Laser-assisted additive technologies for the execution of dental restorative prostheses

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Abstract. In the paper the authors present a technology with a great development perspective applied in restorative dental prosthetics based on the action of the laser. Also, there is presented an additive manufacturing method for obtaining dental prototypes from special materials, which can have multiple applications in the dental field. By this, dentists can replace the traditional outdated methods of prosthesis. A 3D printer for dentistry is a real opportunity to automate the most important stage in the work of dental laboratories, as well as move to a new level of quality. High productivity, waste-free production, possibility of realization of complex geometries - this is only a small part of the advantages of these technologies for metal and polymeric printing. The researches in this article even show that the prostheses made by selective laser melting have some better mechanical properties than the conventional casted prostheses from the same material.

1. Introduction
In modern dentistry, prosthetics remains a very important part of tooth restoration. The manufacturing of dental prostheses does not stand still and constantly offers new technologies, the possibilities of using various materials are expanding [1,2,3]. The indispensability of mounting the prosthesis is due to the need to replace the dental crown of the natural teeth due to some anatomical, aesthetic and functional deficiencies. Among the main indications for prosthesis are the destruction of teeth after caries or other dental diseases, developmental abnormalities, pathological abrasion of hard dental tissues, aesthetic improvement of natural teeth and others. However, some local or even systemic contraindications must be considered. In general, for each type of prosthesis there is a specific set of indications and contraindications. Considerable multidisciplinary research efforts in recent years form the basis for continuous improvement in the field of dental prosthetic restorations.

Dental prostheses are classified from several points of view, but probably the most important criterion of differentiation is the method of obtaining them. There are many techniques and procedures for obtaining dental prosthetic constructions at present, which differ according to the material and equipment used, increasingly being used CAD CAM technologies for this scope [4, 5]. Due to these technologies, the dental technician's activity is successfully performed by the automation systems. It is noted that these technologies are practically error-free - the exact mathematical calculation allows the realization of future prostheses with special precision. CAD-CAM modelling also has notable advantages over conventional prosthetic work techniques. The equipment is compact, but at the same time with high performance, which reduces the waiting time for patients. Figure 1 summarizes the main techniques for obtaining dental prostheses at the present time [6, 7, 8, 9].
Lately, additive technologies are gaining more and more interest, namely those based on the action of the laser beam by melting or sintering the raw material in powder form. These methods of making dentures allow to realize very complex and diversified geometries and configurations of biocompatible materials [10, 11, 12]. These methods can cover many shortcomings of conventional casting technologies and even computerized dental milling technologies, which are recognized in the dental field for accuracy and precision of execution. Being a technology that operates by adding material, the unused raw material can be reused in the following processes, which makes these technologies more economically efficient than milling. Certainly, these additive technologies will have a continuous direction of development and improvement, representing a maximum area of interest in the dental prosthetic field and not only, surely having a hard word in the contemporary world through its usefulness in various applications. The paper presents the steps to make dental prostheses through these emerging laser additive technologies, using as raw material metallic and polymeric fine powders. There will be presented some mechanical and surface characteristics, highlighting the advantages over the prostheses made by classical technologies. Also, there will be presented an additive manufacturing method for realizing prototypes for the final prosthesis, as well as a special material used in this area.

2. Material and methods
Dental restorative prostheses are realized of special materials for which the specialists have very high requirements. The main things taken into account is excellent survival in the tissues of the human body and the absence of biological hazard. In addition, the material of the dentures must have increased resistance to biological fluids and food. Finally, prosthetic materials must have enough strength, elasticity and abrasion resistance to serve a person for many years.

Selective laser deposition represents additive manufacturing processes for metallic, ceramic or polymeric powders that offer the possibility of obtaining highly complex dental structures from biocompatible materials by consolidating the successive layers of the sprayed material on top of each other. In this article it will be presented dental prostheses made from metal powders (Co-Cr alloy) on the SISMA MySint 100 equipment [10] using selective laser melting technology and polymeric powders (nylon) on the FORMIGA P110 printer [13] using selective laser sintering technology (Figure 2).

The dental prosthetic restorations from the Co-Cr alloy (Figure 3) were performed by selective laser melting in the "Precident" Buzau dental laboratory, and the detailed description of the process of obtaining them can be found in the authors previous works [10, 14]. Regarding the prostheses made of
polymeric material, they were obtained by using selective laser sintering technology, and the material is in the form of polymeric powder. The installation used was FORMIGA P110 from The National Institute of Research and Development in Mechatronics and Measurement Technique (Bucharest, Romania). FORMIGA P 110 represents the laser sintering technology in a compact class. With a workspace size of 200 mm x 250 mm x 330 mm, FORMIGA P 110 produces polyamide or polystyrene components in just a few hours using only three-dimensional virtual data [13].

Figure 2. Equipment used for realization of dental prostheses by selective laser deposition: a – SISMA MySint 100 for metallic selective laser melting; b – FORMIGA P110 for polymeric selective laser sintering

Figure 3. Dental prostheses made by selective laser melting in rough state [10]

This unit is ideal for small and individual series manufacturing of parts of a complex geometry - which, for example, are required in the medical field. At the same time, this installation ensures speed and flexibility in the manufacture of functional prototypes and casting models. This equipment uses a laser with gas (CO₂) active medium with a power of 30 W. It is based on an optical scanning system made of Galvano mirrors, which allow a laser speed of up to 5 m/s. The thickness of the layers made depends on the material used and can be 0.06, 0.1 or 0.12 mm. The print speed depends on the material and is up to 20 mm / hour in height. Also, the installation has an LCD screen on which the process parameters can be set and viewed. Mainly, the work platform can be divided into two regions: the actual working chamber (Figure 4) where the current layer is sintered and the removal chamber, where the sintered layers are lowered after processing exactly with the thickness of the set layer. To avoid thermal shocks, deformation and shrinkage during cooling, the working chamber is heated to 169° C and the removal chamber to 150° C. To achieve the dentures, 3D models were obtained in STL format and were introduced in the software Materialise Magics RP from EOSint [13] (Figure 5a). In this program, the necessary information from the STL model is taken and it can be ensured: the visualization of the pieces in STL format; the correct placement of the prostheses on the working platform; repair and modification of STl files; checking the quality of STL files; location of supports if necessary.
After the files have been manipulated through the Materialize Magics program, they are saved in a format known to EOSint (.sli) systems [13]. After saving in this format the newly generated file is passed through PSW (Process SoftWare - Figure 5b) to cut the part into cross sections and to obtain the entire process to be followed by the selective laser sintering equipment, including setting the process parameters of the laser such as the temperature of the execution chamber and the removal chamber, the type of material used (in this case polyamide powder P2200), the thickness of the layer (in this case 0.1mm).

![Figure 4. Working platform: powder bed and heating elements](image)

![Figure 5. Equipment program interface: a - Materialise Magics; b - PSW with the simulation of the deposited layers [13]](image)
After the virtual dentures have been passed through the process programs, they are sent to the equipment via the wireless network. After the program is fully loaded, it will appear on the installation screen. From this phase it can be chosen the program that will execute the installation. The working chamber and the removal chamber are heated to the recommended temperature of 169°C and 150°C respectively. After reaching the required temperatures, the equipment levels with the help of a special mechanism the surface of the powder bed, to ensure the lack of air voids and the uniformity of the powder bed disposing. Once the mechanism has leveled the powder bed, the laser guided by the optical system formed by galvanometric mirrors scans the surface of the powder bed, sintering only the area in accordance with the layers of the workpiece, previously set in process program systems. The selected layer is followed by the CO\textsubscript{2} laser that melts and unites the material (Figure 6). Once the first layer has been completed, the work chamber goes down to exactly the value of the layer thickness (100 µm).

**Figure 6.** Sintering view of selected areas

After the dental prostheses have been obtained and the execution chambers have cooled down to room temperature, they are removed from the powder (Figure 7). The resulting dental prostheses need some post-processing steps to have the desired aspect. From Figure 7 it can be seen that the obtained parts must be cleaned of the remaining powder (this can be reused in subsequent prints) during processing. After they are removed, the dentures are placed on a vibration table to recover the remaining powder in the cavities of the parts and to clean them preliminary, after which they are better processed in a blasting chamber with glass balls so as not to damage the prostheses realized.

The material used as a raw material for the manufacturing of dental prostheses by selective laser sintering was PA 2200 fine powder, based on polyamide 12. This thermoplastic material, also known as nylon, has suitable thermo-mechanical properties and a wide variety of applications. Due to its excellent mechanical properties and chemical resistance, the material is often used to replace the materials used as molds for injection molding [15]. Dental prosthetic elements made by selective laser sintering are shown in Figure 8. Another additive technology intensively developed in the field of restorative dentistry is the technique of vat photopolymerization with the raw material in liquid state. This technology can be implemented to obtain dental prosthetic models / prototypes with multiple applications in the field [16]. For example, dental structures made by DLP (Digital Light Processing) technology can be used as a model for the future prosthesis or to present the patient a prototype for the final work, thus improving the dialogue between the specialist and the patient. Also various surgical interventions can be practiced on these models or they may even constitute surgical guides.
If previous studies aimed at obtaining dental models using DLP (Digital Light Processing) technology from conventional photocurable resins [14, 16, 22], in this article a photopolymer material specially designed for applications in the field of prosthetic dentistry mentioned above was used. The DruckWege Type D Dental resin allows three-dimensional printing of high-precision distinguished models of the teeth. After solidification, the resulting material has an appearance and properties that are incredibly close to the usual dental gypsum material. However, this material has not been tested or approved for medical or pharmaceutical applications. This resin is intended for modeling only and not for use in the oral cavity. Figure 9 shows a dental model made by DLP technology on the Wanhao Duplicator 7 printer [17] from DruckWege special dental resin [18]. The three-dimensional model of the teeth was obtained based on a personalized digital intraoral scan [16].
3. Results and Discussions

Dental prostheses made using SLM (Selective Laser Melting) technology have been tested regarding some mechanical properties and surface characteristics. The raw material for these prostheses was the Co-Cr alloy, which is known for its special biocompatibility [10]. Apart from these two basic metals, the composition of the alloy includes a lower composition of tungsten, molybdenum and other elements. The powder and dentures were investigated on the Olympus BX 51 microscope, which is a universal microscope with direct measurement and is designed to solve complex tasks that require non-standard approaches and the application of the latest advances in the optical and mechatronics industry. Figure 11 shows the Co-Cr coarse powder over 50 micrometers in diameter 200 times magnified. It can be observed spherical granules with a relatively large diameter, where granules with diameters greater than 0.1 mm are distinguished. These powders are separated before the start of the process of selective laser melting through a special spherical sieve, the optimum diameter for granules being in this process below 30-35 µm [10]. From the figure it can be seen the smaller spherical granules that are attached to the larger granules. Figure 12 shows the comparison between the conforming powder (under 30 µm) and the coarse powder (over 50 µm) magnified 500 times.
Figure 1. Coarse metallic Co-Cr powder (over 50 µm in diameter)

Figure 2. Mixed metal powder (over 50 µm and below 30 µm)

A dental prosthesis made by selective laser melting technology which was finished by mechanical polishing was examined on this microscope to see the efficiency of post-processing (Figure 13). Figure 14 shows the result of this microscopic investigation, the magnification being of 50 X. It is observed that the surface condition is glossy, but with internal irregularities marked on the figure with variable dimensions of about 100 µm. These small defects can significantly affect the performance of the future restoration, especially in the ceramic coating process for aesthetic aspect rendering, in which case a more efficient finishing process is required. A possible successful variant for this purpose may be electrochemical polishing [19].

Also, this dental prosthesis made by SLM technology has been tested in terms of hardness [20], as its value should be one of the highest priority when choosing enamel replacement materials. It is preferable that the hardness of the dentures be at least equal to the hardness of the replacement material - of the enamel (275 HV).

The equipment used to determine the hardness was the HMV Schimadzu microdurimeter, which uses the Vickers method, which consists of penetrating the test material with a diamond penetrator, in the form of a regular pyramid with a square base and an angle of 136° at the tip of the penetrator between the opposite faces [20].
Figure 13. Examination of the dental prosthesis realized by selective laser melting on the Olympus BX 51 microscope

Figure 14. Microscopic image of the polished dental prosthesis

Also from the equipment it can be set the conversion of Vickers units to other hardness units. The microdurimeter used HMV Schimadzu (Figure 15) is designed to measure the hardness of small parts and the metal structures used in precision and medical equipment. It has an interface with a touchscreen LCD screen combined with a high-performance optical system, with a minimum diagonal measuring unit of 0.01 μm for extremely high accuracy. In addition to the Vickers method used in this study, the Brinell and Knoop methods can also be used on this microdurimeter to determine the hardness, and to change the determination method, it is necessary to change the penetrator. There are 9 loading modes, from 98,07 mN to 2,942 N. In this case, the 980,7 mN penetrator actuation force (HV0.1) was used.

The optical system is used to set the measuring position and to check the height of the sample surface, and then measures the penetration.
Figure 17 shows microscopically the trace left by the regular pyramid-shaped diamond penetrator with the square base. In total, five different areas have been chosen and it is desired to compare the hardness value resulting from the experimental determination with the hardness values of this material made by traditional technologies. Following the experimental determination, the following results were obtained: area 1 - 526 HV or 50.8 HRC; zone 2 - 554 HV or 52.6 HRC; zone 3 - 513 HV or 50 HRC; zone 4 - 531 HV or 51.1 HRC; area 5 - 495 HV or 48.7 HRC. All the five values obtained far exceed the hardness of the 275 HV enamel and even the hardness of this alloy made by traditional technologies [21]. An average value of 524 HV was obtained, with a maximum of 554 HV and a minimum of 495 HV.

Also, a comparative study was made regarding the dimensional accuracy of the materials made by additive technologies based on the raw material in liquid state compared to those made by thermoplastic extrusion – FDM technology [14]. In order to compare the materials, additive technologies and equipment used to obtain the dental models in terms of dimensional accuracy, several relatively simple parts of identical parallelepiped shape were designed and made. Undoubtedly, the parts made by DLP technology [16] gave the best results, the average relative errors being less than 1%, even in thickness compared to the nominal size, a problematic feature known in these technologies. In the future, it is desired to develop a larger research to study the dimensional accuracy of these additive technologies for the realization of dental models.
4. Conclusions
In the article were presented additive technologies based on the action of the laser to realize dental prostheses from metallic and polymeric powder raw materials, as well as to make dental models through additive technologies using special photopolymer resin. Parts made using selective laser sintering have adequate properties and compared to other 3D printing technologies for thermoplastic materials, they can be used as functional parts, not just as prototypes. Another advantage is that this technology does not require supports and extremely complex geometries can be obtained. The continuous implementation of these additive technologies will favor more intensively the development and refinement of restorative dentistry, eliminating many of the disadvantages of the dental prostheses manufacturing by conventional technologies such as the casting or even the manufacturing of subtractive CAD-CAM milling. After the experimental investigations regarding the hardness determination of the dental prostheses realized by selective laser melting, it can be concluded that after mechanical polishing they have a conforming hardness, considerably higher than the material to be replaced. Moreover, all five hardness values determined exceed the hardness values for the same alloy, but achieved by classical methods. This is a major advantage for the long-term performance of dental prostheses, and with the compensation of other deficiencies existing at this time, dental prostheses made by laser selective melting will certainly be the first choice for dental specialists, patients and dental technicians. However, after obtaining them through the SLM process, their surface is rough, and the post-processing stage becomes vital and indispensable. The mechanically polished prostheses showed minor surface defects, and a more efficient finishing method can lead to the improvement of their mechanical performances and properties. The possible solution for improving the process of finishing the dental prostheses made by SLM can be electrochemical polishing.

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