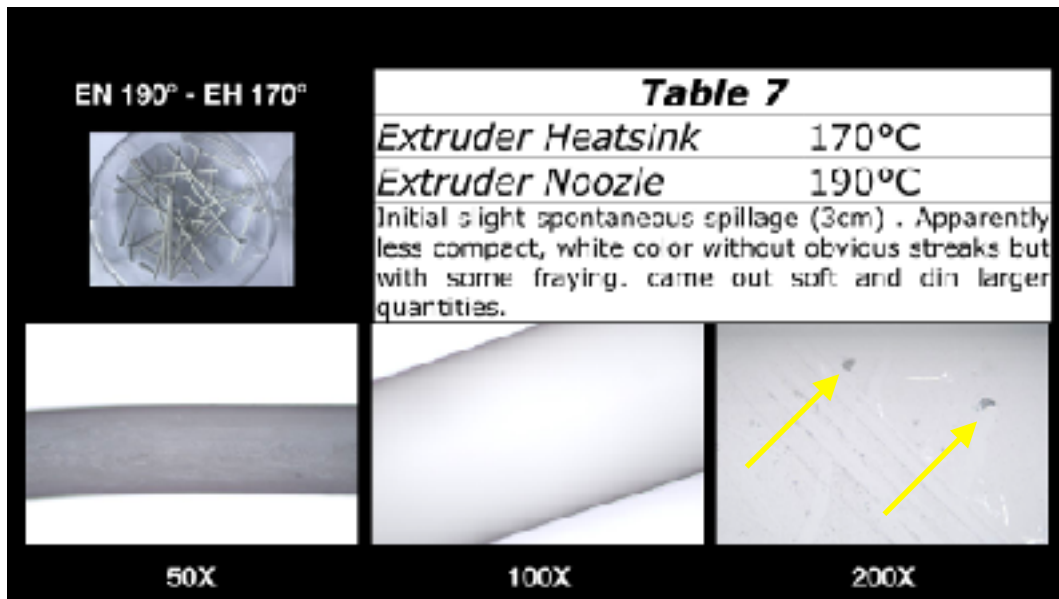


Table 4.7: EHT 170°C - ENT 190°C

At this point, with the intention of continuing with the evaluations and producing a sufficient quantity of material to be analyzed, I continued extruding with the manual program, always changing the material, emptying the chamber and reassembling everything with different temperatures to evaluate the limit performance and we arrived at the block of the process, without allowing anymore material to leak, regardless of the set temperatures . Disassembling the loading hopper it was evident that there was an excessive accumulation of material, in pellets and dust, at the entrance to the chamber. (Fig. 4.23)



Fig.4.23 : Is well visible the material clogging in pellet and dust, this situation can avoid new pellets slide into the screw and till the bottom of the chamber.

Removing the screw, the entire path inside it was full of condensed material which, however, also had a metallic dark color, a reason for future further evaluations. (Fig.4.24)

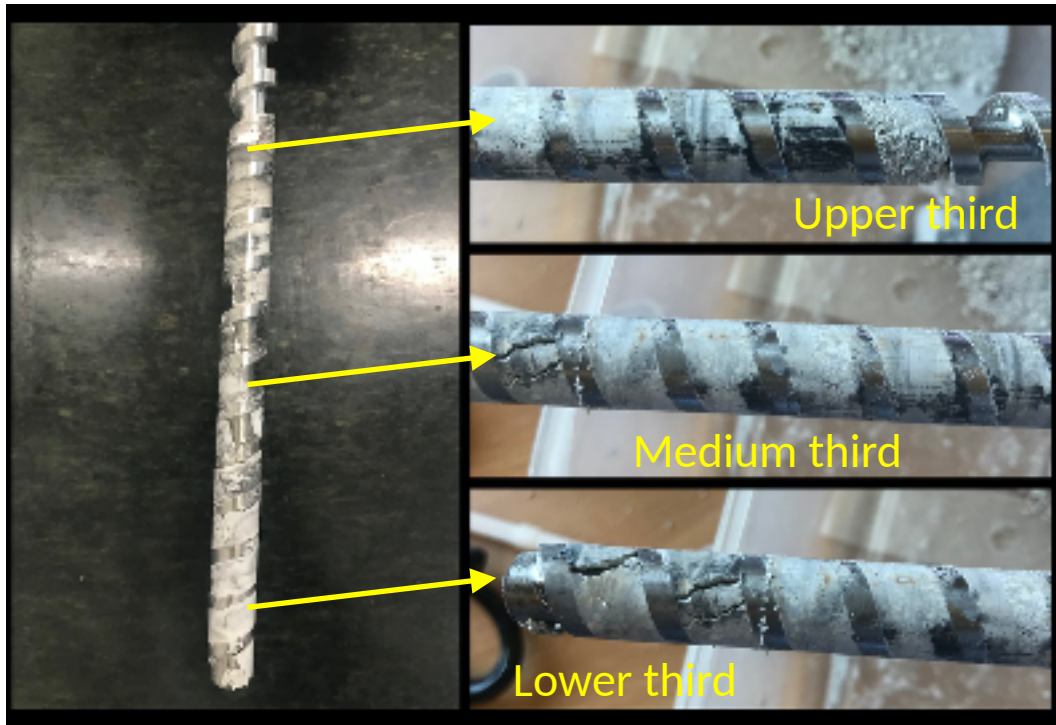


Fig.4.24 :The material removed with the screw, no evident differences has been detected due to the position of it. Metal dark area are well visible mainly on the upper third but this detail can also be caused by the mixing and the movement of the material all other the screw.

4.2.4 CRITICALITY

During meeting with the R&D Teams I have formulated some theories about the reason of this sudden stop:

- Material reflux - the internal characteristics of the chamber are still not suitable for favoring the extrusion of the material, as a consequence of this, by clogging at the bottom tends to rise towards the top of the screw
- Not adequate temperature gradient in the chamber - the temperatures ,even if under the indications of the Owner Company, are not sufficient for extrusion and therefore the material, still not very fluid, tends to accumulate inside the chamber, in its lower portion

As an immediate attempt to solve the problem, it was decided to carry out a manual extrusion test cycle with a higher T (200-220 °C) and reduced screw speed, trying to load 1g. of material to see the output material, but the result was not different and also the

pellet amount was not enough to fill the chamber and the low compactness of the inadequate material detected confirmed the need to insert it in abundance to favor a sliding of the pellets towards the bottom of the chamber which would, in any case, favor the compaction of the material, even though at this moment the cause of the extrusion block is still under evaluation. (Fig.4.25)



Fig.4.25 :Charging just a small pellet amount determinate many gaps and a lack of condensation

Going on with some other test, I reduce the size of the pellets with the idea of favoring their slippage and limiting the compaction stress which could be excessive compared to the ability of the screw to slide the material downwards.(Fig. 4.26)



Fig.4.26 :details of the ceramic ball mill

Even the results of this latest test were not satisfying, thus suggesting that, together with limits on the material and its ability to pass through the entire system, the problem could also lie in the final part, at the level of the *Extruder Nozzle*, which, despite the development performed on *Prototype # 1*, it was not yet suitable.

4.2.5 NEW NOOZLE DEVELOPMENT

It was therefore decided to try to enlarge both the external orifice and the internal portion of the nozzle using a new nozzle with a diameter greater than the 0.8 mm used up

to now and opted for a new brass nozzle, a material selected exclusively because it is already present in BTK Dental, with a diameter of 1.2 mm. (Fig. 4.27-4.29)

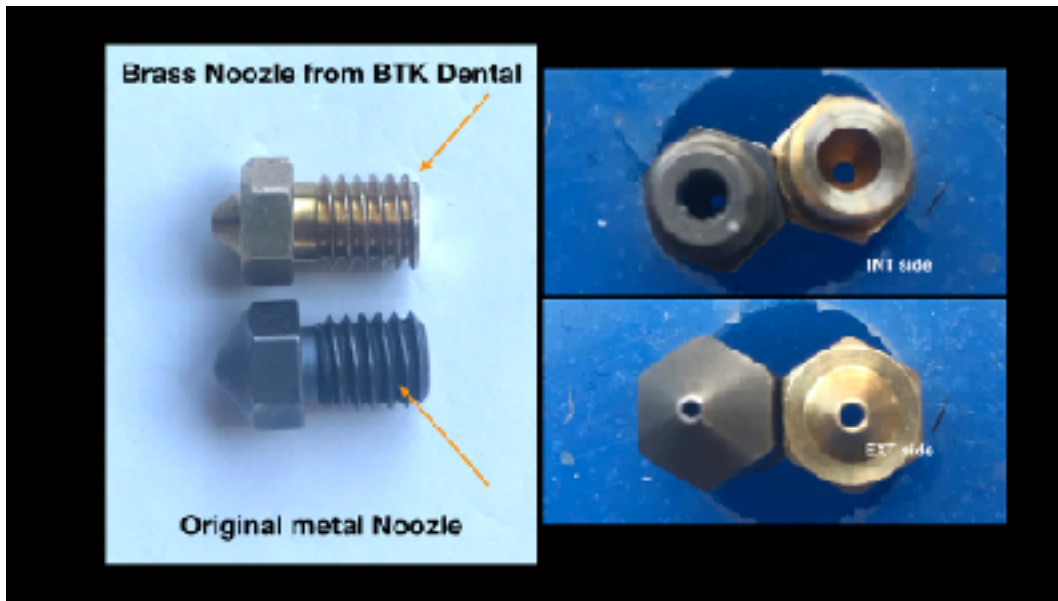


Fig.4.27 : Comparison between the original metal *Extruder Nozzle* and the new brass *Extruder Nozzle* 1.2 mm diameter.

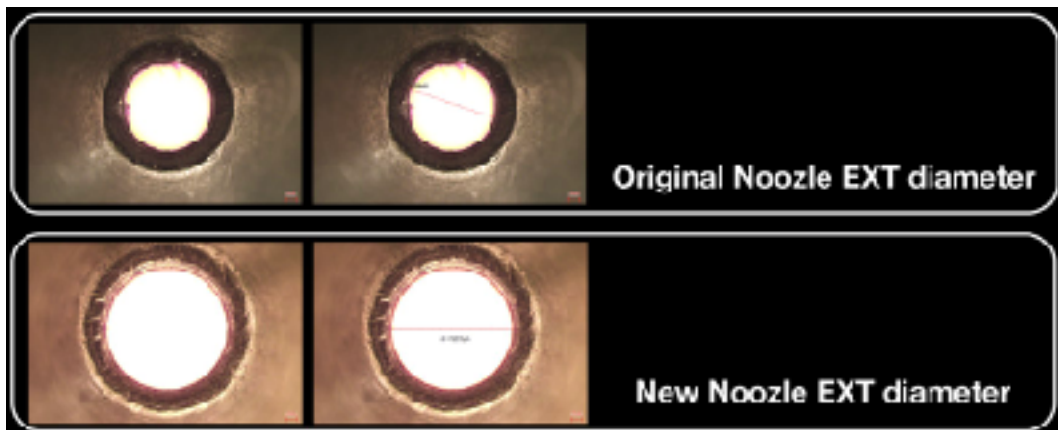


Fig.4.28 : A control with Nikon Eclipse LV100 on different *Extruder Nozzle* diameters

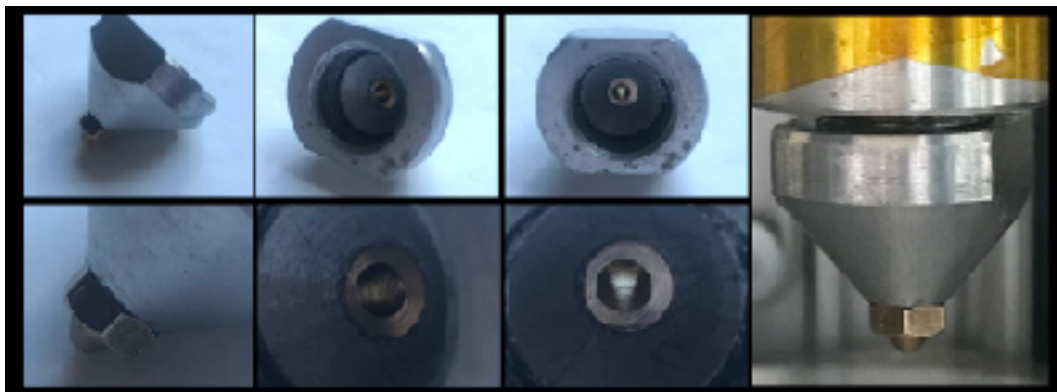


Fig.4.29 : A control of accuracy and fitting of the new brass *Extruder Nozzle* 1.2

4.2.6 EXTRUSION

Summarizing in table 8 the various attempts to solve the extrusion blocking problem, we can see how the turning point is attributable to the enlargement of the nozzle, with the use of the new *Extruder Nozzle 1.2mm*, while maintaining the utmost attention on what was in any case found to be an evident criticality, such as clogging in the loading / entrance hopper area of the chamber.

Type of test	Result
<i>Extruder Heatsink</i> (EHt) and <i>Extruder Nozzle</i> (ENT) temperature changes	Not Satisfying
Internal <i>Extruder Nozzle</i> different tapering (from 140° to100°)	Not Satisfying
Pellet dimensions reduction	Not Satisfying
Increasing <i>Extruder Nozzle</i> diameter (from 0.8 to 1.2 mm)	Satisfying

Table 8: The experimental phase focused on material extrusion has given different results

After having performed several extrusion tests of the ceramic material, i was able to see how all the modifications I made on the *Prototype #2* allowed me to finally obtain interesting results in terms of extrusion with continuity, not yet constant but still considerable as a good starting point for next tests .(Fig. 4.30)

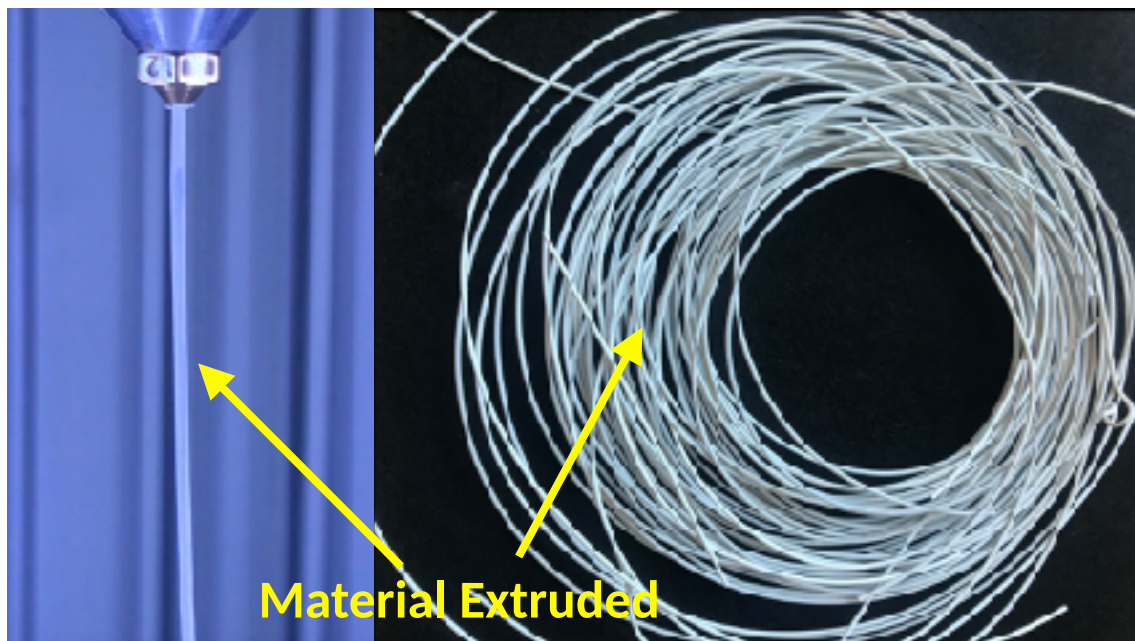


Fig.4.30 : The 1,2 diameter ceramic filament extrusion (on the left) is in this phase continuous (on the right)

Showing and discussing these results with R&D team I was thus able to undertake the subsequent development phase dedicated to the creation and optimization of the 3D printing process. I immediately dedicate optical tests with analysis under microscope NIKON ECLIPSE LV 100 to identify any porosity or surface gaps that did not seem to exist on a direct optical examination but which were instead detected, albeit of an insignificant amount. (Fig.4.31)

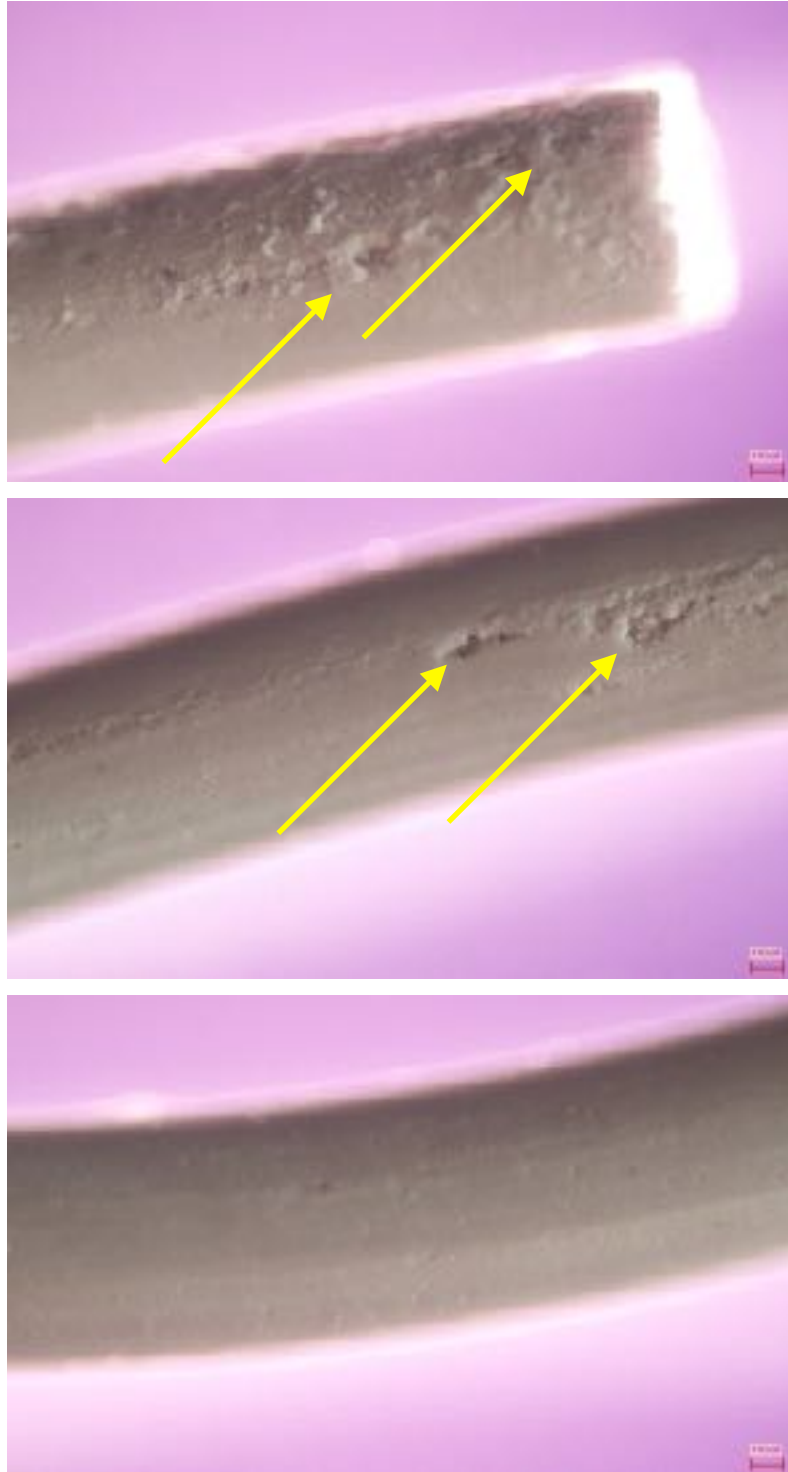


Fig.4.31 : Under Microscope, are visible some defect whose presence deserves further investigation to define its origin

4.2.7 3D PRINTING

The first step is to proceed with the print tests, evaluating the results by going forward and setting new features, such as the calibration of some software parameters, the adjustment of the motor or system flow rate, then I elaborate with BTK and WASP, using the design software (software Simplify3D, version 4.1.2), a file with a cylinder (40mm height X 35 mm diameter) which, as a first idea, I thought might be the simplest shape to print.

The first printing process was performed with the .gcode file, named *Cilindro_ceramica_0.8mm.gcode*. (Fig.4.32-4.34).

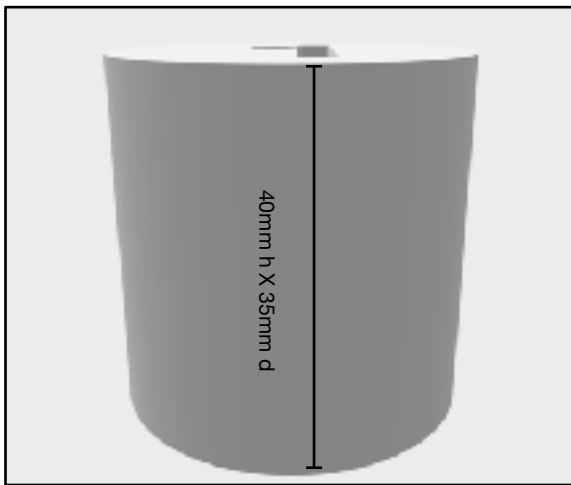


Fig.4.32 : The file
Cilindro_ceramica_0.8mm.gcode



Fig.4.33 : The 3D printed object
on which is evident some
adjustments are necessary

It is immediately evident how many discontinuities are present :

- an unsatisfactory layering because it is clearly visible that in some points the filament is just resting on the previous one instead of joining with, creating a poor density of the 3D printed object.

- In the internal part, due to the designer's pleasure of inserting the shape 1, the filament is not straight and evident, probably due to the difficulty of the extruder to follow the planned path
- In relationship to the external walls, the internal filament looks to be collapsed, probably due to a discontinuity in layering associated to a difficult path.

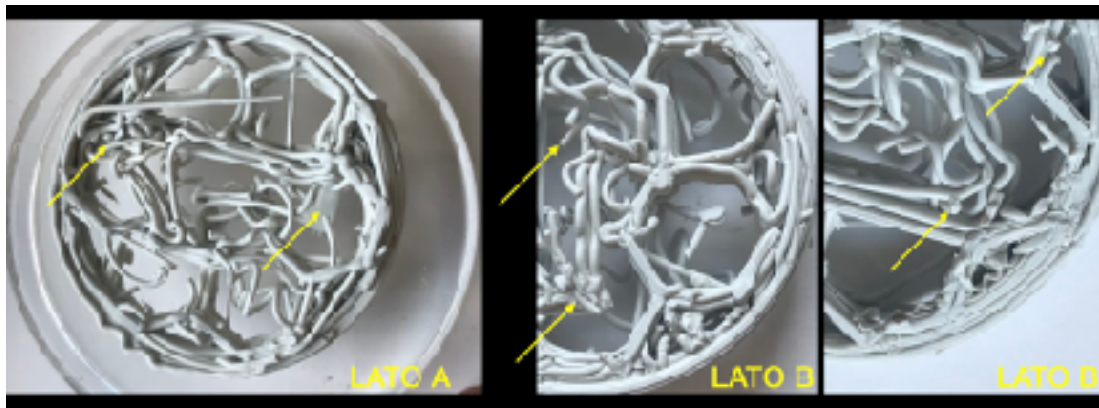


Fig.4.34 :On both sides, A and B , is evident the discontinuity of the filament that, especially in the internal area, ha underlined how much is still have to be done.

Table 4.9 is related to the .gcode file by which I have maintained some parameters just to underline the most evident ones that, due to some live necessity, I can modified on the Operator Display. The .gcode parameters chart is much more longer and complete with the need, however, on some settings to request intervention from WASP.

```
G-Code generated by Simplify3D(R) Version 4.1.2
Oct 19, 2021 at 1:40:00 PM
Settings Summary
processName,Process1
applyToModels,1cil
profileName,PELLET HD CERAMICA 0.8mm
profileVersion,2021-10-12 09:50:31
baseProfile,DeltaWASP 2040 Dual (modified)

layerHeight,0.25

temperatureName,Nozzle,Barrel,Heated Bed
temperatureSetpointTemperatures,170,150,40

maxCoolingFanSpeed,100
bridgingFanSpeed,100
```

Table 4.9 : On the top are visible informations about Date, Software, file name, 3Dprinter and some others like layer height, temperatures, speeds.

Making an analysis of this result obtained, my first evaluation refers to the Z dimension of the layers which in my opinion, as just described, is excessive and I therefore requested,

while keeping the cylindric design unchanged just to evaluate one parameter per time , to prepare the new file *V3CERAMIC_CYLINDER_08mm.gcode*. From table 4.10, referring to the printing details, it can be seen how this dimension has varied from 0.25mm to 0.15mm.

```
G-Code generated by Simplify3D(R) Version 4.1.2
Oct 28, 2021 at 6:05:22 PM
Settings Summary
processName,Process2-1-1-1-1
applyToModels,1c1l
profileName,PELLET HD CERAMICA 0.8mm (modified)
profileVersion,2021-10-19 13:40:02
baseProfile,DeltaWASP 2040 Dual (modified)

layerHeight,0.15

temperatureName,Nozzle,Barrnel,Heated Bed
temperatureSetpointTemperatures,170,150,100

maxCoolingFanSpeed,100
bridgingFanSpeed,100
```

Table 4.10 : With the intention to avoid confusion, in this phase I planned to change just the parameter

I considered most effective to increase performances

The results immediately appeared in support of my hypothesis as, despite the still unresolved extrusion discontinuity, some gaps were filled by the short distance of the next layer allowing a better adaptation and a better stratification, even if not yet complete. Is now visible the 3D print geometry with well-defined edges and also a greater ease of the extruder to follow the internal lines, making me think that the union of successive layers would act, even though in a relative way but not to be underestimated, as a guide for the next layer thus favoring the 3dimensionality of the printed object.(Fig.4.35-4.36)

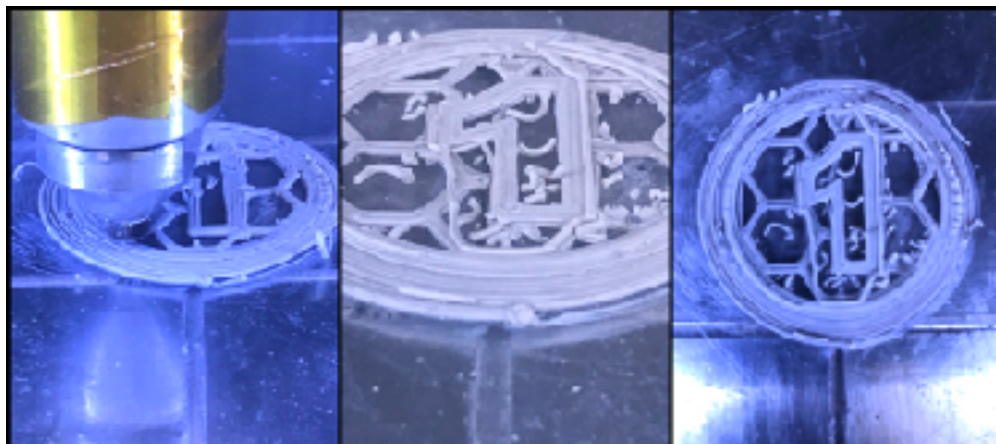


Fig.4.35 : Due to this new setting, the geometry start to be visible still disturbed by the material discontinuity

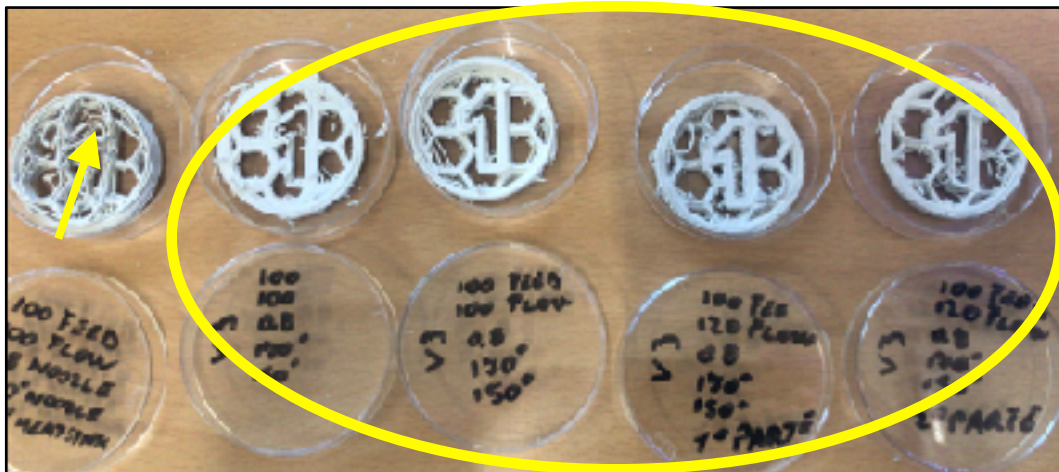


Fig.4.36 :Differences are evident. On the left it is difficult to distinguish a defined geometry and this lack further favors the displacement of subsequent layers, causing the entire structure to collapse rapidly. In the group on the right, on the other hand, a repetitiveness can be identified which, although absolutely not yet complete or satisfactory, underlines the importance of contact between successive layers.

At this point I can start make a first evaluation of what produced:

- Thickness layer is very important and at this point can be considered effective at 0,15mm
- The cylindric geometry has not to be considered wrong but, due to many curves and direction changes , especially caused by the internal design of the project, it would be simplified
- Due a still not obtained ability to have a constant continuous material extrusion, we can see and guess the final geometry but not achieve the completion of the whole process.

I abandoned the cylindrical drawing and, using the Ultimaker Cura 4.9.1 software, I created a parallelepiped (file name *Provino Solimei 8x3x50 mm.stl*)(Fig.4.37) whose measurements could be compared with samples highly qualified commercial Zirconium oxide ZrO_2 obtained from bars of the most popular Katana (Kuraray Noritake, Tokyo, Japan) brands, in collaboration with Mr. Daniele Rondoni dental laboratory, through milling and subsequent sintering at 1600 °C, as for INMAFEED K1013 indicated by the company.



Fig.4.37: Provino Solimei 8x3x50 mm.stl file

With same parameters set on .gcode I can start new 3Dprinting sessions. The first results of this new print design (*v1provino.gcode*) have given me confirmation, having set aside the geometric printing problem, that the laboratory activities would now be concentrated on the improvement of the parameters useful for the completion of the parallelepiped and its possible development.(Table 4.11)(Fig.4.38)

```
G-Code generated by Simplify3D(R) Version 4.1.2
Nov 9, 2021 at 2:55:32 PM
Settings Summary
processName,Process1-1
applyToModels,Provino Solimei 8 x 3 x 50 mm
profileName,PELLET HD CERAMICA 0.8mm
profileVersion,2021-10-19 13:40:02
baseProfile,DeltaWASP 2040 Dual (modified)

layerHeight,0.15

temperatureName,Nozzle,Barrel,Heated Bed
temperatureSetpointTemperatures,170,150,40

maxCoolingFanSpeed,100
bridgingFanSpeed,100
```

Table 4.11: *v1provino.gcode* settings

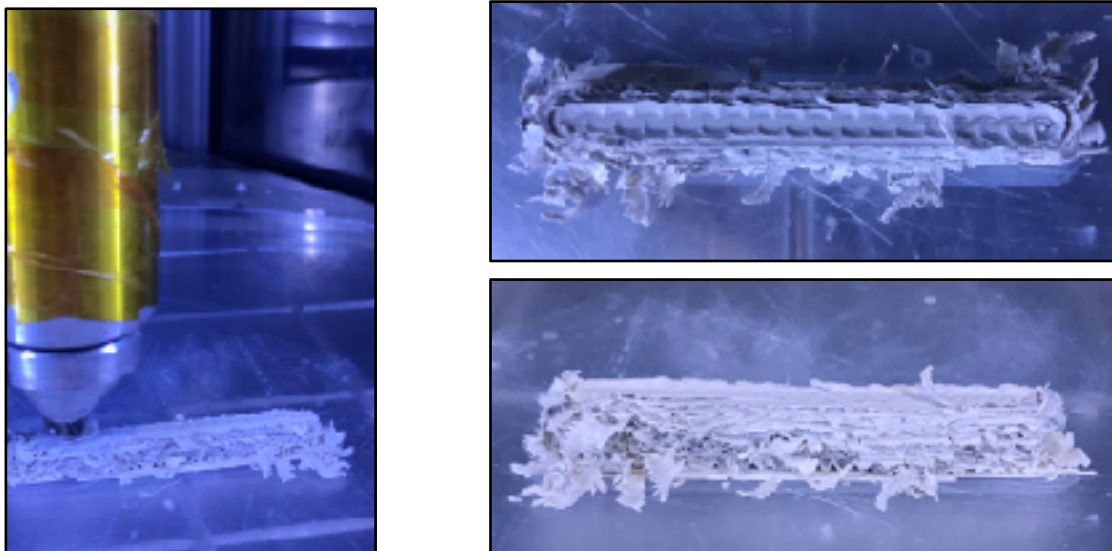


Fig.4.38:The printed parallelepiped *v1provino.gcode* from which a new phase of analysis begins

4.2.8 PARAMETERS IMPROVEMENT

Now I had the idea of carrying out an exploratory campaign of the Feed and Flow parameters, now possible as the system is functioning, to optimize the results of the current machine, *Prototype #2*, and increase the reproducibility of the samples.(Fig.4.39)

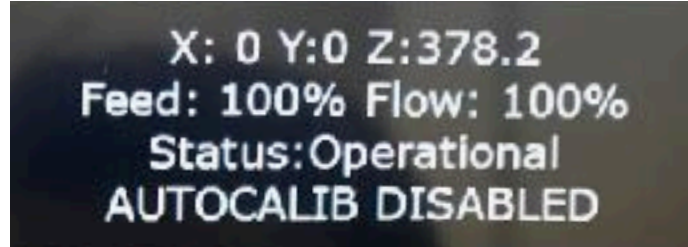


Fig.4.39:The operator display show the Feed and Flow parameters

- **Flow** : is a multiplier (indicated as a percentage) that determines the amount of material the printer extrudes at any given time, so related to ceramic.
- **Feed** : is a multiplier (indicated as a percentage) used by the printer to calculate the speed of movement for all axes, so related to the Extruder.

My attention is focused on the research of the *Feed* and *Flow* parameters to obtain a homogeneous product that at the same time does not have too many surpluses to be eliminated in post-production. Compared to the factory settings of Feed 100% and Flow 100% I wanted to explore different combinations.(Table 4.12) This type of research was of great importance because it allowed me to find combinations to get the desired results. (Fig. 4.40)

Therefore, given the validity of the project, this also allowed me to resume evaluating an element left in abeyance, that is the continuous extrusion capacity with respect to the unexpected block due to clogging at the level of the loading hopper. The hypothesis to be supported is that of having a printing process that allows me to produce the drawn object, according to the parameters set on the .gcode and those modified directly on the operator's display.

The only way to understand the validity of these settings is to repeat consecutive prints from the moment of cleaning and refilling the loading hopper to see if a drop in print quality is identifiable and, if so, after what happens.

<i>Extruder Heatsink 170°C - Extruder Nozzle 150 °C</i>		
FEED %	FLOW %	SPECIMENTS
<u>100</u>	<u>100</u>	<u>2</u>
100	90	3
100	80	3
100	70	3
100	60	3
100	50	2
90	50	2
90	60	2
90	70	2
<u>90</u>	<u>80</u>	<u>2</u>
80	80	3
80	70	3
80	60	3
<u>80</u>	<u>50</u>	<u>2</u>
TOT		56

Table 4.12: The scheme with all the specimen groups, the number of each group are different due to the ability to 3Dprint them: the groups with only two specimens are those where the printing process was interrupted prematurely because it was considered unsuitable.



Fig.4.40: an overview of some of the samples

The results (Fig.4.41-4.44) showed that the combinations of parameters that gave better results were:

- Flow 100 - Feed 100
- Flow 90 - Feed 80
- Flow 50 - Feed 80



Fig.4.41:Group Flow 100 - Feed 100



Fig.4.42:Group Flow 90 - Feed 80



Fig.4.43:Group Flow 50 - Feed 80

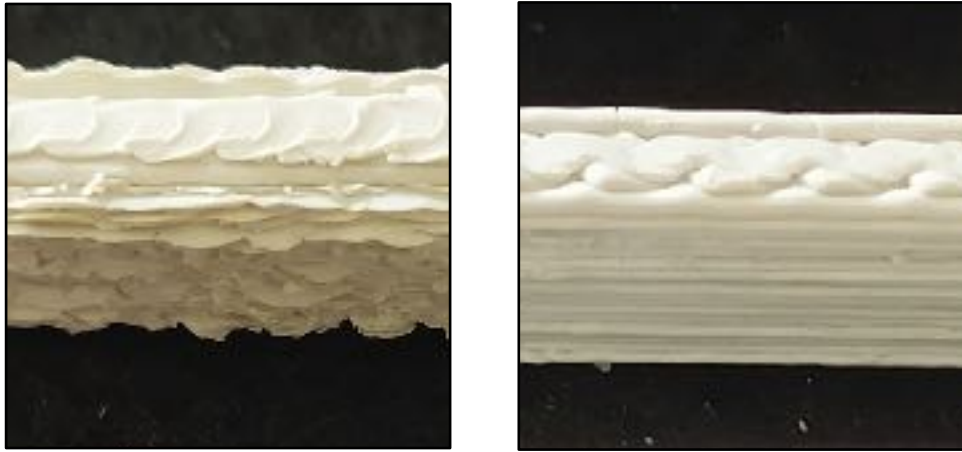


Fig.4.44: some details of the 3D printed final results in different samples that have to be grinded and refined

4.2.9 3D PRINTED MATERIALS WORKABILITY

Having identified the winning combinations, I conceived a continuation of the experimental campaign aimed at identifying the workability of the materials, in this regard I subjected the samples of the most promising combinations to mechanical processing on the Struers grinder (Fig.4.45), with the initial need to regularize the printing blank forms. (Fig.4.46)

I have used different waterproof silicone carbide paper :

- Grit 320
- Grit 1000



Fig.4.45: Wet grinding

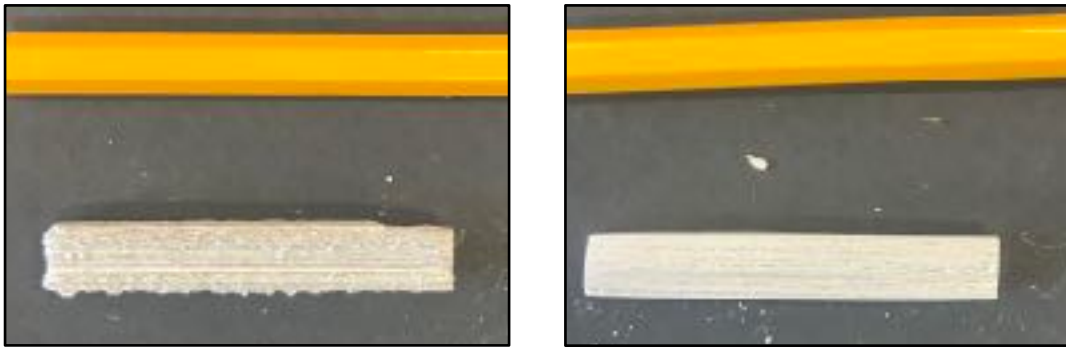


Fig.4.46: One specimen before (on the left) and after wet grinding (on the right)

The tests on the samples in green phase were carried out on 27 samples (9 each group), they led to great success as none of the samples broke or suffered any damage and the shapes obtained were greatly regularized.

This result proved some points:

- The material was distributed homogeneously
- There was excellent adhesion between the subsequent layers in the deposition phase
- I suppose there are no residual stresses by printing process
- There was no evidence of gaps due to sublimation of the polymeric phase

The processed samples allowed us to further extend the experimental campaign and then were placed in the Memmert UM500 Lab oven at 60 degrees to mature 48 hours, to remove the liquid phase from the green.(Fig.4.47)

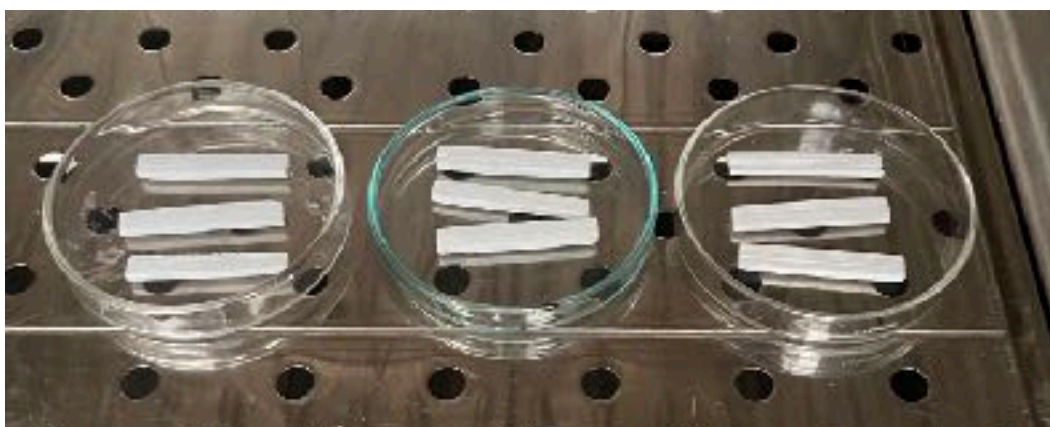


Fig.4.47: Before proceeding on next experimental tests is necessary to remove the liquid phase from the green to avoid any fracture during the sintering

The samples were then subjected to a sintering process at a temperature of 1600°C, according to the indications of INMATEC company, at DICCA laboratory with INSint 1600 oven of the Sirio Dental company (Meldola(FC), Italy)(Fig.4.48) which I sincerely would like to thank for the important contribution provided to the my PhD. The results were extremely satisfactory as no sample fractured, shattered or skewed(Fig.4.49) and I went on analyzing the samples obtained.

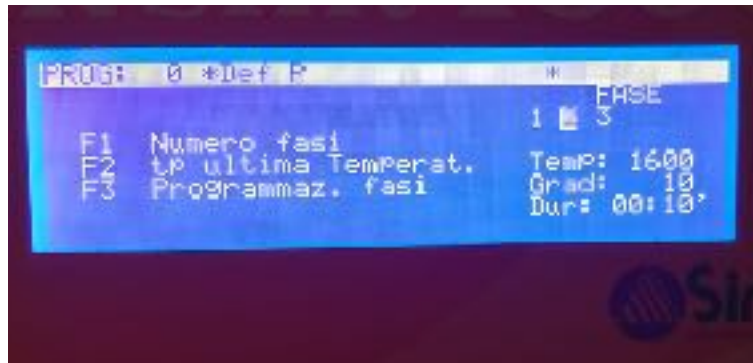


Fig.4.48: First sintering phase



Fig.4.49: Specimens after sintering show the same characteristics as previously, without any damaging. The defects visible are the one already obtained through the 3D printing

4.2.10 SPRAY COATING

Due to the satisfactory results on previous tests, I extended the experimental campaign to verify the compatibility of the samples printed with ceramic coatings prepared at DICCA Department according to the deposition procedure through Vacuum Plasma Spray (VPS) refined by Prof. Antonio Barbucci (Table 4.13) :





Deposition procedure through Vacuum Plasma Spray (VPS)		
insert zirconia spheres of different sizes and then the following components into the jar in the order described		
Ethanol	Solvent	10g
YSZ-Tosoh		3g
PEI	Dispersant	0.09/0.1g (2 drops with spatula)
	Ball Milling	78 rpm x 4h
Add		
PVA	Binder	0.04g
	Ball Milling	78 rpm x 4h
Add		
PEG	Plasticizer	0.06g (3 drops with spatula)
	Ball Milling	78 rpm x 4h
Ethanol	Solvent	35g
	Ball Milling	78 rpm x 1h
Compressor 2bar		
Spray timing 300 seconds		

Table 4.13 : Deposition procedure through Vacuum Plasma Spray (VPS)

I then proceeded to carry out the coatings with the airbrush My OLIMPOS HP 23-BC on the samples selected by me and divided into 5 groups (Table 4.14):

Group A	Green aluminium oxide (Al_2O_3) spray coated with aluminium oxide (Al_2O_3)
Group B	Sintered aluminium oxide (Al_2O_3) spray coated with aluminium oxide (Al_2O_3)
Group C	Green plasma treated aluminium oxide (Al_2O_3) spray coated with aluminium oxide (Al_2O_3)
Group D	Green plasma treated aluminium oxide (Al_2O_3) spray coated with zirconium oxide (ZrO_2)
Group E	Green treated aluminium oxide (Al_2O_3) spray coated with zirconium oxide (ZrO_2)

Table 4.14 Groups based on specimens treatment and different coating material. Each group include subgroups divided on Feed and Flow different percentage chosen (100-100 A; 90-80 B; 50-80 C)

After this phase I placed all the specimens in the Memmert UM500 Lab oven at 60 degrees to mature 48 hours, to remove the liquid phase of the coating before sintering as already described procedures.

The structure of these 5 groups experimental campaign was organized according to this logic:

1. test the compatibility of aluminium oxide (Al_2O_3) coatings on printed aluminium oxide (Al_2O_3) bars before and after sintering with the aim of analyzing whether one single sintering (group A) rather than two (group B) could have repercussions: satisfactory results, without fractures or delaminations (Fig.4.50).



Fig.4.50: Samples treated with aluminium oxide (Al_2O_3) and different sintering phases

2. Study of the effect of plasma treatment in oxygen (Fig.4.51) for the purpose of promoting adhesion of the coating on the ceramic specimens.

Although I have not identified any problems, I have subjected green samples to treatment in Gambetti Low pressure Plasma Colibrì at 100Watt for 60 sec. on each side in order to interact with the residual polymer phase that may remain after the printing phase. (Fig.4.52) This comparison allows me to evaluate any



differences with respect to the coating on the green not subjected to plasma. Apparently no differences has been found.

Fig.4.51: Samples are inserted into Gambetti Low pressure Plasma Colibrì



Fig.4.52: Gambetti Low pressure Plasma Colibrì set at 100 Watt per 60 seconds, each samples surface

3. Finally, upon completion, the compatibility of aluminum oxide with another ceramic. An exposure was made of 3D printed bars with zirconium oxide (ZrO_2) coating on sintered and molded greens. The results were apparently satisfactory. (Fig.4.53)

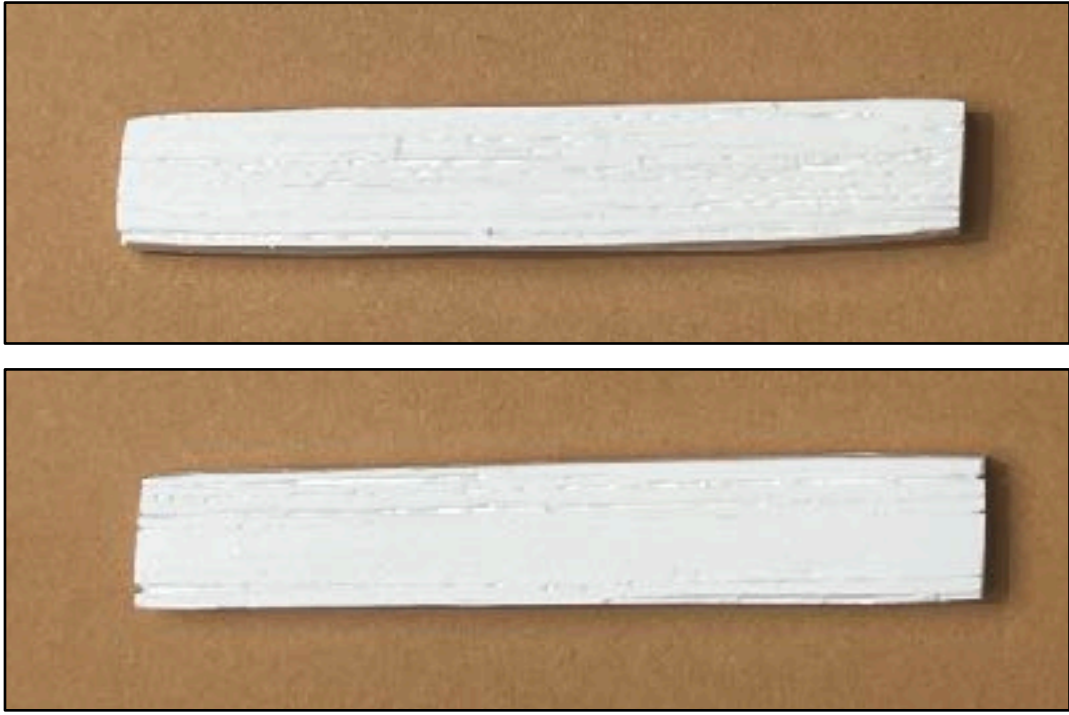


Fig.4.53: Two samples coated with zirconium oxide (ZrO_2) on sintered and molded green

4.2.11 SAMPLE DEVELOPMENT: BENDING TO MESH

The always satisfying results of all previous experimental campaigns push me further to develop a new STL file (*Swanky Juttuli .stl*), from which to extrapolate a new .gcode (*v1Swanky.gcode*). (Fig.4.54)(Table 4.14)

The main difference respect the previous geometries printed and analyzed so far lies in the design of a curved geometry, to go and test the performance of *Prototype # 2* even further.

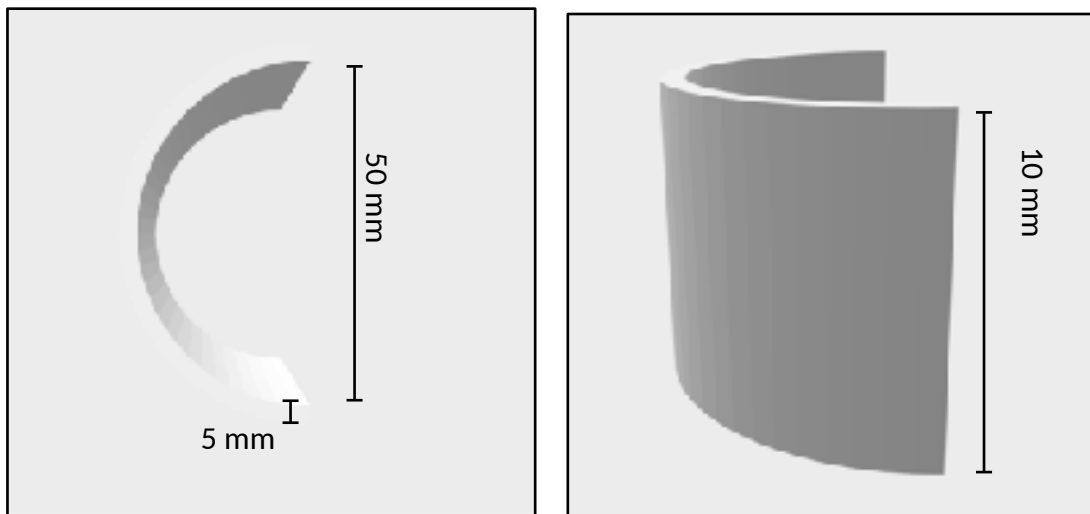


Fig.4.54: The *Swanky Juttuli .stl* file from different point of view. It has an hemisphere shape with 50mm diameter, wall thickness 5mm and height 10mm

```

G-Code generated by Simplify3D(R) Version 4.1.2
Jan 11, 2022 at 2:43:28 PM
Settings Summary
processName,Process1
applyIcModels,Swanky Juttuli (1)
profileName,PELLET HD CERAMICA 0.8mm
profileVersion,2021-10-19 13:40:02
baseProfile,DeltaWASP 2040 Dual (modified)

layerHeight,0.15

temperatureName,Nozzle,Barrel,Heated Bed
temperatureSetpointTemperatures,170,150,40

maxCoolingFanSpeed,100
bridgingFanSpeed,100

```

Table 4.14: The v1Swanky.gcode has the same main parameters already tested and confirmed by the 3D printing

I therefore embarked on a new experimental campaign with this new printing project, repeating the same procedures that have already occurred successfully on parallelepiped specimens:

1) *PROTOTYPE #2 3D PRINTING* (Fig.4.55)

- Extruder Heatsink 170°C - Extruder Nozzle 150°C
- Flow 100 - Feed 100
- Procedural time 18 minutes



Fig.4.55: The v1Swanky.gcode 3D printed specimen



Fig.4.55: Some other details on v1Swanky.gcode

2) *SAMPLE FINISHING* :(Fig.4.56)

- Wet grinding with Struers grinder - external surface
- Dry manual grinding (made by my own in my clinic Lab) - internal surface





Fig.4.56 : Due to the internal concavity, not possible to be post-processed just on DICCA Lab grinder and thanks to all those finishing instruments I daily use in my clinic, I could refine the surface manually achieving a very satisfying result

2) COATING (Fig.4.57) :

- Green aluminium oxide (Al_2O_3) spray coated with aluminium oxide (Al_2O_3)
- Memmert UM500 Lab oven at 60 degrees to mature 48 hours, to remove the liquid phase from the green



Fig.4.57 : After coating the 3D printed curve sample has been treated like others specimens

2) *SINTERING* (Fig.4.58,4.59) :

- INsint 1600 oven of the Sirio Dental company



Fig.4.58 : The 3D printed curve sample v1Swanky.gcode has been sintered

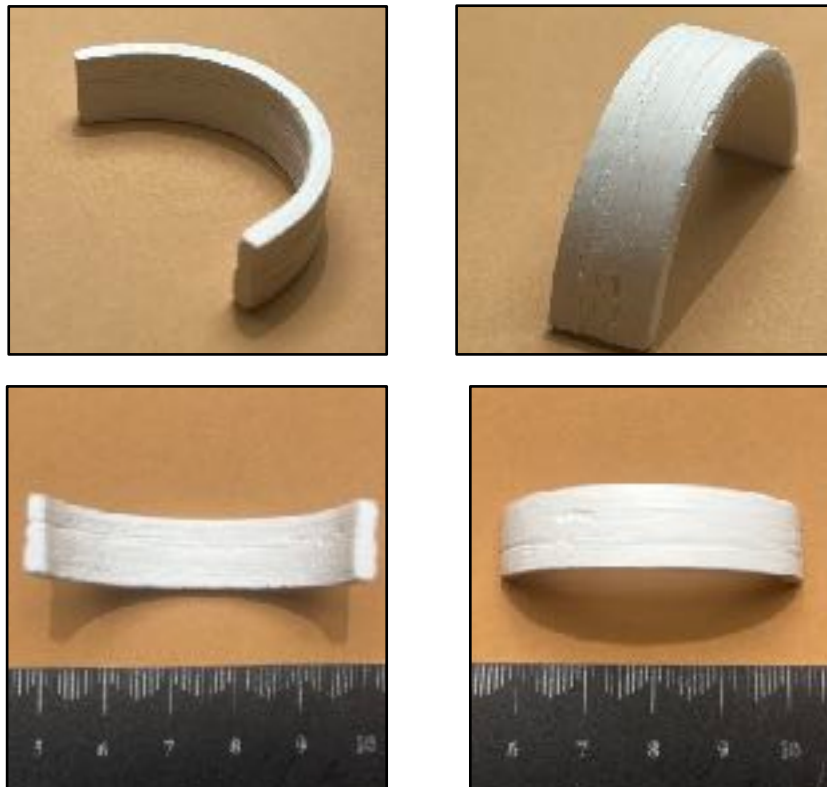


Fig.4.59 :Some details of The 3D printed curve sample v1Swanky.gcode

4.2.12 NON-DESTRUCTIVE AND DESTRUCTIVE MECHANICAL TESTS

On the samples thus obtained we have set up the experimental campaign with Non-Destructive and Destructive mechanical Tests.

Specifically the internal friction and the fracture module with ZwickRoell AllroundLine universal testing machine Z050.

1) In the *Non-destructive tests*, (Fig.4.60) a remarkable homogeneity of printed samples was highlighted testifying the good level of repeatability of what was obtained, but an evident, quantifiable difference in the natural frequencies of vibration of the internal friction denote a clear difference in density of the printed material compared to the milled one. In the scheme below is referred to Table 4.14 (Nomenclature each sample, Ex.: AC2 : A Group coating; C Subgroup of Feed&Flow parameters, 2 specific specimens)

Test internal friction - Solimei											
Specimens: allumina (3Dprinted) and zirconia (Milled) with different coating -Table 4.14											
Hardware settings:											
velocity	25mm/s/V										
lowpass	25kHz	highp	8kHz				TEST 1	TEST 2	TEST 3	TEST 4	TEST 5
Campi	L [mm]	W [m]	H [mm]	mass	densità	posizion	f [Hz] Q-1	f [Hz] Q-1	f [Hz] Q-1	f [Hz] Q-1	f [Hz] Q-1
AC2	46,80	8,00	3,80	3,40	2389,8	10,5	10723.24	10722.63	10807.05	11227.29	10976.00
BC2	44,00	7,70	3,00	3,00	2951,6	9,9	12287.75	12447.11	11836.31	11914.86	12290.01
CC2	44,80	6,60	2,60	2,20	2861,7	10,0	10326.25	10326.57	10326.18	10326.42	10326.53
DC2	43,60	6,10	3,00	2,10	2632,0	9,8	11351.37	11310.51	11399.76	11690.90	11536.61
EC2	44,00	7,40	3,10	2,70	2675,0	9,9	11726.13	11548.80	11800.77	11502.21	11502.21
C16	50,00	8,00	2,90	6,90	5948,3	11,2	7538.68	7542.33	7910.75	7703.59	7887.70
A16	50,00	8,00	2,90	6,90	5948,3	11,2	7926.99	7552.22	7921.76	7926.25	7921.98

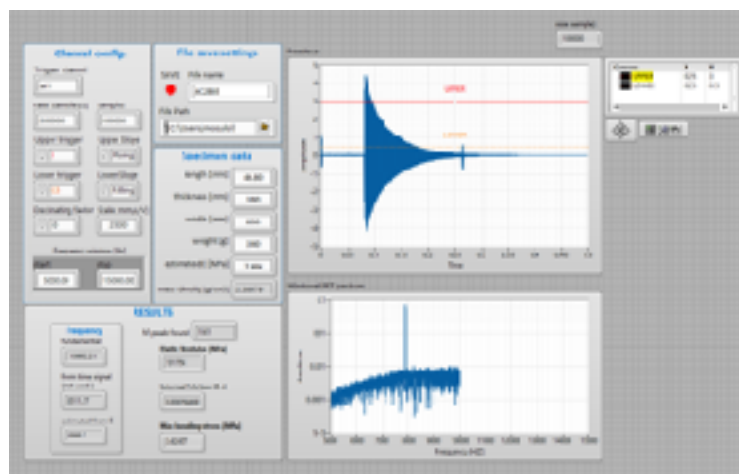


Fig.4.60 : Internal Friction results

For each horizontal series of 5 tests on each sample there is a limited variation due to 1 repositioning did not guarantee the exact position, 2 to the inevitable geometric differences due to the processing procedure in relation to the repositioning itself. Between the vertical series of samples there are inevitable differences in geometry and weight (printing, processing and coating) which lead to a different energy distribution.

This is an expected result that shows a difference in each family quantifiable around 10-15%, due to the just described differences that suggests promising possible implementations .

The whole family of milled samples (in the Table samples A16 and C16) show a 30% lower and constant difference with the 3D printed parts. A direct comparison could not be done due to different materials and manufacturing technologies.

2)In the *Destructive mechanical Tests* the same samples were fractured with the Zwick 3-point fracture method (Fig.4.61) which showed that the breaking point of the milled samples is around 150% higher than the printed samples, this also dictated at a density higher than about 60%.As expected by the previous observed differences by milled zirconia samples and alumina 3D printed ones the same trend has been confirmed in the destructive tests.

	E _f	σ _{fM}	ε _{fM}	σ _{fB}	ε _{fB}	L _v	h	b
	MPa	MPa	%	MPa	%	mm	mm	mm
A16	183753,57145	333,650014	0,1822844	333,650014	0,18228444	42,7	2,9	8
C16	168462,20544	331,418958	0,2016903	331,418958	0,20169035	42,7	3	8,3
CC2	144816,72504	129,668860	0,1063546	129,668860	0,10635467	32,7	2,6	6,6
DC2	176687,53095	129,034438	0,0984765	129,034438	0,09847656	32,7	2,6	6,6

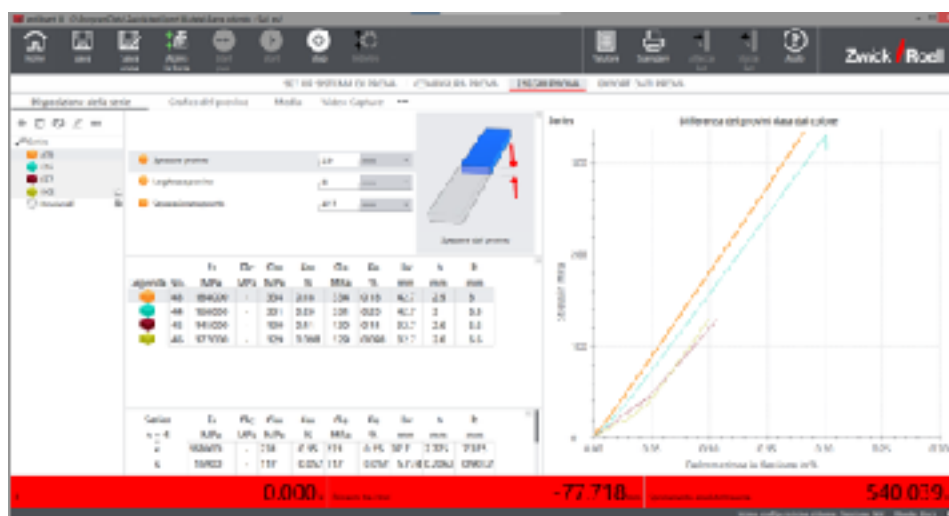
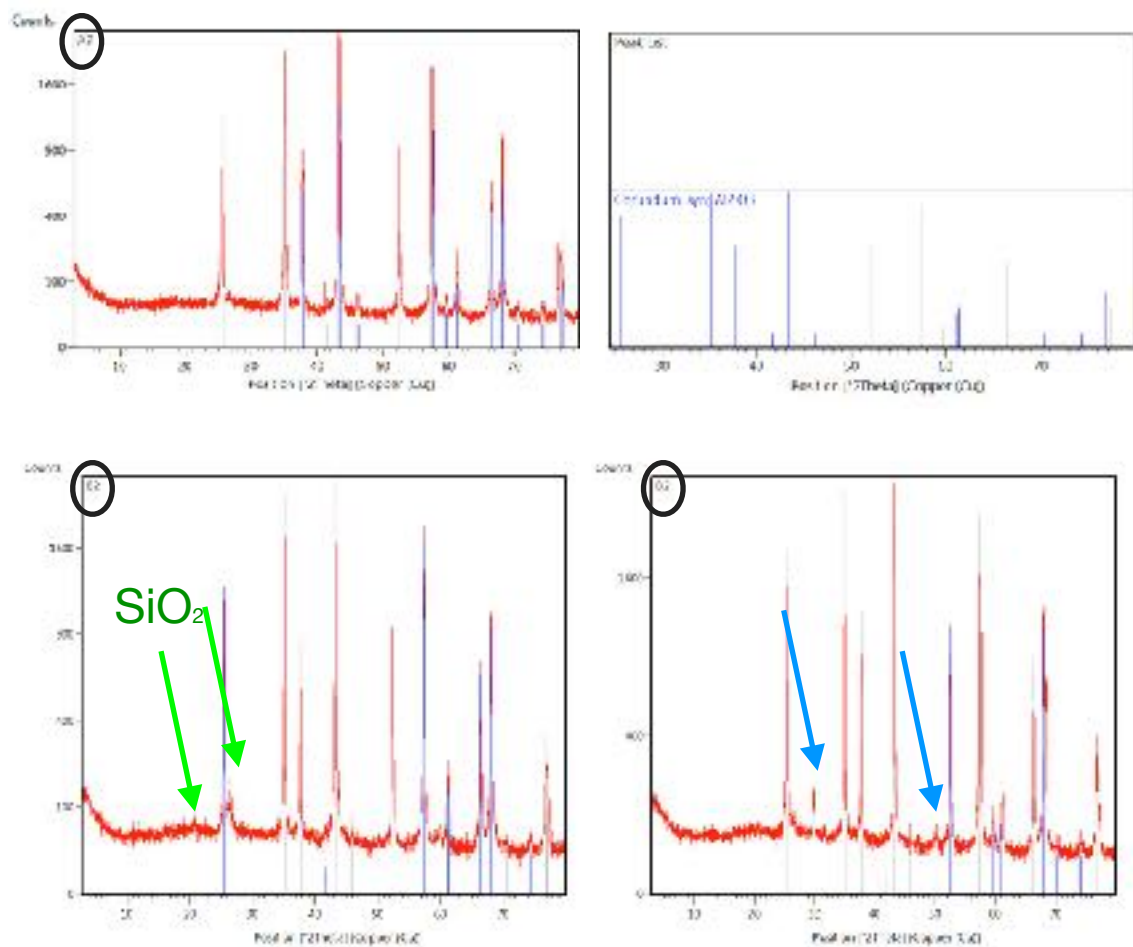


Fig.4.61 :3-point fracture strength

3) The same samples (Fig. 4.62) were then subjected to XRD (X-Ray Diffraction) at the DISTAV University of Genova XRD laboratory by Prof. Cristina Carbone. The mineralogical analyzes were performed on these samples using the PW 3710 powder diffractometer with Philips X'pert High Score as crystalline phases above 1% interpretation and quantification software.



Samples Group A	Pure crystalline phase - aluminium oxide (Al_2O_3)
Samples Group B	New phase appears which could be a small one amount of crystalline SiO_2
Samples Group C	New phase appears which could be a small one amount of crystalline SiO_2
Samples Group D	New crystalline phase (ZrO_2) with 2 peaks
Samples Group E	New crystalline phase (ZrO_2) with 2 peaks

Fig.4.62 : The XRD (X-Ray Diffraction) of some samples

At DISTAV XRD laboratory it has also been made by Prof. Cristina Carbone and me the same XRD (X-Ray Diffraction) on some of the first samples extruded and 3D printed (Fig.4.63) to make an evaluation of INMAFEED K1013 during the working flow and after sintering.

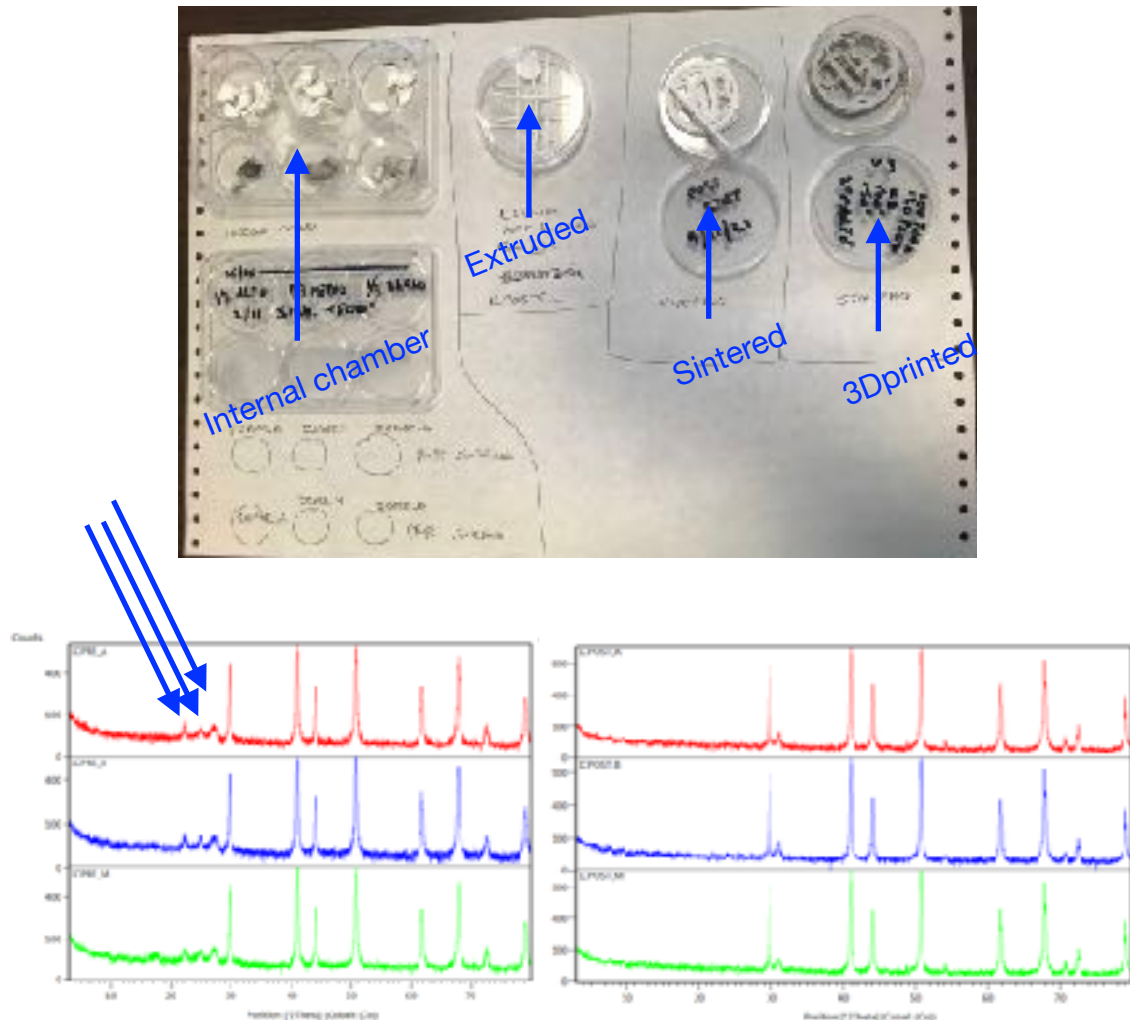


Fig.4.63 : The specimens examined at XRD (X-Ray Diffraction)

Also in these results is confirmed homogeneity between PRE and POST samples which are all characterized by aluminium oxide (Al₂O₃), it can be observed also that PRE samples are characterized by the presence of 3 peaks which are not present in POST samples, thing to be deeply analyzed through the SEM.

The reticular structure of what was obtained should be compared with the tests that at the beginning of the doctorate I did at DCCI University of Genova with Prof. Adriana

Saccone and me on zirconium oxide (ZrO_2) samples that Dental Companies delivered me in commercial disk. (Fig.4.64)

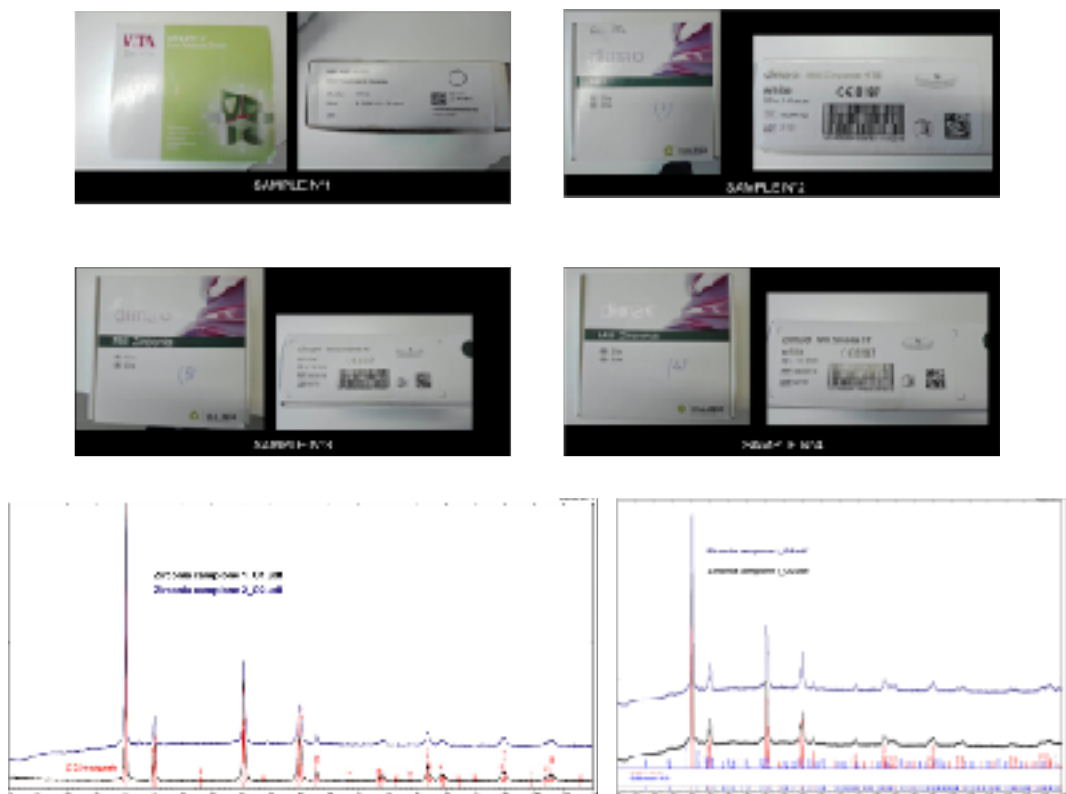


Fig.4.64 : zirconium oxide (ZrO_2) commercial disk test used in preliminary test

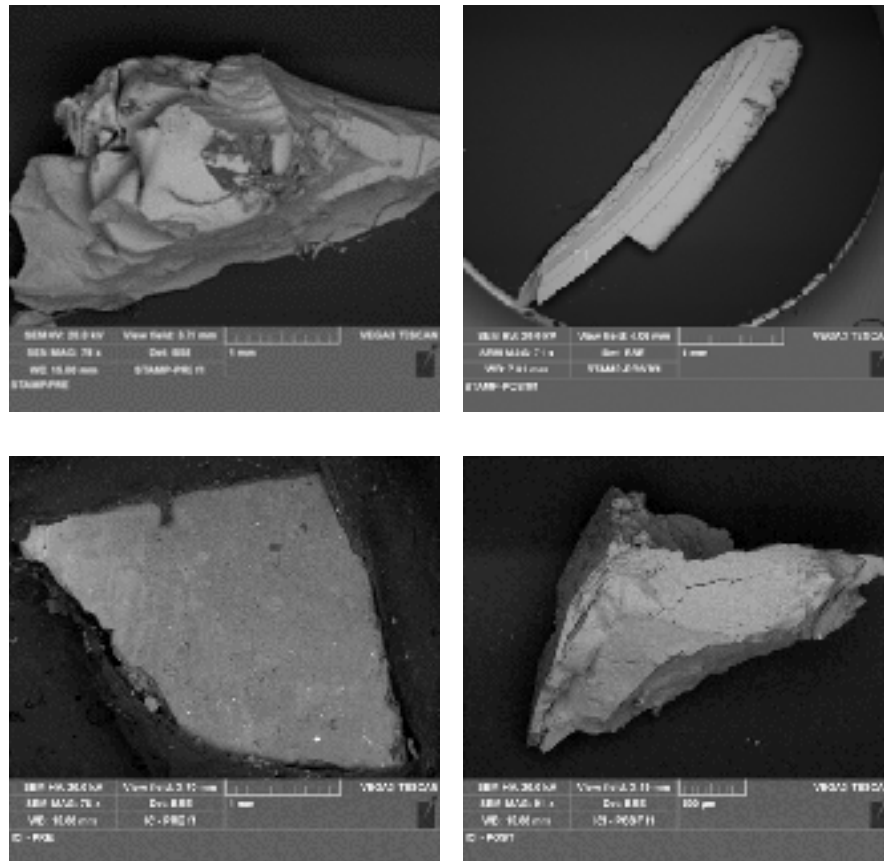
Samples 1	It is β ZrO_{2-x} tetragonal.
Samples 2	It is β ZrO_{2-x} tetragonal.
Samples 3	Monoclinum (α ZrO_{2-x}) and Tetragonal form (β ZrO_{2-x})
Samples 4	Monoclinum (α ZrO_{2-x}) and Tetragonal form (β ZrO_{2-x})

The zirconia is the reference ceramic and had been taken as a benchmark of current dental practice while alumina was kept as a fixed parameter of my doctoral activity as a material used by the printer manufacturer.

4)Finally, the analyzes were performed at the DISTAV Electron Microscopy and Microanalysis Laboratory by Prof.Cristina Carbone and me on all the samples with the SEM Vega3 - TESCAN type LMU scanning electron microscope, equipped with an EDAX APOLLO XSDD detector from EDAX with a DPP3 type analyzer, associated with the TEAM EDS (Texture and Elemental Analytical Microscopy) software for the acquisition and

processing of all the data deriving from the analyzes performed on 4 representative samples provided from the preliminary extruded from Prototype#2 material.

The SEM images of the 4 samples showed in Fig. 4.65 an organic part (polimer residual on green samples as original TGA test - Fig.3.25)on the STAMP PRE sample. Below are the 4 3D photos of the samples.



The photographs show a certain compositional homogeneity, as can be seen from the EDS analyzes carried out at the point and in the below picture on the right in Fig.4.65 (all aluminium oxide (Al_2O_3)).

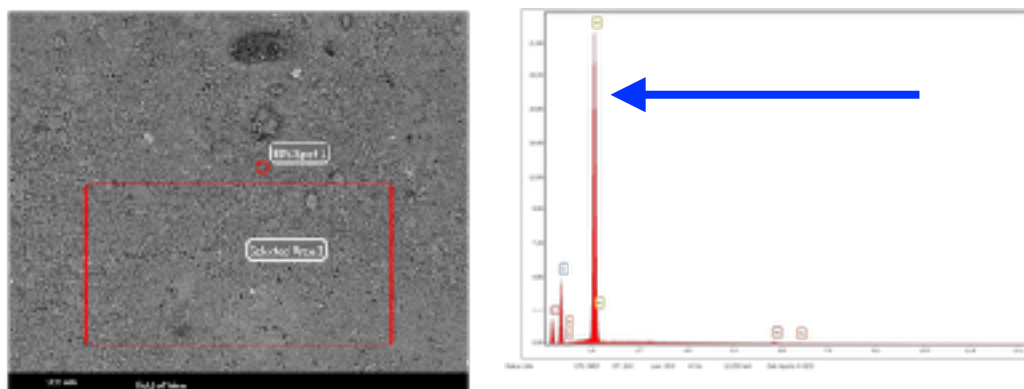


Fig.4.65 : From the picture is evident the main Allumina presence

A survey was carried out on the STAMP_PRE sample as it has a part of organic matter in both pieces as shown in the photographs (dark part in the photos - Fig.4.66).

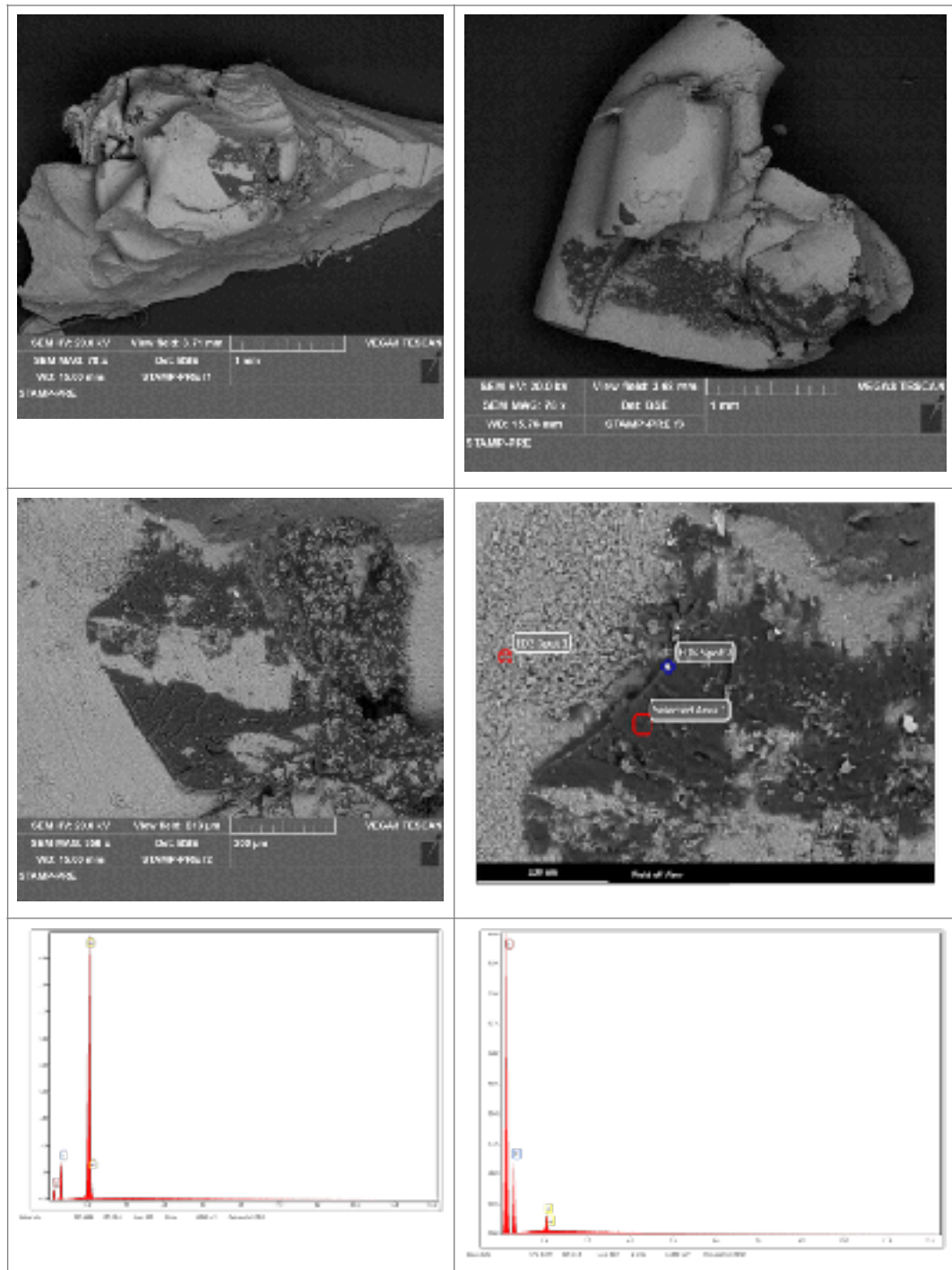


Fig.4.66 : In the 4 photos are visible dark areas attributable to organic component, confirmed also by the spectrum

In particular, the spectrum on the right: the EDS analysis testifies to the total absence of elements, for which there is the certainty that all the dark part is attributable to organic matter.

In this sample there are also micrometric particles of iron and not very abundant, which I suppose can be attributed to residues of the cochlea or of the chamber in the friction phenomena that occur during extrusion (Fig.4.67):

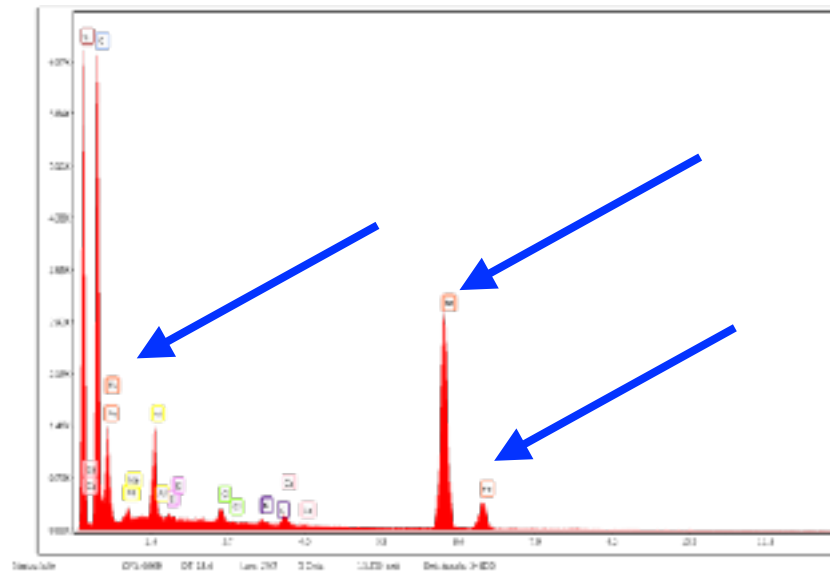


Fig.4.67 : In the spectrum are identifiable some iron particles

*

CHAPTER 5 - CONCLUSIONS

This Project was possible also by the continuous support and skills of BTK, a leading company in the design and printing of dental implants, present on world markets that allowed me to keep the attention on the most important technical issues of my PhD project.

Thanks to BTK, in the person of Dr. Andrea Peloso, for having supported financially and technically the following PhD Program and to the technical team composed by Ing. Andrea Trentin, Ing. Marco Zoppo and Ing. Matteo Marsetti whose collaboration has been fundamental to proceed with the implementation of the changes each time agreed between the University of Genoa, BTK and WASP.

Thanks to WASP, in the person of Mr. Massimo Moretti, for having provided the prototype on which to set up my experimental campaign and the technical collaboration for its development in the person of Mr. Flavio Gioia.

My PhD was focused on the development of a 3D printer for end-users such as advanced dentists able to produce sub-gingival structures in material other than metal, a medical need that was explained in detail in Chapters 1 and 2.

The focus was on helping to develop an industrial prototype.

The collaboration with two primary companies in the field of medical implants and 3D printing has allowed to coordinate a collaboration with the laboratories of DICCA-University of Genoa that has brought to obtain two successive prototypes (*Prototype #1* and *Prototype #2*) whose results have been presented in the previous Chapters.

Starting from a low TRL (Technology Readiness Level) and an equivalent level of MRL (Manufacturing Readiness Level), it was possible to identify the technical parameters able to characterize the effectiveness of the printer according to the original settings.

This PhD has been oriented to an incremental innovation aimed to obtain a working device with reliable technology and at an affordable cost for the advanced dental professionals.

The results obtained are not dependent on a tailored material but have been obtained and studied keeping the choice of a commercial feedstock allowing me to obtain a robust and usable product with what is currently available on the market.

The technical evaluation carried out has allowed to indicate in the printing temperature the first point of attention for the continuity of the process. The consequences on the ceramic composite flow appeared of extraordinary importance as demonstrated by the continuous failures of *Prototype #1*. The optimization of the feeding device (auger, coupled with a new design of the thermal chamber) improved the material supply and a further significant optimization was obtained with the redesign of the nozzle profile and the variation of the internal flow angles of the material itself.

The surface tension of the material in the fluid viscous state has imposed a study of the nozzle diameters, finding at the moment the optimal solution in 1.2 mm.

A further increase in performance was obtained by studying the combination of the Feed and Flow parameters and the speed of movement of the printer head.

A further positive contribution has been obtained by the hypothesis of decoupling the heating temperatures of the heating chamber (*Extruder Heatsink*) from the area where the nozzle is positioned (*Extruder Nozzle*).

In fact, it has been possible to understand that, with polymer-based ceramic compounds, it is essential to review as much as possible the exposure to melting temperatures.

To reduce transmission and printing efforts the fuel crushing phase was also explored to assess the effectiveness of powder rather than pellet feed. Although the latter measure brought initial advantages it was noted that the powder system was even more sensitive to the effects of thermal loading and was therefore considered less efficient at present.

Taken together the results presented enabled repeatable samples to be obtained with continuous printing activity and with a remarkable quality appearance depending on the prototype stage.

The flow of production of samples has therefore become continuous and constant allowing me to create the samples analyzed in Chapter 4 that have shown consistency in performance, density and functional characteristics.

The achievement of this result has allowed me to make a further development towards the printing of non rectilinear shapes, prelude to the creation of a mesh.

Finally, to evaluate the goodness of the management of sintering processes I was able to experience the absence of severe stress from shrinkage through the deposition of thin films of ceramic surface coating (zirconia and alumina) that have never fractured or broken as a result of previous stresses.

This Doctorate has therefore indicated a way for an individual device for advanced dentists. What collected in this experience has allowed me to define the technical indications for the construction of future *Prototype#3*, based on the reduction of mechanical stress due to the crushing of the pellet and the great reduction of the exposure of the feedstock to thermal stress pre-printing. *Prototype #1* was developed with the objective of printing; *Prototype #2* was developed with the objective of achieving production repeatability; *Prototype #3* will be designed with the target of achieving a product quality at the level expected by the market.

These results will be achieved with an integral redesign of the extruder in agreement with the manufacturer WASP.

Similarly, based on the experiences of this PhD Program, indications will be provided for the logistical management of the printing phase, currently not user friendly.

Finally, this Doctorate Program wanted to keep a single material originally recommended by the manufacturer of the prototype while evaluating alternative proposals (presold Mishimura ceramic in Appendix C). This choice has been made for the aforementioned need of alignment with the production choices rather than the need to make the prototype completely functional thus avoiding the use of medical grade ceramic at the time not essential.

Next steps, in agreement with the company, will be to complete *Prototype#3* and to open an experimental phase on the performance of becoming ceramic compounds functional to the technical choices pursued by the technical team University of Genoa - BTK -WASP.

* * *

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APPENDIX A

PRODUCTION TECHNIQUES

• Stereolithography SLA

Stereolithography involves the creation of a CAD model followed by CAM (Computer-Aided Manufacturing) processing to translate the model. Developed and patented by Chuck Hull in 1986, SLA is the best known technique among those that use the principle of photopolymerization to give life to new models.

The necessary elements to realize the SLA are: a beam of ultraviolet light, a system of mirrors, a tank destined to contain the liquid polymer, a platform-lift that supports the object to be made and moves it progressively downwards after the completion of each single layer, an ultraviolet light oven and possible supports to support the parts of the object during the construction.

After virtually subdividing the CAD figure into horizontal two-dimensional planes, software transmits the information to a laser source. The laser, through the system of mirrors, strikes the liquid photopolymer contained in the special tank causing it to harden. The process takes place through Digital Light Processing (DLP), which is a photochemical transformation of a particular polymer, usually a liquid resin. Then a concentrated ultraviolet light is focused on the surface of a tank containing photopolymer drawing each layer of the object on the liquid surface, which hardens and polymerizes.

In the first phase, the final positioning of the piece to be made is prepared on the workstation and, if necessary, the supports are generated.

Subsequently, the laser, focused on the work surface by means of optical systems, polymerizes the first section of the prototype. Then the plane is lowered and the process continues with the polymerization of the next layer. At the end of fabrication, the solid extracted from the liquid resin is placed in an ultraviolet light oven to complete polymerization. Any substrates used in the construction of complex parts are removed at the end of printing.

A CAD/CAM system maneuvers the light by shaping the shape of the object in a large number of layers, starting from the lowest to the top.

• Selective laser sintering SLS

Also in 1986, Carl Deckard, Joe Beaman and Paul Forderhase (and several other researchers) at the University of Texas at Austin studied Chuck Hull's ideas and developed Selective Laser Sintering (SLS). Sintering, or the joining of material into granules, is a process similar to the one previously described by Hull, but with an important modification, replacing liquid with liquid plus powder. As the powder is a solid it does not require specific supports giving a number of advantages especially from a practical point of view. The system comprises a laser source,

a mirror system, a control system and a working chamber in which the process takes place. The chamber consists of a build platform, a powder cartridge and a levelling roller. In the SLS process, microscopic particles of plastic, glass or ceramic are exposed to a high-power laser that fuses them together to form a three-dimensional solid object. The powder is initially released onto a platform to create a layer of about 0.1 mm, which is then hit by the laser that fuses it into a compact layer. The non-sintered powders on the platform form the support for subsequent layers until the complete object is produced. At the end of the process the object is removed and separated from the non-sintered powders, which can be partially or totally reused.

In detail, the sintering process involves a layer of material being spread out on a platform and being leveled with a roller. The laser traces a two-dimensional horizontal section of the part, sintering the material into granules.

After the completion of each layer, a special piston moves downwards lowering also the layer just made. Then new material is forced out of the cartridge in which it is contained and onto the build platform, where the new section is sintered to the previous one.

This process continues until the part is built and once ready, the model is removed from the chamber to be finished by removing the waste material.

Unlike SLA and FDM, the SLS process does not require support structures as the object being made is completely immersed in the material. Sintering is ideal for durable and functional parts with a variety of applications.

• **Selective Laser Melting (SLM)**

In 1995, the Fraunhofer-Gesellschaft Institute in Germany developed the method of Selective Laser Melting (SLM), a technique that made it possible for the first time for 3D printers to produce truly solid objects.

This technology, therefore, does not sinter, but melts the metal powders in a solid and homogeneous mass thanks to a very high power laser, according to the designed 3D drawing.

The operating scheme is almost entirely analogous to SLS. Unlike sintering, it uses integral metal powders, i.e. without the aid of low melts, as a construction material. The result is that the laser is more powerful and that at the end of the processing you get an object similar to those obtained with mass production, without the need for surface finishing and that can be subjected to traditional processing. An inert atmosphere is used in the work chamber to prevent metal oxidation.

Both SLS and SLM are used in many fields including aeronautics and architecture, design, medical and dental.

• **Laminar Structure**

The Laminated Object Manufacturing (LOM) technique involves laminating and depositing together sheets of paper, plastic or metal impregnated with a carbon dioxide adhesive

glue. A mechanism pulls the sheets onto the work platform and a special heated roller glues the paper to the substrate.

Next, a laser head cuts the contours of the section, creating a rectangular profile that is used for the backing. The platform then lowers one layer and the process continues until the product is manufactured.

Post-production treatments such as sandpaper finishing and waterproofing treatment are required to prevent and avoid layers from peeling off. Prototypes, models or molds can be created with this production method.

• **Fused Deposition Modeling (FDM)**

In 1988, Scott Crump, founder of the well-known 3D printer manufacturer Stratasys, patented Fused Deposition Modeling (FDM), which is printing with molten material that is deposited layer by layer according to the object to be made.

Using a heated nozzle, layers of a molten polymer are released onto a support structure that is removed at the end of the process. Basically, a plastic filament or metal wire is unwound from a spool, which supplies the material to the extrusion nozzle through which the flow can be managed.

The nozzle is heated by radiators that keep the temperature above the melting point of the material so that it can flow out smoothly and is guided in both horizontal and vertical directions by a numerical control mechanism, i.e. following a path traced by CAM software.

Once the patent on this technology expired, Open Source development communities sprang up to develop cheaper variants of Stratasys, calling the printing technique Fused Filament Fabrication (FFF). Fused Filament Fabrication (FFF) involves an extrusion operation almost identical to FDM. Quantities of plastic or wax material are released from a nozzle that builds the two-dimensional planes of the object layer by layer. The temperature of the extrusion head and the working surface is very important for the success of the object. The nozzle contains radiators to keep the plastic just above its melting point, so it can escape and build the layer easily.

The platform, on the other hand, has a lower temperature so that the plastic hardens as soon as it is deposited. Once each layer is completed, the platform lowers one layer and the extrusion head deposits another layer of material.

The thickness of a layer and the accuracy of the vertical dimension are determined by the diameter of the extrusion punch. It varies from 0.013 to 0.005 inches. In the X-Y plane, 0.001 inches of resolution is achievable. The maximum size of objects created using FDM systems is 36.00x24.00x36.00 inches. No post-processing is required. FFF has restrictions on the shapes that can be fabricated: structures with hollow parts must be avoided or supports must be used that will be removed once the process is complete.

• PolyJet

PolyJet technology also falls into the DLP category and is an advanced additive manufacturing method that allows for the creation of prototypes, parts and tools with smooth surfaces and accurate details. PolyJet printers are the most expensive of AM's, but as a result, this technology offers a good trade-off between resolution, speed, material quality and final price. With a high layer resolution of around 16 microns and a level of accuracy as low as 0.1 mm, it is possible to produce thin walls, complex geometries, intricate details and refined elements using a wide range of materials. It also incorporates a wide variety of colors and materials into a single model with high efficiency.

It is then used to make precise and detailed prototypes that perfectly render the final aesthetics. 3D printing using this technology works similarly to inkjet printing, but instead of depositing ink droplets on paper, they are deposited on a tray with layers of solidifiable liquid photopolymers.

Preparation software automatically calculates the placement of the photopolymers and support material using a 3D CAD file. Then the 3D printer begins depositing and curing tiny droplets of liquid photopolymers immediately through UV light. In this way, thin layers accumulate on top of each other over the tray, creating one or more precise three-dimensional models or parts. Where there are protrusions or complex shapes that require support, the 3D printer deposits a removable support material at the end of the print by hand, with water or in a solution bath. As soon as they leave the printer, models and objects are ready for manipulation or use, without much further treatment.

PolyJet/Multijet technology is therefore able to develop prototypes very close to reality by making prostheses for the medical and dental sector.

• Digital Light Processing (DLP)

This process is similar to stereolithography in that it is a 3D printing technique that works with photopolymers. The main difference is the light source.

Digital Light Processing (DLP) uses conventional light sources, such as an arc lamp, with a liquid crystal display or a deformable mirror device (DMD), which is applied to the entire surface of the photopolymer resin tank in one step. The photopolymer hardens right where the light hits the surface. Once the layer is completed, the platform inside the tank lowers by a fraction and the next layer is traced. This continues until the entire object is completed.

• Paper 3D Laminated Printing

In 2005, the Irish company Mcor Technologies Ltd, developed yet another method: Paper 3D Laminated Printing. This technology involves the superimposition of sheets of paper that are previously modified according to the feature they must have. It is therefore to be considered as an alternative additive method, but which allows the use of all colors. Basically, instead of using plastics which are more expensive, objects are made with

sheets cut and glued on standard office paper. Thus, the printed objects cost 10-20% compared to the cost of other techniques and, in addition, toxic fumes or solvent additions are avoided.

Another interesting aspect is that since it is standard paper, it is possible to print on it in color before cutting and assembling it, giving overall high quality and high color resolution on the final object. In addition, if the final object is not strong enough you can dip it in a solid glue.

- **Electron Beam Melting (EBM)**

2002 was the year of Electron Beam Melting (EBM), a technology whereby a high-energy source, consisting of a concentrated and accelerated beam of electrons, strikes a material in micro-grain form causing it to melt completely. With this method it is possible to obtain metallic objects with an even higher density than Selective Laser Melting.

Electron Beam Melting (EBM) is very similar to SLM but, unlike SLM, to allow for proper focusing of the beam on the work surface thus creating a vacuum in the chamber, which also avoids the formation of metal oxides in the powders. By focusing a higher spot power than the laser used for SLM, the electron beam can melt high melting powders such as titanium.

In particular, this technique is used for the construction of titanium biomedical prostheses for the use of powders with high biomedical compatibility.

- **Inkjet Printers**

It is counted among the 3D printing techniques that use granular materials. Inkjet printers are becoming quite popular in the 3D printing landscape due to their time, cost and ease-of-use advantages. The model is built one layer at a time and the material is spread out on the build platform and leveled with a special roller.

Unlike the SLS method, the powders are not sintered but rather bonded with an adhesive liquid dispensed from a special head. As with the other production techniques, the layer just made is lowered and the process is repeated until the object is complete.

- **3D Bioprinting**

3D Bioprinting is the process of generating cellular models using 3D printing technologies, in which cell function and viability are preserved within the printed construct. Living tissue can be reproduced using this technique.

The first bioprinters were called Regenovo and Organovo and were designed in China and the United States, respectively. These machines are still in development, but show a number of promising results. The Regenovo printer at Hangzhou University of Science and Technology already boasts the reproduction of numerous jellies, 3D printed semi-

transparent ears, kidneys and various other conglomerates of cells obtained in a sterile environment.

The printer uses medical polymers, living cells, inorganic materials and hydrogels to create scaffolds in which cells are grown to produce living tissue. Research is focusing on refining the size of the cells. Longevity is something that still needs to be improved, however, the results so far are really good. Cornell University is working on 3D printed spine discs, while the University of Iowa is designing a two-arm 3D printer that can define different types of cells at once.

San Diego-based Organovo is using these techniques to test cancer drugs on specific cell types. Also, at Wake Forest University they are developing a method to scan and print layers of skin cells after burns.

APPENDIX B

This PhD Program is based on 3D printing process based upon ceramic/polymer composites.

I evaluated to do not include in Appendix B those materials well known by the scientific community that are not strictly related to this dental medical field.

3-D PRINTED MATERIALS

- Resins for 3D Printing : Photopolimers

In terms of printing materials, unlike extrusion systems, for light source printing technologies (SLA/DLP), there are not yet products on the market that can be used with all 3D printing machines.

The main materials used for laser and DLP stereolithography systems include:

Standard Resins

Standard resins are 3D printing materials used to create functional prototypes that require good aesthetic resolution of geometry. There are lighter resins used for 3D modeling and darker resins used for functional prototypes that require a high degree of precision. Conversely, standard resins are inexpensive resins that have low impact resistance and react strongly to changes in temperature or light.

Standard resin is available in 4 colors. It allows you to streamline your orthodontic workflow for 3D printing by printing models directly in the lab for appliance design and manufacturing.

With these resin models, clear aligners, splints, braces and other devices can be fabricated on them, even using the thermoforming technique.

- *Burn-out Resins* . is designed to replicate details and smooth model surfaces in metal. Casting the resin to obtain metal models that can be used as bridges and crowns is currently being tested. As for surgical templates, the resin allows practitioners to speed up the fabrication of guides.
The resin is certified as a Class 1 biocompatible material, making it suitable for applications such as surgical guides for the oral cavity.
- *Castable resins* are the 3D printing materials that have revolutionized the dental industry. Castables enable 3D prototypes with crisp detail and smooth surfaces.
- *Tough/Hard: Resins for Tough Models*. Tough resins are used for making models or prototypes that must withstand high levels of mechanical stress. In addition to good levels of tensile strength, hard 3D printing resins retain good elasticity. The combination of these characteristics makes them very similar to ABS, so much so that they are often referred to as ABS-like. Hard resin is not the ideal material for printing very thin walls and is characterized by high brittleness and heat sensitivity.

- *Transparent Resin.* Photosensitive resins share the same basic characteristics as standard 3D printing materials. The added value of such additive manufacturing materials, lies in the possibility of obtaining completely transparent objects. It turns out to be a biocompatible resin, has high fracture resistance and can be installed directly into the patient's mouth. Perfect for forming braces, retainers and splints to be printed instantly. Being transparent, it is a non-invasive and aesthetically pleasing product.
- *Durable 3D printing resin* is a material for 3D printing objects that require wear resistance. This 3D printing material is also characterized by its flexibility, to the point that it is compared to polypropylene (PP-like). 3D models made from these printing resins have a good surface finish and like many of the other resins on the market, durable has very low tensile strength and heat resistance.
- *Resins for Dental Models.* This resin is designed to make bridges and crowns with removable abutments. It is a high-precision resin, with fits that support tolerances down to ± 35 microns. It has a smooth, matte, plaster-like surface, making it scannable and easily transportable from analog to digital systems.
- *Heat resistant.* These are materials for additive manufacturing capable of withstanding temperatures up to 300°C. They are often used for the realization of moulds, models or parts used to channel or contact hot air flows or tools for casting or thermoforming systems. On the other hand, their respectable surface finish is counterbalanced by their high fragility.
- *Elastic Resins .* Rubber-like resins are 3D printing resins that simulate rubber. Using these materials, it is possible to create objects that are resistant to both stretching and bending with good impact resistance. The downside of using these materials for 3D printing is that they are particularly sensitive to UV light. Prolonged exposure to sunlight leads to premature geometry degradation.
- *Ceramic filled resins* for 3D printing are among the most suitable for the creation of highly defined objects in terms of detail and surface appearance. Prototypes made with these materials are very fragile but boast moderate elasticity, high heat resistance and good thermal stability.

- Metallic materials for additive manufacturing: the "powders" for three-dimensional printing

The new industrial revolution passes through new additive manufacturing technologies but also through the raw material: metal powders. Most AM systems with metals, both professional and industrial, use some of these materials listed below.

- *Titanium powder.* Being highly reactive, titanium 3D printing always takes place in a controlled atmosphere with Argon gas or in vacuum systems. It is among the most widely used metal additive materials for medical and prosthetic fabrication. Titanium is 3D printed by either binder jetting, powder bed casting or Electron Beam Melting technology.
- *Stainless Steel* The creation of 3D printed models in steel has become very popular due to the material's strength and ductility characteristics. The earliest applications of metal additive manufacturing with steel were in the medical and endoscopic surgery fields.
- *Chrome Cobalt* It is probably the most widely used material in metal additive manufacturing technologies as it is applied in the most diverse areas. From the realization of orthopedic or dental implants, to the realization of turbines and more.
- *Copper and Bronze.* Considered as materials of little interest in the industrial field, Copper and Bronze are commonly used in 3D printing processes with lost wax metals. However, due to good conductivity characteristics, copper in particular is also used in FDM 3D printing processes to create real printed circuit boards.

- 3D printing substrate materials

The list of materials that can be used in additive manufacturing could not miss a section dedicated to the materials that can be used for the creation of printing media.

- *HIPS Filament - High Impact Polystyrene.* More than a printing material it is considered a support material for printing, having big adhesion problems in fact, in 3D additive manufacturing processes HIPS is used to create printing supports.
- *PVA Filament* .Literally in support of 3D printing. Polyvinyl Alcohol is water-soluble by nature, and like HIPS is used to make print substrates in multi-extruder systems. Wax Wax is one of the most widely used substrates in jet printing systems. Removal is very simple and usually occurs by exposing the 3D model to controlled temperatures (between 70° and 80°) in order to activate the liquefaction process.

- Ceramics

The new systems of 3D printing with metallic materials, make use of metallic materials for the production of printing supports. The advantage of using ceramics is the possibility to obtain the detachment of the supports without the use of specific tools for metal but with the simple use of the hands.

In the article "Three-Dimensional Bioprinting Materials with Potential Application in Preprosthetic Surgery" by Mina D. Fahmy, Hossein E. Jazayeri, Mehdi Razavi, Radi Masri, Lobat Tay published in 2015, 3Dbioprinting is examined and the different materials that can be used are analyzed. Through that article, advantages and disadvantages of

commercially available materials are evaluated, which allow, for example, the creation of custom 3D scaffolds for use in dentoalveolar defect repairs. The following tables summarize the results of the research.

- **Bioceramics**

- *Calcium Phosphate* compounds have been used for their ability to chemically bind to hard tissue. Tricalcium phosphate (TCP) exists in the form of three polymorphs, including the less dense but more soluble monoclinic and hexagonal α , and the higher density rhomboidal β form. The first alpha forms are formed at high temperatures and can be converted from the β state between 1100°C and 1200°C, whereas a conversion from β to α requires slow cooling. TCP ceramics have been shown to have greater biodegradability than other candidate materials including hydroxyapatite (HA). Lacey et al. found that bone formation is aided by the release of Ca and PO₄ ions around the implant. Klein et al. noted that compared with HA coatings, α -TCP induced more bone one week after implant placement. TCP materials resorb slowly under physiological conditions and can be molded into the bone defect in the form of granules; however, these granules can only be placed in defects surrounded by intact bone. In contrast, calcium phosphate cements (CPCs) can be freely molded and will provide the necessary soft tissue mechanical support after curing. Despite this drawback, the use of CPC is limited due to the lack of macroporosity. Custom-made calcium phosphate implants with a patient-friendly structure are designed to circumvent the problem of lack of macroporosity. β -TCP is the most favorable form of TCP because of its mechanical strength and chemical stability, although there are several challenges associated with it including maintaining a low sintering temperature so as to avoid a transformation to α -TCP. Miranda et al. noted that β -TCP scaffolds containing a rod network were designed by direct write assembly, while optimization of β -TCP printing materials was investigated.
- *Hydroxyapatite (HA)* . Because of the stoichiometric similarity to the mineral phase of natural bone, HA was considered a bone replacement with good potential for biocompatibility. HA implants have been assembled by numerous techniques, including hydrothermal conversion, the use of polymeric sponges, and ceramic material processing techniques. However, all of these methods are limited in their ability to control implant porosity. Several methods have recently been developed to enable 3D HA scaffold design and engineering. The stereolithography (SLS) technique has been used to construct HA scaffolds using the lost mold technique. In addition, direct-write assembly using colloidal inks with tailored viscoelastic properties has also been used to construct 3D HA scaffolds. Michna et al. developed HA scaffolds with the desired characteristics by customizing their architecture and sintering conditions

using HA printing material suitable for direct-write assembly. Chumnanklang et al. describe how the adhesive binder can be incorporated by two methods in HA powder preparation :either by mixing them as separate granules or by coating the HA powder. Leukers et al. have used HA granules to create porous ceramic constructs. The patient's own cells can be implanted directly into the construct for tissue engineering. Leukers et al. noted that the scaffolds produced can act as 3D templates for primary cell attachment, followed by tissue formation. Irsen et al. pointed out that HA granules may not meet all the requirements for use in 3D printing because HA is expensive and does not interact optimally with the binding liquid. Optimization of bioprinting techniques is necessary to provide good surface quality in addition to achieving better resolution.

- *Bioactive glasses or Bioglass Bioactive (BG)* have shown great potential for both healing and regeneration of bone defects because of their ability to support osteoblastic cells and to bind to both soft and hard materials. BG appears to be an attractive alternative to other materials because of its ability to stimulate angiogenesis in the presence of vascular endothelial growth factor (VEGF). BG exhibits the characteristics of osteoconductivity and osteoproducity; both are features that enhance progenitor cell proliferation and differentiation. An important feature of BG is the development of a biologically active surface layer of HA and carbonated hydroxyapatite (CHA) that allows interfacial adhesion to surrounding tissues without formation of scar layers. However, BG usually does not degrade at a sufficiently rapid rate and thus may remain within the body for an extended period of time. One concern regarding the use of porous BG scaffolds is their cytotoxicity on the surrounding environment, perhaps caused by high ion concentration.

The advantage of using ceramics such as HA, bioglass, and calcium phosphate is that they can over-regulate osteogenesis. Another advantage is their ability to allow maintenance of the space, making them materials of interest for reconstruction of craniofacial defects. Printed scaffolds with bioceramic materials allow for rapid population of cells on the surface of the scaffold and promote proliferation; however, ceramics are too fragile for implantation into craniofacial weight-bearing sites.

- Metals

• *Titanium*

The amount of load distribution between the bone and the implant depends on the elastic modulus of the implant. Therefore, it is important that the implant has a mechanical behavior similar to that of natural bone, particularly in the elastic modulus. Potential biomaterials for bone scaffolds, ceramics, and polymers have been extensively studied; however, they are sometimes unable to provide the necessary

mechanical requirements under the specified loads. As a metallic biomaterial, titanium (Ti) has been widely used in recent investigations because of its high corrosion resistance, high strength-to-weight ratio, and confirmed biocompatibility. Ti has low density and suitable mechanical properties such as elastic modulus, fatigue strength, and toughness.

It has been widely used for the construction of implants, such as prosthetic joints, trauma locking plating systems, dental prostheses, screws, membranes, and heart valves. Although the bulk elastic modulus of Ti is more than natural Ti, it is still less than other biomaterials such as stainless steel or cobalt alloy.

Introducing Ti volume porosity to produce titanium scaffolds through approaches engineering, its mechanical properties could be manipulated. In addition, porosity provides pathways for cells to grow within the porous implant.

However, none of the conventional methods allowed the fabrication of porous materials with desirable shape and interconnected pores. To overcome the problems associated with conventional methods, AM technology has been used. Until recently, AM focused primarily on polymeric and ceramic materials. Using AM on metals for bone tissue engineering posed significant challenges.

Ryan et al. used a commercial 3D printer (Thermojet) to produce a porous Ti scaffold from a wax prototype. Powder metallurgy was employed to create porous Ti by filling Ti mush around the wax model. The results of this research indicated that porous Ti scaffolds with porosity of about 66.8% exhibited strength at 10.4 and 23.5 Mpa in axial and transverse directions, respectively, showing anisotropic titanium properties.

The cultured osteoblast cells also maintained their metabolic activity on the surface of the Ti materials.

Wiria et al. also produced a porous Ti scaffold using 3D printing with an elastic modulus of about 4.8 to 13.2 GPa and compressive strength of 167 to 455 MPa. The elastic modulus of the fabricated Ti scaffolds was in the range of natural bone.

Cytocompatibility tests in this study demonstrated that the fabricated Ti scaffolds could provide a suitable surface for cells to live, proliferate, and grow.

Ti alloy (Ti6Al4V) was also used to produce scaffolds with adequate amounts of porosity, pore size, and interconnected pores.

Li et al. developed 3D fiber deposition as an AM technique.

The experimental result of this study illustrated how the parameters control the construction of porous scaffolds. In summary, the Ti and Ti alloy implants produced by 3D printing and tested by biomechanical and in vitro investigations show good mechanical properties and biocompatibility, which confirm the potential use of tissue engineering.

APPENDIX C

- INMAFEED datasheed

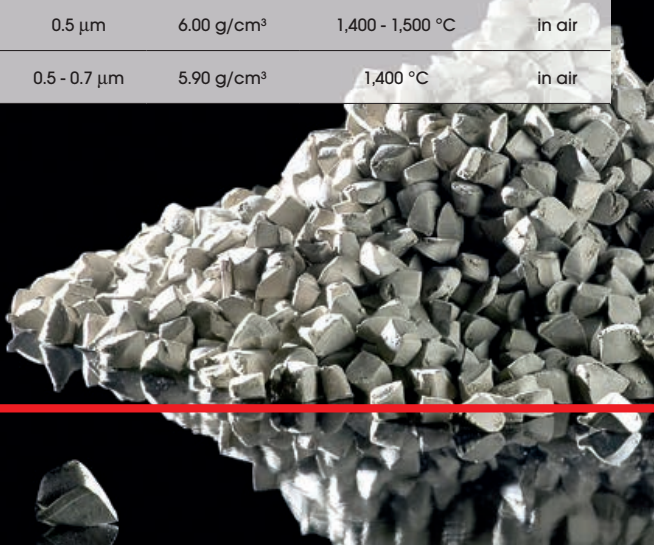

INMAFEED

Ceramic Feedstocks – Product programme

	Ceramic Powder	Colour	Particle Size d_{50}	Theoret. Density	Sintering Temperature	Atmosphere
Al₂O₃ - Feedstocks						
INMAFEED K1008	Al ₂ O ₃ , 96.0 %	white	1.8 - 2.2 µm	3.80 g/cm ³	1,620 °C	in air
INMAFEED K1010	Al ₂ O ₃ , 99.7 %	white	1.0 - 1.5 µm	3.92 g/cm ³	1,680 °C	in air
INMAFEED K1013	Al ₂ O ₃ , 99.8 %	ivory	0.5 µm	3.94 g/cm ³	1,600 - 1,650 °C	in air
INMAFEED K1021	Al ₂ O ₃ , 99.99 %	white / translucent	0.4 - 0.6 µm	3.99 g/cm ³	approx. 1,800 °C for translucent applications	H ₂
ZrO₂ - Feedstocks						
INMAFEED K1009	ZrO ₂ 3Y (Tosoh)	white	0.6 µm	6.05 g/cm ³	1,400 - 1,450 °C	in air
INMAFEED K1012	ZrO ₂ 3Y (Tosoh)	white	0.6 µm	6.05 g/cm ³	1,500 °C	in air
INMAFEED K1015	ZrO ₂ 3Y (Tosoh)	black	0.5 µm	6.00 g/cm ³	1,400 - 1,500 °C	in air
INMAFEED K1016	ZrO ₂ 3Y (DK)	black	0.5 - 0.7 µm	5.90 g/cm ³	1,400 °C	in air

To all INMAFEED-Feedstocks applies:*
 Debinding: 2 steps, in water & thermal
 Processing temperatures: approx. 150 - 165 °C
 Mould temperature: approx. 50 - 65 °C

* Process conditions are depending on part dimension and design.

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- INMAFEED K1013 datasheed



INMAFEED K1013

- Technisches Datenblatt

Der Feedstock basiert auf einem Aluminiumoxid-Pulver (Al_2O_3 , 99,8 %, AES-11C (Solvadis)) und einem wachsbasierten Bindersystem für den Pulver-Spritzgießprozess.

Das Spritzgießen dieses Feedstocks ist auf einer Standardspritzgießmaschine möglich. Bedingt durch die materialeigene Abrasivität von keramischem Pulver wird der Einsatz von Zylindern, Schnecken und Werkzeuginnern empfohlen, die aus Hartmetall gefertigt sind.

Die hergestellten Bauteile sind, bevor sie der Sinterung zugeführt werden können, in einem zweistufigen Entbinderungsprozess zu entbindern.

Der erste Entbinderschritt umfasst das Herauslösen des Binders in einem Wasserbad.

Im zweiten Entbinderungsprozess wird der restliche Binder thermisch herausgelöst.

Diese allgemeinen Richtlinien basieren auf einer Wandstärke von ca. 5mm. Bitte berücksichtigen Sie bei Anwendung dieser allgemeinen Empfehlungen unbedingt, dass es sich hierbei ausschließlich um Richtwerte handelt, die in der Praxis, entsprechend der jeweiligen Bauteil-Wandstärken und -gestaltung, optimiert werden sollten.

Wir beraten Sie gerne anhand der bauteilspezifischen Daten.

Feedstock Kennwerte

Typische Materialeigenschaften	
<i>Produkt</i>	Feedstock für den keramischen Spritzgießprozess
<i>Binderbasis</i>	Polyolefinbasiertes Bindersystem
<i>Aussehen</i>	Weißes bis gräuliches Granulat
<i>Lagerung und Haltung</i>	Bei trockener Lagerung und Raumtemperatur kann die Feedstockmenge pro Verpackungseinheit bis zu sechs Monate nach Öffnung eingesetzt werden. Nach Materialentnahme muss der Behälter wieder luftdicht verschlossen werden.
<i>Typische Zusammensetzung nach den Sintern</i>	Al_2O_3 , 99,8 %, AES-11C (Solvadis)
<i>Theoretische Dichte</i>	~ 3,94 g/cm ³
<i>Schwindung, ca.</i>	16,5 %
<i>Werkzeugaufmaß-Faktor, ca.</i>	1,19

Typische Verarbeitungseigenschaften	
<i>Werkzeugtemperaturen</i>	50 – 60 °C
<i>Verarbeitungstemperaturen Spritzgießen</i>	155 – 165 °C
<i>Entbinderung</i>	Zweistufig
<i>Erste Entbinderungsstufe</i>	Wässrige Entbinderung
<i>Zweite Entbinderungsstufe</i>	Thermisch bis 300 °C
<i>Sintertemperatur</i>	T _{max} 1600 °C, an Luft

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- NISHIMURA Feedstock economical proposal



NISHIMURA
ADVANCED CERAMICS
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QUOTE

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FABRIZIO BOMBARDI, PhD
Associate Professor
Material Science / Composite Materials

DATE: MAY 11, 2021
VALID DATE: UNTIL 11, 2021

QTY	DESCRIPTION	PRICE	FREIGHT	LINE TOTAL
30kg	N-999 Alumina 99.9% CoA Feedstock (N/A required) (Our material data, price, or any relative information is confidential.)	Japanese Yen 14,500	Japanese Yen 55,800	Japanese Yen 471,800
30kg	N-99 Alumina 99% CoA Feedstock (N/A required) (Our material data, price, or any relative information is confidential.)	Japanese Yen 4,800	Japanese Yen 55,800	Japanese Yen 216,800
	Subtotal			Japanese Yen 688,600

TOTAL Japanese Yen
688,600

THANK YOU!

*1 Quotes were based on above mentioned quantity base per order per lot. In case such quantity couldn't be reached,
Nishimura Advanced Ceramics shall reserve the right to re-examine and revise quotes.
2 Payment Method: Advanced payment by wire transfer.
3. BANK INFORMATION
PAYING BANK : WATBIO BANK, LTD.
A/C WITH BRANCH : KYOTO BRANCH
ADDRESS : 20 NAGAHATAKEDCHO, KAWASUMI-HASHIRU, SHUJO-CHO, SHIMOGUCHI-KU, KYOTO 600-8008 JAPAN
SWIFT CODE : WBCJJPJT
A/C NUMBER : 430-0021632

AKNOWLEDMENTS

La presente per esprimere la mia piena soddisfazione nell'aver compiuto questo percorso che mi ha permesso di entrare in contatto con gli aspetti ingegneristici del mio lavoro quotidiano.

La professione medico-odontoiatrica si focalizza sul paziente, dando per conclamate le tecnologie e gli strumenti con cui si eseguono le terapie , e l'aver avvicinato, studiato e sviluppato gli aspetti più profondi delle stesse mi ha sicuramente arricchito personalmente e culturalmente.

Il percorso ha visto numerose insidie che con caparbia ed impegno sono riuscito a superare rendendomi oltremodo orgoglioso del lavoro svolto e del risultato ottenuto.

Intendo sinceramente ringraziare l'azienda BTK per aver supportato economicamente e aver contribuito allo svolgimento del mio Dottorato.

Esprimo altrettanta gratitudine all'azienda WASP per avermi fornito, senza vincoli alcuni, un prototipo su cui sviluppare la fase sperimentale raggiungendo ottimi risultati.

LUCA SOLIMEI