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# Mechanical Properties Comparison of Engineering Materials Produced by Additive and Subtractive Technologies for Dental Prosthetic Restoration Application

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Additional information is available at the end of the chapter

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## Abstract

Comparative investigations are presented into the structure and properties of selected engineering materials used for dental prosthetic restorations manufactured alternatively by the subtractive method by milling on computerised numerical control (CNC) milling machines and by the additive selective laser sintering (SLS) method of solid and porous elements using computer-aided design/computer-aided manufacturing (CAD/CAM) techniques; moreover, an original technology was presented of manufacturing the elements used in prosthodontics, produced with titanium and Ti6Al4V alloy powders with the SLS technique. Suitability was confirmed of applying the manufacturing technologies used in prosthodontics from powders by the SLS technique. The results were compared of the executed tests of strength micro-samples and of the selected prosthetic Bridges. The SLS technology for titanium, and even more for Ti6Al4V alloy, ensures the achievement of mechanical properties comparable or better than a reference Co-Cr alloy commonly used for prosthetic restorations, including prosthetic bridges fabricated by milling solid discs with CNC milling machines. For all the examined engineering materials, the milled and then sintered ZrO<sub>2</sub> material exhibits the lowest strength properties. The results presented in this chapter can be directly applied in dental practice.

**Keywords:** prosthodontics, machining, additive machining, selective laser sintering, titanium and its alloys, Co-Cr alloys, zirconium oxide

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## 1. Justification and scope of comparative investigations of selected alloys and technologies of dental manufacturing of prosthetic restorations

Practical dental engineering encounters numerous problems with selecting the most suitable material and technology of dental manufacturing of a prosthetic restoration by a dental

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surgeon conducting treatment. One of the important reasons is inability to compare directly the properties and structure of analogous prosthetic restorations but produced using various technologies and from different alternative engineering materials accepted for medical, especially dental, uses as compared to the restorations used most often until now. It is beyond any doubt that dental surgeons are responsible for the strategy and quality of dental treatment. The literature studies carried out as well as the Author's long-term own engineering experience in running medical practice and a dental engineering workshop show that—parallel to clinical experience of a dentist conducting treatment of dental system diseases—the successfulness of such activities also depends on the results of a dental engineer's activities, consisting of the appropriate execution of prosthetic restorations and implants, depending on the selection of the most appropriate engineering material and appropriate manufacturing technology, ensuring, respectively, the required biocompatibility, mechanical properties and corrosion resistance, as well as high production accuracy and aesthetic requirements. Such activities require, therefore, close cooperation of a dentist and a dental engineer having extensive and interdisciplinary engineering knowledge of the principles of construction, technology and science of materials and computer-aided methods of engineering and dental works.

The dental system, especially teeth, is still subject to numerous disease processes, especially tooth decay, so widespread in many countries and practically across the globe [1–4]. This disease has a considerable social range and is a serious medical problem, not only due to local mouth cavity disorders but also due to a high risk of systemic complications stemming from the dental pulp disease, and is a direct cause of a majority of tooth losses among a wide group of people in many countries. The extraction of unhealthy teeth was a dominant practice in such cases for a long time. There may also be inborn causes of missing teeth, for example, due to missing tooth buds. The basic method of producing permanent prosthetic restorations, which is still often used, is to cast metal alloys requiring successive machining, mainly to remove elements of the gate system, and to ensure required surface roughness and dimensional accuracy. Apart from conventional technologies of manufacturing prosthetic restorations including especially powder metallurgy, casting technologies, metallic foam manufacturing, also additive technologies of fabricating solid and microporous materials in medicine and dentistry are exceptionally useful. The potential of additive technologies is much larger than of other technologies and is represented chiefly by opportunities ensured by three-dimensional designing and the related control of the structure, sizes and shape of the materials produced and the repeatability of geometric features of the elements produced, and because no wastes are produced and because the simplicity of the technology is comprised of two key stages only: designing and manufacturing.

Considering the additive technologies employed most extensively in industry, only few have found their application in prosthetics, with selective laser sintering/selective laser melting (SLS/SLM) offering the biggest opportunities [5–15]. This issue is even more important to clarify whether such additive technologies, applied in dental engineering, are competitive for conventional technologies, because original own works [5, 16–36] have been undertaken concerning constructional solutions and fabrication technologies of a new generation of custom, original, hybrid, microporous, high-strength engineering and biological

materials with microporous rigid titanium and titanium alloy skeletons manufactured by selective laser sintering, whose pores are filled with living cells. The aim of such constructional and technological solutions is to ensure conditions for natural ingrowth of living tissues in the connection zone of prosthetic/implant elements, with bone or organ stumps, to eliminate the need to apply for patients the mechanical elements which are positioning and fixating the implants. In order to manufacture engineering and biological materials and implant scaffolds, it is required to seek the most advantageous proliferation conditions of living cells inside the pores of a microporous skeleton made of titanium and titanium alloys, because the adhesion and growth of living cells are dependent on the type and characteristics of the substrate. A porous zone requires surface treatment inside pores to improve proliferation conditions of living tissues, which are not advantageous for a substrate made of titanium or Ti6Al4V alloy. It appears that the improvement of proliferation conditions of cells is ensured by a substrate made of fully compatible materials, including  $\text{TiO}_2$ ,  $\text{Al}_2\text{O}_3$  oxides and a hydroxyapatite,  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ , used as coatings of internal surfaces of pores of a microporous skeleton fabricated by SLS. Thin layers inside pores were deposited by two technologies ensuring the uniform thickness of coatings on all the walls and openings of a substrate, that is, the so-called atomic layer deposition (ALD) [19, 37–43], and the sol-gel technology of coating deposition from the liquid phase by the immersion method [37, 40, 44–52]. In order to be able to accomplish the above-mentioned general aims of the investigations, it has to be confirmed that additive technologies, especially SLS, do not lead to unacceptable deterioration of useful properties of the so-produced prosthetic restorations.

Apart from permanent prosthetic restorations made traditionally on a metallic substructure, new technologies of introducing ceramic materials have been launched, including so-called fully porcelain systems made of zirconium oxide and aluminium oxide. For dimensional accuracy and aesthetics as well as biocompatibility and dental strength of prosthetic restorations, the constant development of manufacturing technologies of prosthetic restorations is required along with the evolvement of the engineering materials currently employed in prosthetics. Highly varied conditions of joining the artificially produced prosthetic restorations and implants with a body's natural tissues, mainly in the oral cavity, are driving especially high requirements for the engineering material applied for prosthetic restorations and implants. The reason for this is not only special conditions of using various prosthetic and implantological restorations but also different economic and technological conditions and differentiated availability and level of clinical methods and also important aesthetic reasons. Computer-aided design/computer-aided manufacturing (CAD/CAM) techniques [53–59], allowing to improve dimensional accuracy of the fabricated prosthetic restorations, have become increasingly vital over the last decade. CAD/CAM techniques find their application in dental engineering in machining, in plastic forming, in additive manufacturing technologies and in special technologies and both in metal and ceramics working. Computer-aided design enables, in particular, to produce a digital prosthetic model by scanning with an intra-cavity scanner and also to customise the designing and manufacturing of each prosthetic restoration under constant supervision of a doctor conducting the treatment. Cone beam computed tomography (CBCT), used often in dental surgeries these days as the basic diagnostic tool for comprehensive dental treatment, mainly

implantological, prosthetic and endodontic treatment, creates excellent possibilities in this field. A widespread application of CBCT also permits to utilise the information acquired about the condition of a patient's tissues in planning and performing implant and prosthetic treatment [55, 60].

The assumptions made require special interest in the selected engineering materials finding application in dental engineering, including mainly casting alloys of cobalt, titanium and its alloys and ceramics on the zirconium oxide matrix [61–72]. The essential aspects underlying the investigations described here were the questions whether—in each case—it is feasible to apply prosthetic restorations made on a metallic substructure of zirconium oxide, guaranteeing currently best aesthetic results, for prosthetic restorations and to explain if it is possible to use a zirconium oxide substructure in the side sections and in circular restorations together with recognising the limitations for the use of this material. Another practical aspect is to develop a methodology for application of titanium and its alloys as compared to Co-Cr alloys of the Vitalium type for implantoprosthodontic restorations so as to guarantee the lowest possible mass of the completely manufactured prosthetic restoration while ensuring aesthetic requirements and the maximum, possible strength properties. For production of metallic substructures, it is necessary to ensure space for veneering porcelain, among others, in intermolecular spaces on abutments between crowns and bridge spans but also on the vestibular space, so that the dark colour of the substructure does not influence the colour of the ready veneering ceramics. Considering that disadvantages and limitations are known of casting and machining technologies such as computerised numerical control (CNC) milling currently used in dental engineering laboratories, it was decided to compare the state-of-the-art manufacturing techniques currently applied in dental engineering, including completely innovative additive techniques which—due to high implementation price, but very low price of producing a single prosthetic point—are rarely used in practice. As Co-Cr alloys are most often used in dental practice and, therefore, most often described in the literature, such were used as a reference point for the works performed already described in literature. This will allow practitioners, especially dentists, to easily transfer the results presented in this article to everyday uses and to consider such results for designing the extensiveness of prosthetic restorations and for cost valuation. The matter is very complex and requires multi-criteria optimisation, which cannot be performed individually by any prosthetic laboratory. The matter requires, therefore, methodologically planned research which can demonstrate—to the practising therapists and prosthetic workshops cooperating with them—the advantages of some material and technological solutions over those commonly in use these days. This will surely have a major impact on the outcomes and durability of dental treatment and on satisfaction, comfort and patients' improved health condition. The aspects highlighted were the reasons for outlining the topic of the chapter presenting the results of the work [18], after making a thorough literature analysis of the status of research into the dental system, its diseases and treatment methods of tooth losses as well as materials and technologies applied in prosthetics. A concept presented in this article is covered by a broader range of works followed in the recent years [5, 7, 16, 17, 21–26, 34, 55, 56, 73–79], in which the author has participated actively. The works concern

principally the possibility of producing solid and porous titanium parts by additive technology, for use in dentistry and reconstructive medicine.

This chapter depicts the outcomes of comparative investigations into the structure and properties of selected engineering materials used for dental prosthetic restorations manufactured alternatively by the subtractive method by milling on CNC milling machines and by the additive SLS method of solid and porous items using CAD/CAM techniques; moreover, an original technology was presented of manufacturing the elements used in prosthodontics, produced with titanium and Ti6Al4V alloy powders with the SLS technique. The assumptions made in this chapter are focussed on the selected engineering materials finding application in dental engineering, including mainly casting alloys of cobalt, titanium and its alloys and ceramics on the zirconium oxide matrix.

Materials for milling were delivered in the form of discs with the diameter of 98.3 mm and height of 10–16 mm, and the chemical composition, according to suppliers' attestations, is shown in **Table 1**.

Two types of powders with a spherical shape were used, respectively, for selective laser sintering and with the composition shown in **Table 2**, also confirmed with spectral examinations with the energy dispersive spectrometry (EDS) method:

- Titanium powder with Grade 4 and grain size of up to 45 μm, oxygen concentration reduced to 0.14%, while average oxygen content in titanium powders is about 0.5%, the aim of which is to ensure process safety,
- Ti6Al4V alloy powder with the grain diameter of 15–45 μm, for medical applications.

The results of comparative investigations are presented into the structure and properties of the mentioned engineering materials used for dental prosthetic restorations manufactured alternatively by the subtractive method by milling on CNC milling machines and by the additive SLS method of solid and porous items using CAD/CAM techniques; moreover, an original developed

Material	Mass concentration/fraction, %					
Ti grade 2	Ti	Others N, C, H, Fe, O altogether				
	> 99.6	< 0.4				
Ti6Al4V	Ti	Al	V	Others N, C, H, Fe, O altogether		
	89.4	6.2	4.0	≤ 1.0		
Co-Cr	Co	Cr	W	Mo	Si	Others C, Fe, Mn, N altogether
	59.0	25.0	9.5	3.5	1.0	< 1.0
ZrO <sub>2</sub>	ZrO <sub>2</sub> + HfO <sub>2</sub> + Y <sub>2</sub> O <sub>3</sub>					Including Y <sub>2</sub> O <sub>3</sub>
	> 99.0					4.5-6.0

**Table 1.** Chemical composition of the examined materials manufactured by CAD/CAM by milling solid discs.

Powder	Mass concentration of elements, %									
	Al	V	C	Fe	O	N	H	Others total	Others each	Ti
Ti	–	–	0.01	0.03	0.14	0.01	0.004	< 0.4	< 0.01	remainder
Ti6Al4V	6.35	4.0	0.01	0.2	0.15	0.02	0.003	≤ 0.4	≤ 0.1	

**Table 2.** Chemical composition of the powders used for selective laser sintering.

technology was presented of manufacturing the elements used in prosthodontics, produced with titanium and Ti6Al4V alloy powders with the SLS technique. Experimental comparative investigations were carried out of selected engineering materials recommended for clinical use for permanent dental prostheses manufactured by CAD/CAM. The properties and structure were also compared directly of analogous prosthetic restorations but produced using the various technologies mentioned and from different alternative engineering materials already mentioned, as well, as compared to the restorations made of Co-Cr alloy by milling solid discs, used most often until now. In order to create a ranking of the materials and technologies applied, analogous elements were produced by milling from solid discs made of ZrO<sub>2</sub> ceramics and then by sintering. Such material and technology are commonly regarded by dentist practitioners as the most avant-garde solution. Elements were produced from titanium and Ti6Al4V alloy by machining by way of milling solid discs, and analogous elements were made from such materials by the additive method in an SLS process. An original technology was established of manufacturing elements used in prosthodontics, produced with titanium and Ti6Al4V alloy powders with the SLS technique.

## 2. Additive and machining technology of fabrication of materials and dental restorations and research methodology

The elements used for the investigations were fabricated by the machining method by milling solid discs on a CNC milling machine and by the additive SLS method. In the case of the engineering materials manufactured by the machining method by milling on CNC milling machines, technological conditions of manufacturing were chosen experimentally. The technological processes mentioned have no influence on any structural changes, except that ceramic ZrO<sub>2</sub> material of the Cercon type has to be sintered already after milling, so the selection of manufacturing conditions does not have to be verified experimentally and structural changes do not have to be confronted with the mechanical properties obtained of the elements produced. The situation is opposite if the SLS additive technology is applied. Investigations over the selection of technological conditions of selective laser sintering involve the selection of laser power, laser beam diameter, a dependency between the laser beam diameter and the distance between laser beams and the distance between laser remelting paths to desired geometrical features of solid and porous elements produced from titanium and Ti6Al4V alloy and the structure formed depending on such technological conditions and its influence on mechanical properties. Each time before producing the examined elements, design was performed using

the CAD method, and relevant data in the stereolithography (STL) format is transferred for the execution of computer-aided manufacturing in a relevant technological device.

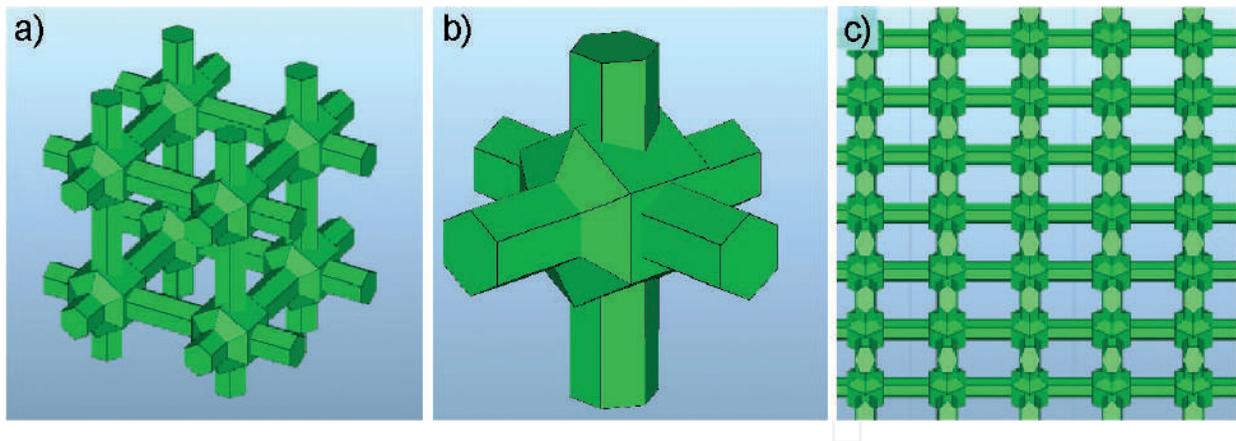
The solid elements used for the investigations, fabricated by the machining method by milling solid discs, were prepared with special CAD software, dental wings operation system (DWOS), by Dental Wings and 3D Marcam Engineering AutoFab software (software for manufacturing applications) for geometrically simpler shapes of test specimens.

The software features the width offset of the tools used for milling, to ensure the highest possible design reproduction in reality. The so-designed elements were verified by the software for surface cohesion and developed as ready designs in the stereolithography (STL) format. The design files are then implemented to a CAM module, Mayka Dental, by Picasoft. The CAM module enables to position the design prepared on a material disc according to the optimum three-axial milling axis and ensures the placement of the milled elements in a way least interfering with the design and to determine the optimum axis of precision five-axial milling to exploit optimally the capabilities of the milling machine. The so-prepared design is transformed into a machine language, and the file produced is transferred to the milling machine's software.

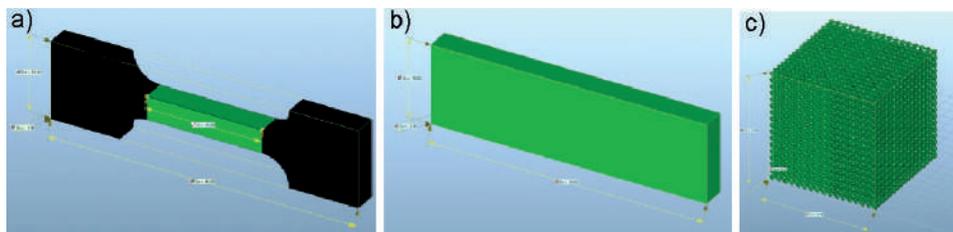
Another group of the examined elements was manufactured by an additive technology of selective laser sintering by designing a given element virtually, in order to develop a 3D CAD model in the STL format, transferred to the machine's software and then by producing in reality the so-designed element layer by layer until producing a ready product. 3D Marcam Engineering AutoFab (software for manufacturing applications) software was used for model designing as a CAD/CAM tool. The software enables to select model dimensions, constructional features and the type of the model volume filling either as solid or porous and to choose the size of a cell unit making up the entire model. A 3D model featuring a layered structure is produced as a result of designing. The surface of the elements modelled in the STL format, which is accommodated to SLS manufacturing conditions, is shown with a net of triangles, with the accuracy of the surface being represented being inversely proportional to their size.

The model size and structure have to be assumed each time and divided into layers with the expected thickness. The number of layers in a virtual model matches the actually designed number of powder layers when the given element is really produced. A set of "hexagon cross" unit cells was used, selected in a geometrical analysis and as a result of preliminary studies, from the set available in the software. By duplicating them, the entire elements were designed, consisting of nodes and single-lattice fibres, linking the particular skeleton nodes (**Figure 1**).

Fabrication conditions were also selected, at the stage of virtual design of elements, available in the selective laser sintering system, including layer thickness, laser power, laser beam diameter, scanning rate and distance between particular remelting paths. A spatial orientation of unit cells of  $45^\circ$  relative to the axis  $x$  of the system of coordinates was also selected experimentally, because other orientations analysed initially, including at the angle of  $0^\circ$ , at the angle of  $45^\circ$  relative to the axis  $y$ , at the angle of  $45^\circ$  relative to the axis  $x$  and  $45^\circ$  to the axis  $y$ , at the angle of  $45^\circ$  relative to the axis  $y$  and  $45^\circ$  relative to the axis  $x$ , turned out to be less advantageous due to the mechanical properties of the elements produced (**Figure 1**).



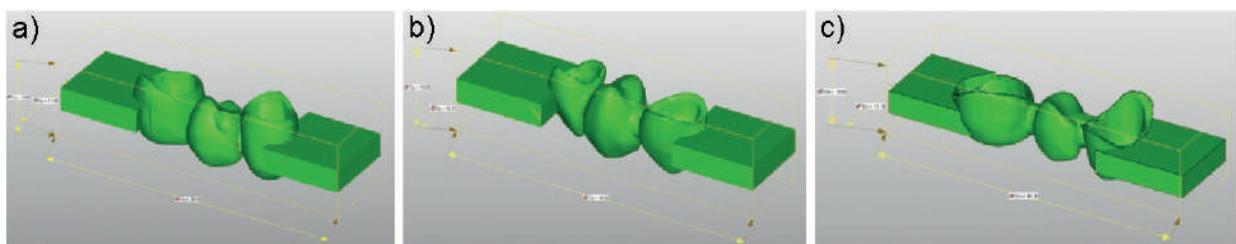
**Figure 1.** (a, b) “Hexagon cross unit cell”; (c) the arrangement of unit cells in the space of the system of coordinates at the angle of  $45^\circ$  relative to the axis  $x$ .



**Figure 2.** Computer model image of solid samples for static test: (a) tensile test, (b) three-point bending test and (c) compression test.

Micro-samples for static tensile, bending and compression tests were specially selected for the investigations (**Figure 2**), made of all the chosen materials manufactured using, respectively, the additive SLS method from powders with individual CAD/CAM and with the machining technology using CAD/CAM techniques by milling solid discs on CNC milling machines. Micro-samples for tensile strength, bending strength and compression strength tests were also designed for the conditions given above with the pore size of  $200\text{--}250\ \mu\text{m}$ .

In order to perform bending strength tests, models were created of three-point prosthetic bridges from three different sections of a dental arch (**Figure 3**), including the front, front-wing and wing section, taking into account first of all the highest possible stresses which may occur in such type of prosthetic restorations. They were made as solid from all the examined engineering materials for bending strength tests with the three-point bending method with the both analysed technologies, that is, machining method by milling solid discs on a CNC milling



**Figure 3.** Computer model of bridges nos. 1, 2 and 3 for bending strength tests with the three-point bending method.

machine and by the additive SLS method. The bending strength was compared to dental bridges made of solid materials, that is, sintered titanium, sintered Ti6Al4V alloy, milled Ti6Al4V alloy, milled Co-Cr alloy and milled and sintered ZrO<sub>2</sub> sinter. The results of strength tests of dental bridges selectively sintered by laser in optimised conditions were compared with the results of tests for bridges milled with CAD/CAM methods from discs of other tested materials, additionally sintered after milling in the case of ZrO<sub>2</sub>. The samples prepared correspond to the prosthetic restorations designed in the author's own clinical practice and in a dental engineering laboratory for particular patients and used by them. Geometrical features were taken into account, such as the fitting of a prosthetic restoration to a pillar, of 0.03 mm; the width of the threshold area; the space for prosthetic cement in the occlusal region, of 0.1 mm; the reduction of the crown shape considering the space for porcelain, of 1.5 mm; and the minimum thickness of the substructure according to the material manufacturer's recommendations, of 0.3 mm, for a substructure made of Co-Cr alloys, titanium and its alloys and 0.6 mm for a zirconium oxide substructure. The software features the width offset of the tools used for milling.

The so-prepared micro-samples and bridges were verified by software for surface cohesion and prepared as a ready design in the STL format (stereolithography), processed into a machine language of a CNC milling machine by Yenadent D43W or AM 125 machine by Renishaw for selective powder laser sintering. After designing the shape of the elements produced, short machining of such elements takes place with a CNC milling machine from a disc of the selected material and additional sintering in a resistance furnace for ceramic prostheses (Table 3). In the case of additive treatment, after designing the produced element the same as previously, the particular layers of metals and alloys are joined layer by layer in the form of powder in an SLS process (Table 3).

As reference results, the results were used of tests of micro-samples and prosthetic bridges fabricated by the machining method with CAD/CAM techniques by milling—with CNC milling machines—solid discs made of Co-Cr alloy of the Vitalium type, used most often in dental treatment, mainly because the alloys are commonly used in casting methods. In order to create a ranking of the materials and technologies used, analogous elements were produced by milling from solid discs made of ZrO<sub>2</sub> ceramics and then by sintering. Titanium elements were fabricated by the machining method by milling solid discs and by the additive SLS method. Elements from Ti6Al4V powder by SLS (Table 3) were also produced for comparative purposes. Apart from examinations of solid materials, examinations of porous elements with the pore size of 200–250 μm manufactured by SLS from titanium and Ti6Al4V alloy powder were also carried out for comparative purposes.

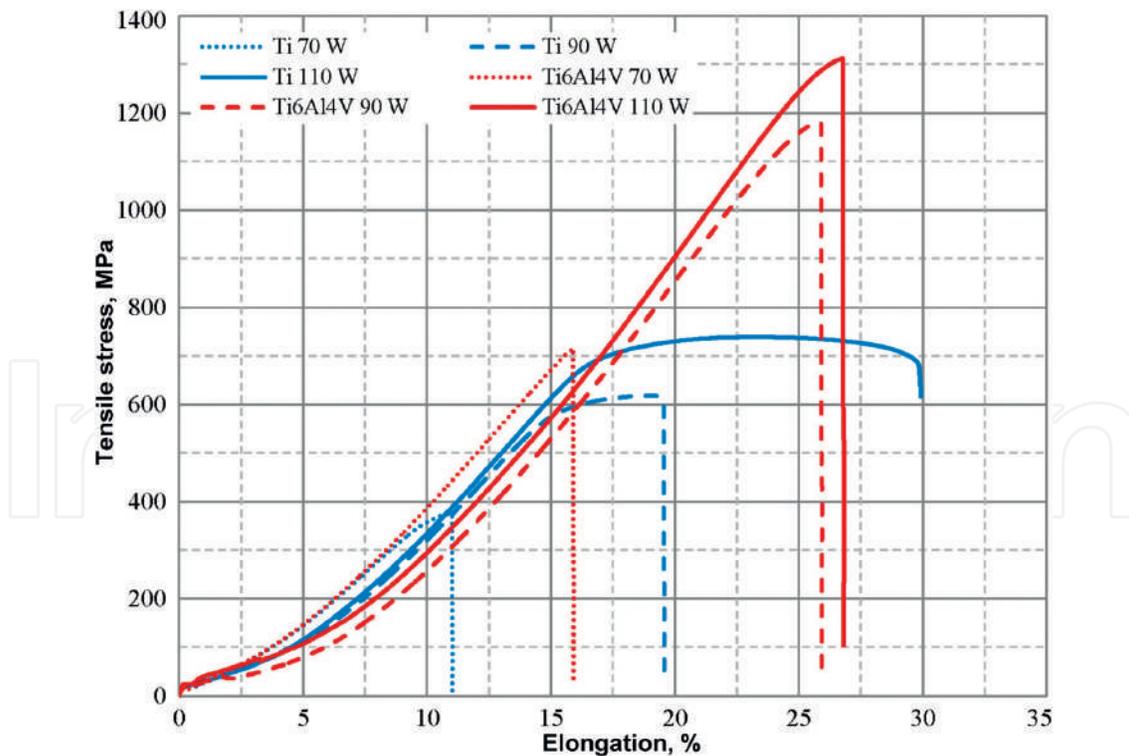
Milling from disc on CNC milling machine			Manufacturing technology
Co-Cr	ZrO <sub>2</sub>	Ti6Al4V	Solid engineering material
Sintered solid engineering material		Ti6Al4V	Ti
Manufacturing technology		Selective laser sintering of powders	

**Table 3.** Diagram of selection of engineering materials and manufacturing technologies of the examined elements.

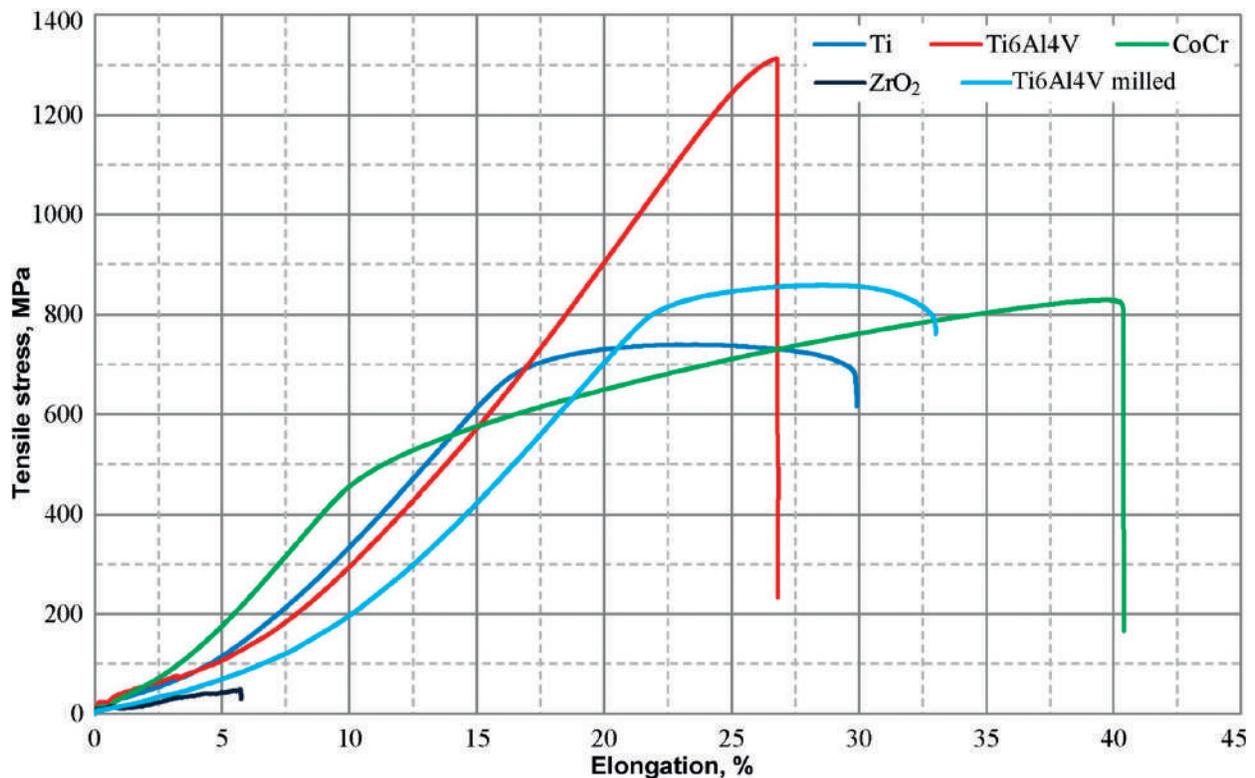
### 3. Comparison of strength properties of the examined solid engineering materials for dental prosthetic restorations manufactured by additive and machining methods

The investigations of mechanical properties of the examined engineering materials were performed in two series in each case. According to the assumed aim of the investigations, mechanical properties were compared in the first series, starting with tensile strength, each time mechanical properties of solid materials produced by the SLS technique for different laser power, that is, sintered titanium and sintered Ti6Al4V alloy. Mechanical properties were compared in the second series of all the examined solid materials, that is, sintered titanium, sintered Ti6Al4V alloy, milled Ti6Al4V alloy, milled Co-Cr alloy and milled and milled ZrO<sub>2</sub> sinter. The results of the examinations were presented in such order for, respectively, tensile strength, bending strength and comprehensive strength.

The impact of laser power, ranging 70–110 W, was investigated in the first place on tensile strength values of sintered titanium and sintered Ti6Al4V alloy (**Figure 4**). The results of tensile strength tests for sintered titanium, sintered Ti6Al4V alloy, obtained in optimum conditions of production, milled Ti6Al4V alloy, milled Co-Cr alloy and milled ZrO<sub>2</sub> sinter, are shown in **Figure 5**.



**Figure 4.** Comparison of diagrams of dependency between tensile stress and elongation for solid samples made of Ti6Al4V alloy and pristine titanium sintered at different laser powers.

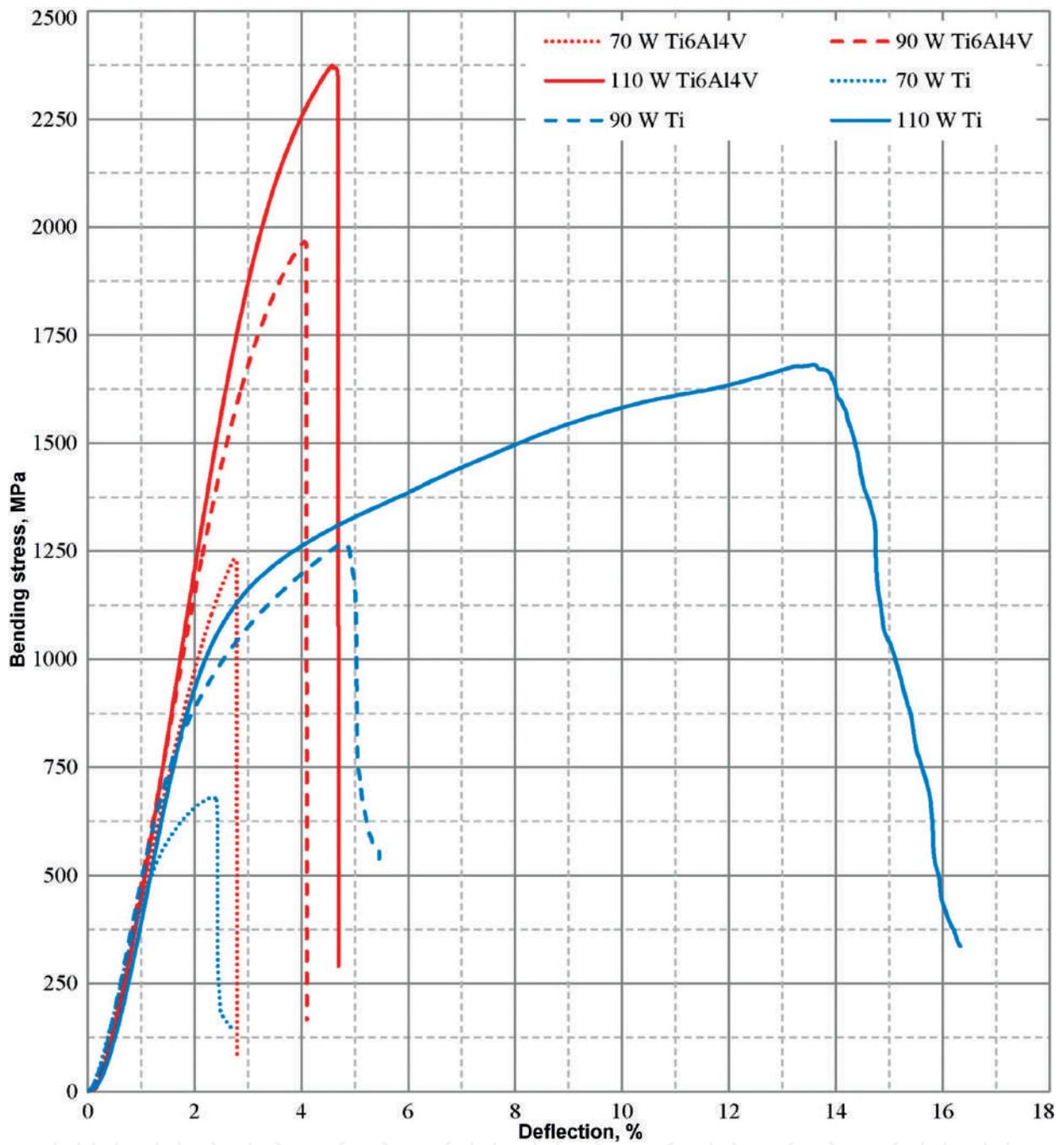


**Figure 5.** Comparison of diagrams of dependency between tensile stress and elongation for various examined materials, that is, for sintered Ti, sintered Ti6Al4V alloy, milled Co-Cr alloy, milled ZrO<sub>2</sub> sinter and milled Ti6Al4V alloy.

The test results given in **Figure 5** are an interesting reason for application of the tested materials in dental prosthetics. A result of approx. 47 MPa for tensile strength of milled and then sintered ZrO<sub>2</sub> alloys is certainly concerning. Selectively laser sintered titanium exhibits the tensile strength of approx. 740 MPa, slightly smaller than specific for milled Co-Cr alloy samples, approx. 825 MPa, and Ti6Al4V alloy, approx. 858 MPa, and much lower than the tensile strength of approx. 1312 MPa of the selectively laser sintered Ti6Al4V alloy. It is the highest tensile strength value for all the examined engineering materials.

Bending strength tests were performed the same as tensile strength tests. The investigations were performed in relation to solid materials manufactured by SLS for different laser power, that is, sintered titanium and sintered Ti6Al4V alloy (**Figure 6**), as well as in relation to the investigated solid materials, that is, sintered titanium, sintered Ti6Al4V alloy, milled Ti6Al4V alloy, milled Co-Cr alloy and milled ZrO<sub>2</sub> sinter (**Figure 7**). It is noted that the bending strength of the sintered titanium of approx. 1682 MPa is only about 3% smaller than the bending strength of about 1740 MPa of the Co-Cr alloy but strongly smaller than the bending strength of approx. 1959 MPa of the milled Ti6Al4V alloy and much higher than the bending strength of approx. 2374 MPa of this alloy after SLS. The smallest is the bending strength of approx. 605 MPa of sintered ZrO<sub>2</sub> alloys milled from discs and then sintered.

**Figure 8** is the comparison of diagrams of dependency between compressive stress and deformation for selectively laser sintered Ti samples and Ti6Al4V alloy.



**Figure 6.** Comparison of diagrams of dependency between bending stress and bending for solid samples made of Ti6Al4V alloy and pristine titanium sintered at different laser powers.

#### 4. Comparison of results of strength tests of dental bridges manufactured from the investigated materials with the additive and machining technology

The results of comparative investigations are presented of mechanical properties of dental bridges manufactured from the investigated engineering materials. The results of strength

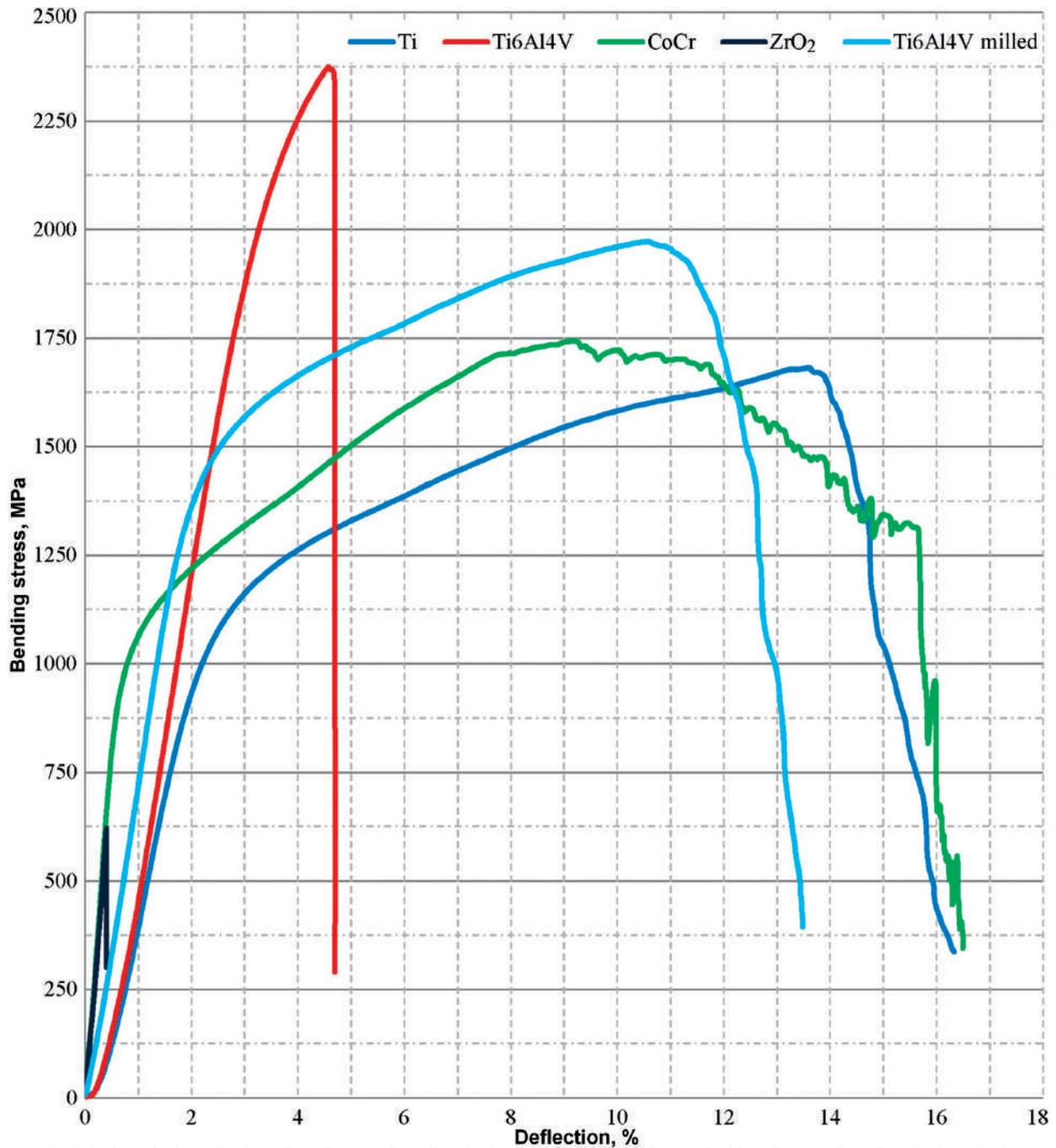


Figure 7. Comparison of diagrams of dependency between tensile stress and bending for various examined materials, that is, for sintered Ti, sintered Ti6Al4V alloy, milled Co-Cr alloy, milled ZrO<sub>2</sub> sinter and milled Ti6Al4V alloy.

tests of dental bridges selectively sintered by laser in optimised conditions were compared with the results of tests for bridges milled with CAD/CAM methods from discs of other tested materials, additionally sintered after milling in the case of ZrO<sub>2</sub>. The impact of laser power, ranging 70–110 W, was investigated in the first place on bending strength values of three bridges manufactured by SLS from sintered titanium and sintered Ti6Al4V alloy. The results of bending strength tests of a dental bridge no. 1 produced from titanium and Ti6AlV4 alloy were compared directly in **Figure 9**. Regardless the material produced by selective laser

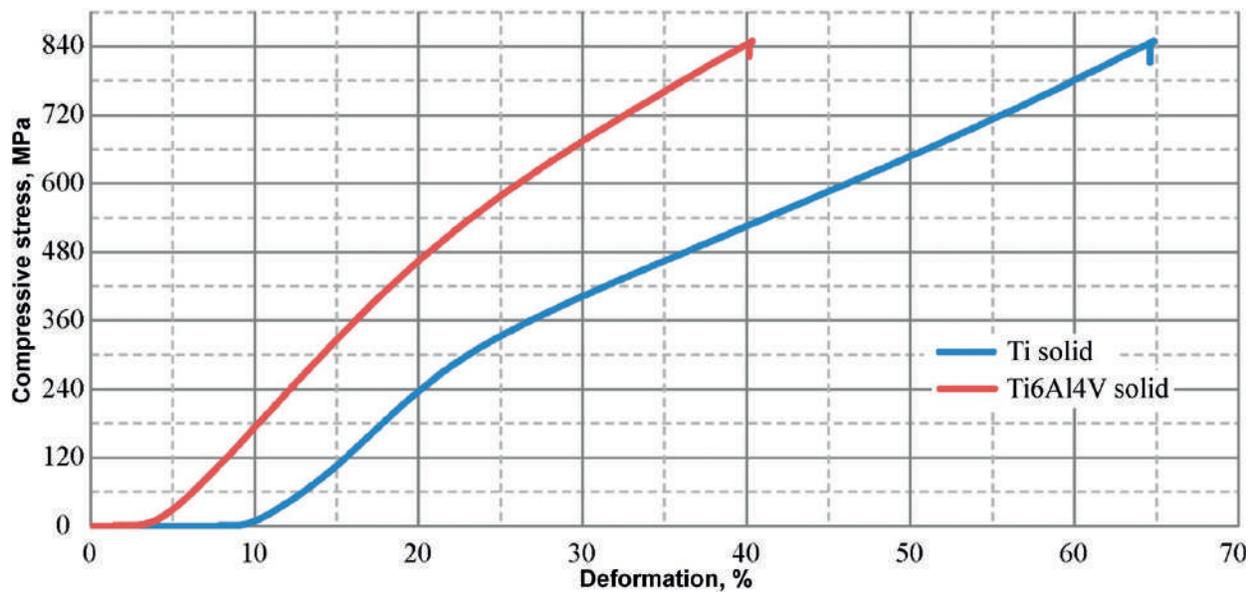


Figure 8. Comparison of diagrams of dependency between compressive stress and deformation for selectively laser sintered Ti and Ti6Al4V alloy samples.

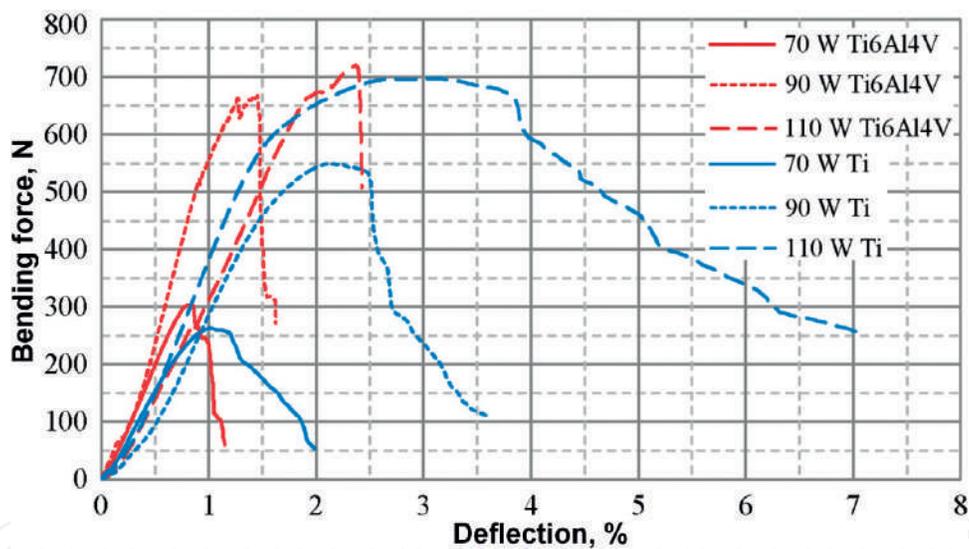
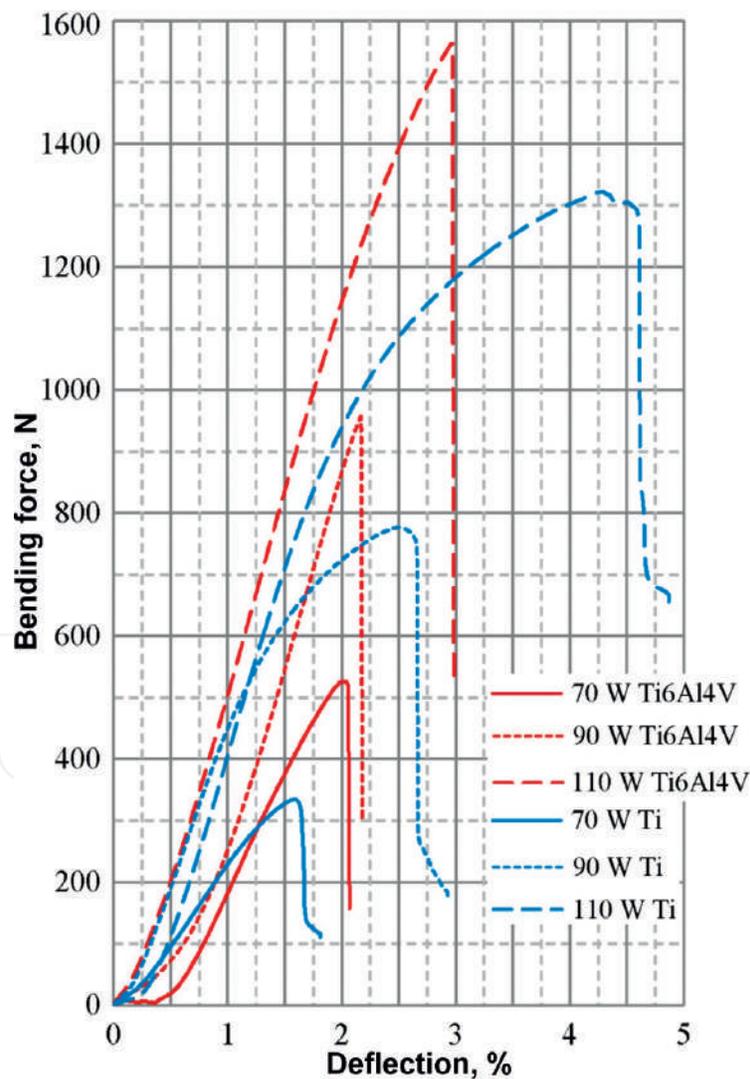


Figure 9. Comparison of diagrams of dependency between bending strength and bending of solid bridge no. 1 manufactured by SLS from titanium and Ti6Al4V alloy for different laser power.

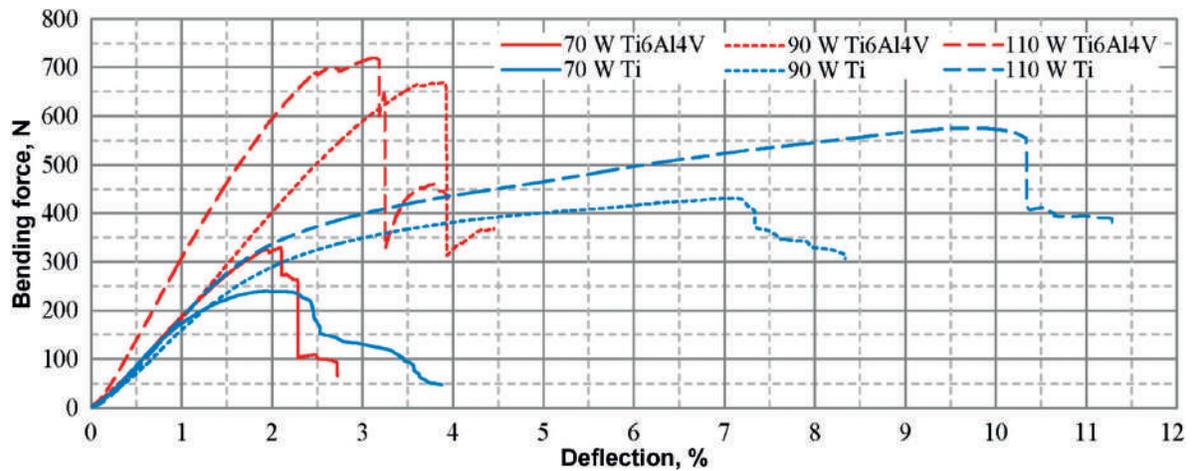
sintering, the maximum bending strength strongly depends on laser power. Sintering with the laser power of 70 W ensures small maximum bending force of approx. 260 and approx. 310 N, respectively, for titanium and Ti6Al4V alloy and is rising almost proportionally to, respectively, approx. 700 and approx. 730 N with laser power increase to 110 W. The maximum bending of the produced dental bridges depends very strongly on the applied laser power and a selectively sintered material. For titanium, this bending—depending on the laser power—varies between approx. 0.9 and approx. 2.4%, when it is much higher for Ti6Al4V alloy and ranges within approx. 2 to approx. 7%, and bending strength is systematically falling as bending is rising (Figure 9).

The analogous strength properties were obtained for a dental bridge no. 2 produced from titanium and Ti6Al4V (**Figure 10**). In the case of a titanium bridge, if laser power is increased from 70 to 110 W, this has a considerable effect on the value of the maximum bending strength, which increases on average from approx. 350 to approx. 1315 N. In the case of a bridge made of Ti6Al4V alloy produced by SLS, if laser power is raised in the same range, the maximum bending strength rises from approx. 525 to approx. 1560 N. In the case of Ti6Al4V alloy, each time, for each laser power, the maximum bending strength causing sample fracture is higher than for bridges produced from titanium, and this takes place in each case for relatively smaller bending. For example, selectively laser sintered solid bridges with laser power of 110 W from Ti6Al4V alloy are damaged at approx. 3% bending, when bending for titanium exceeds 4.5% (**Figure 10**).

As laser power is increased from 70 to 110 W, the value of the maximum bending strength for dental bridge no. 3, produced from titanium, increases from approx. 240 to approx. 580 N, in



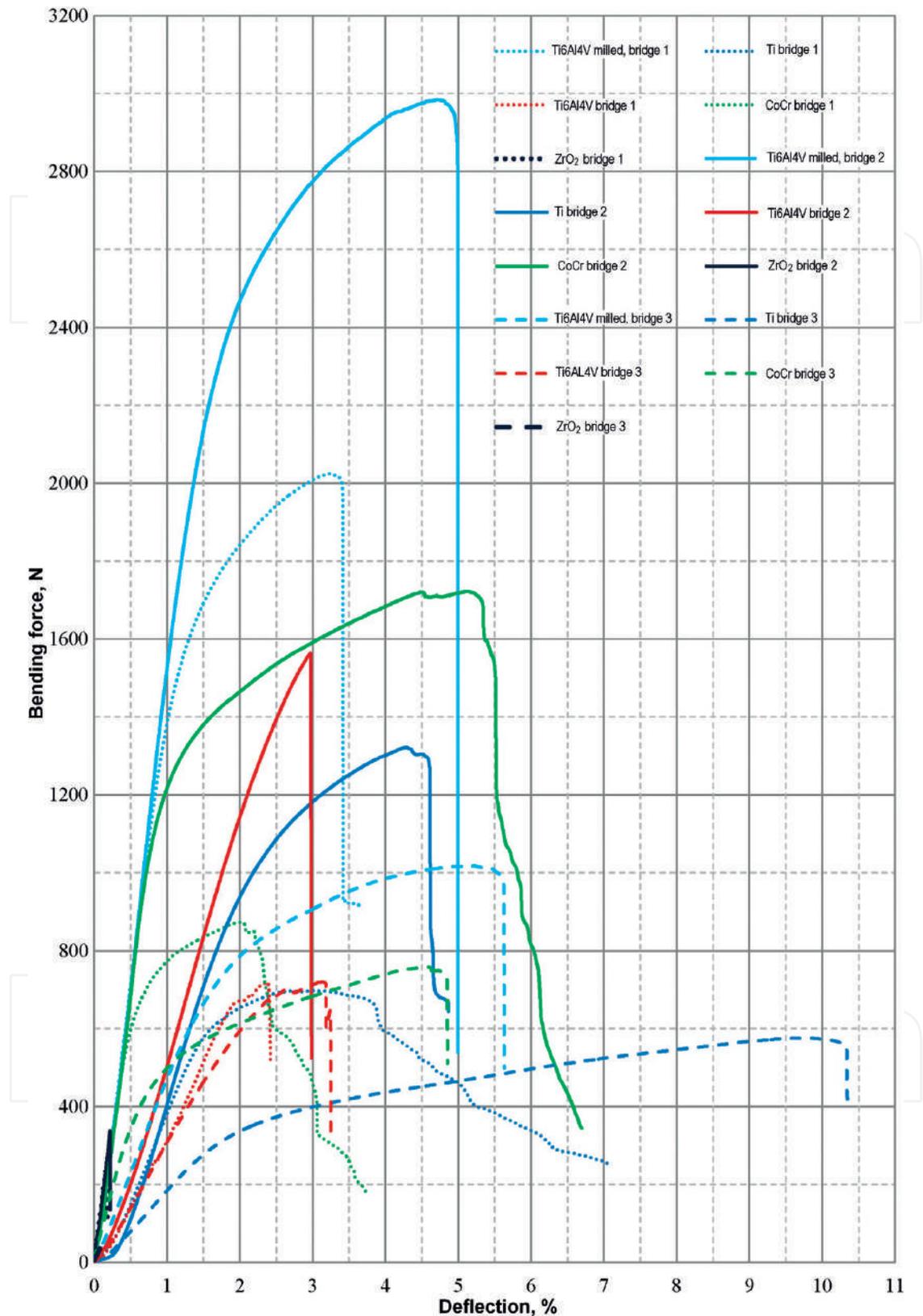
**Figure 10.** Comparison of diagrams of dependency between bending strength and bending of solid bridge no. 2 manufactured by SLS from titanium and Ti6Al4V alloy for different laser power.



**Figure 11.** Comparison of diagrams of dependency between bending strength and bending of solid bridge no. 3 manufactured by SLS from titanium and Ti6Al4V alloy for different laser power.

the case of a bridge made of Ti6Al4V alloy, from approx. 340 to approx. 720 N (**Figure 11**). In the case of selectively laser sintered Ti6Al4V alloy, each time, for each laser power, bending strength causing sample fracture is higher than for bridges produced from titanium, and this takes place in each case for relatively smaller bending (**Figure 11**).

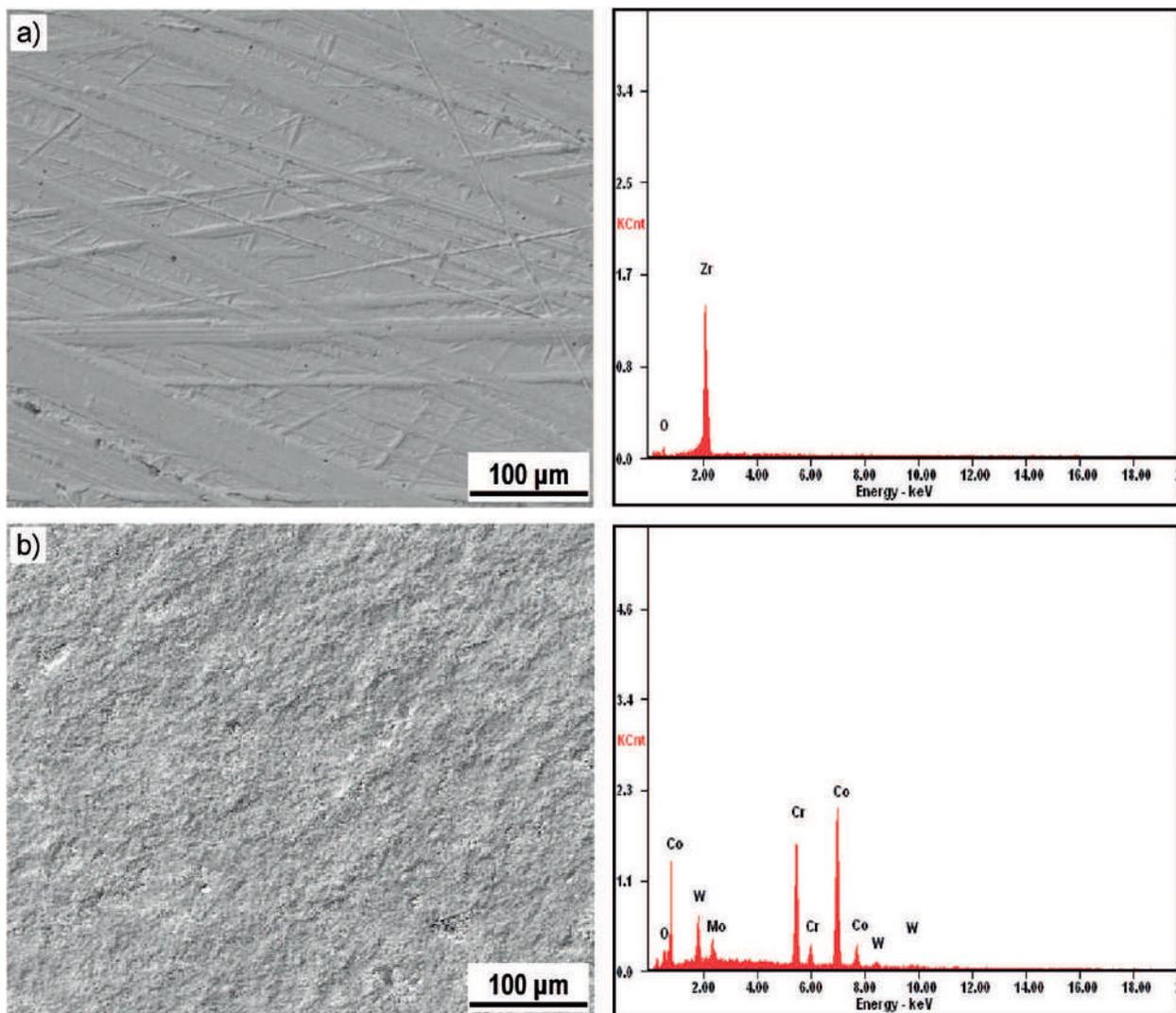
Diagrams were compared of dependency between bending strength and bending of solid bridges nos. 1, 2 and 3 manufactured from all the examined materials, that is, from selectively laser sintered titanium and Ti6Al4V alloy and milled from Ti6Al4V alloy discs, Co-Cr alloy and milled ZrO<sub>2</sub> sinter and then sintered (**Figure 12**). The maximum bending strength highly relies on the dental bridge type and varies from approx. 580 N for bridge no. 3 to approx. 1320 N for bridge no. 2. On the other hand, bridge no. 3 exhibits the maximum bending of approx. 10.4% while bridge no. 2 smallest bending of approx. 4.6%. Bridge no. 1 shows indirect properties. In the case of solid bridges nos 1, 2 and 3 manufactured by SLS from Ti6Al4V alloy with laser power of 110 W (**Figure 12**), the maximum bending strength of approx. 1570 N occurs for bridge no. 2, and the two other bridges show the strength of approx. 720 N. Maximum bending for bridges nos 3, 2 and 1 is, respectively, approx. 3.2, approx. 3 and approx. 2.4%. In the case of bridges nos. 2, 1 and 3 manufactured by CAD/CAM by milling discs from Ti6Al4V alloy, as presented in **Figure 12**, the maximum bending strength is much higher and is, respectively, approx. 2970, approx. 2030 and 1030 N, and maximum bending is, respectively, approx. 5, approx. 3.4 and 5.6%. Diagrams were also compared of dependency between bending strength and bending of solid bridges nos. 1, 2 and 3 manufactured by CAD/CAM by milling discs from Co-Cr alloy and ZrO<sub>2</sub> sinter (**Figure 12**). The comparison of diagrams of dependency between bending strength and bending of solid bridges nos. 1, 2 and 3 manufactured from all the examined materials, that is, from selectively laser sintered titanium and Ti6Al4V alloy and with the CAD/CAM method by milling discs from Co-Cr alloy and ZrO<sub>2</sub> sinter, shows that the highest maximum bending strengths are specific for bridge no. 2 regardless the material applied, and highest bending is seen for bridge no. 3.



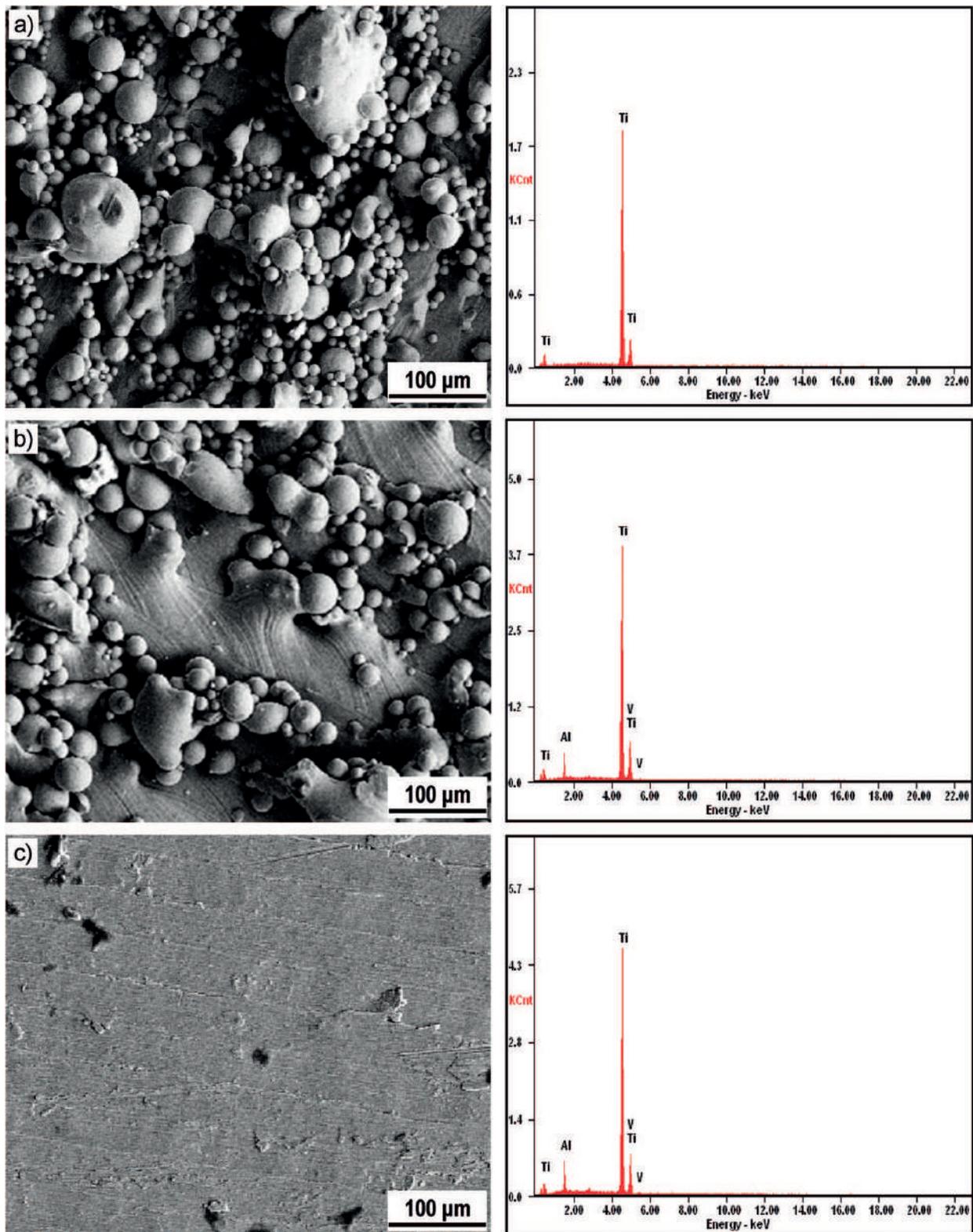
**Figure 12.** Comparison of diagrams of dependency between bending strength and bending of solid bridges nos. 1, 2 and 3 manufactured from all the examined materials, that is, from selectively laser sintered titanium and Ti6Al4V alloy and with the CAD/CAM method by milling discs from Ti6Al4V alloy, Co-Cr alloy and sintered ZrO<sub>2</sub> sinter.

## 5. Structure of the investigated engineering materials manufactured by additive and machining technologies

It was revealed in examinations of the structure of the investigated materials in a scanning electron microscope that in the case of Co-Cr and Ti6Al4V alloy, the surface of the samples produced by CAD/CAM, by milling solid discs, exhibits roughness distinctive for precision machining (Figures 13 and 14), the same as for ceramic ZrO<sub>2</sub> material which is sintered after performing machining (Figure 13). The examinations of chemical composition with the EDS method confirm the presence, in the first case, of Co, Cr and W (Figure 13) and in the second case of, respectively, Ti, Al and V (Figure 14) and in the third case of Zr and O (Figure 13), corresponding to the chemical composition of the materials applied. Figure 14 shows a surface structure of pristine titanium and Ti6Al4V alloy manufactured by selective laser sintering with



**Figure 13.** Surface structure of the samples produced by CAD/CAM by milling solid discs with the results of examinations of EDS chemical composition of (a) Co-Cr alloy, (b) sintered ZrO<sub>2</sub> sinter after machining (SEM).

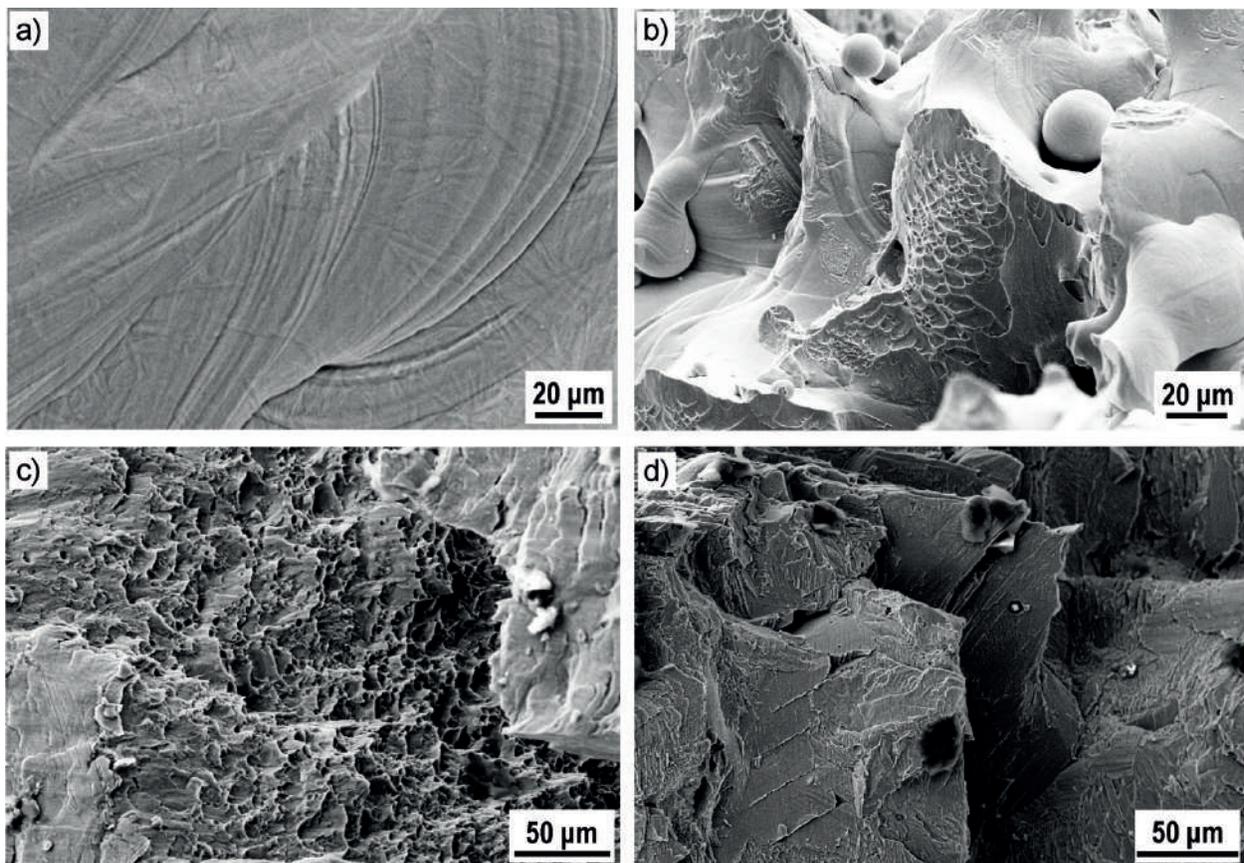


**Figure 14.** Surface structure of samples manufactured by selective laser sintering with the use of laser beam of 50 μm with laser power of 110 W of (a) solid titanium, (b) Ti6Al4V alloy and (c) Ti6Al4V alloy by CAD/CAM method by milling solid discs with results of examinations of EDS chemical composition (SEM).

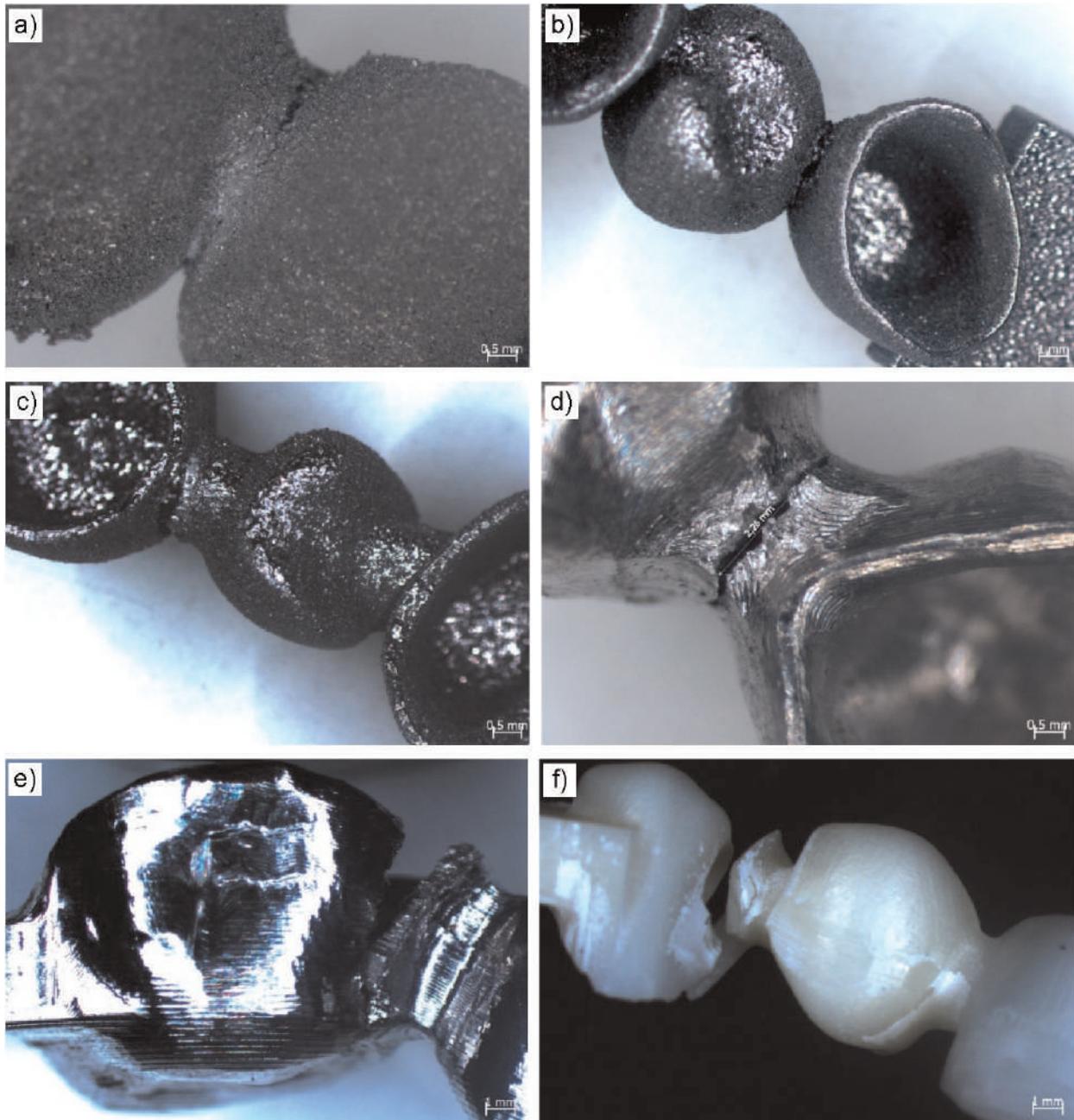
the laser beam size of 50  $\mu\text{m}$  and laser power of 110 W. It was revealed in the both cases that apart from the completely sintered materials, with the shown paths of laser beam transition, fine powder particles exist, as well, which—after sintering—should be removed mechanically or by chemical etching.

X-ray tests allow to establish the phase composition of the investigated materials based on the data derived from international files. The following was identified, respectively, in particular samples: Co and Cr in Co-Cr,  $\text{ZrO}_2$  alloy, Ti in pristine titanium and  $\text{Al}_{0.3}\text{Ti}_{0.7}$  phase and  $\text{Ti}_{0.8}\text{V}_{0.2}$  in Ti6Al4V alloy irrespective of the manufacturing technology by milling from discs or selective laser sintering.

Investigations were carried out into the structure of the examined engineering materials subjected to the examinations of mechanical properties, and the structure was compared, especially of fractures of the examined materials produced by SLS, that is, sintered titanium and sintered Ti6Al4V alloy, and also manufactured by CAD/CAM by milling discs from solid Ti6Al4V, Co-Cr alloys and  $\text{ZrO}_2$  sinter milled and then sintered. The selectively laser sintered materials have a continuous structure without pores, as for titanium (**Figure 15a**), in which



**Figure 15.** Surface structure of solid samples manufactured by selective laser sintering (a) with the use of laser beam of 50  $\mu\text{m}$  with laser power of 110 W, (b) fracture structure after a static bending test of samples of solid Ti6Al4V alloy manufactured by selective laser sintering with laser beam size of 50  $\mu\text{m}$  after sintering with laser power of 70 W and (c, d) fracture structure after a static bending test of the samples produced by CAD/CAM by milling discs from solid alloys of (c) Ti6Al4V and (d) Co-Cr; SEM.



**Figure 16.** View of dental bridges after static bending test, manufactured from (a,b) titanium by SLS, (a) bridge no. 2 and (b) bridge no. 1; (c) from Ti6Al4V alloy by SLS bridge no. 3; and (d–f) fabricated by CAD/CAM by disc milling (d) from Ti6Al4V alloy, bridge no. 2; (e) from Co-Cr alloy, bridge no. 3; and (f) from ZrO<sub>2</sub> sinter manufactured by CAD/CAM by disc milling and then sintering, bridge no. 3; stereoscope microscope.

particular laser paths can be distinguished, provided that laser power for a laser beam with a diameter of 50  $\mu\text{m}$  is 110 W. It is revealed by analysing a fracture of titanium, laser sintered with the laser power of 70 W, subjected to a static bending test, that—especially—finest powder particles are not sintered fully and also that a ductile fracture occurs in bridges of the sintered material. The samples sintered with the laser power of 110 W are solid and show a ductile fracture. A fracture structure of the samples from the laser sintered Ti6Al4V alloy after a static bending test is analogous to this obtained for titanium (**Figure 15b**) and—after

sintering with the laser power of 110 W—shows a ductile fracture. A ductile fracture also exists in the case of fractographic tests of Ti6Al4V alloy but in the form of discs for sample milling (**Figure 15c**). The samples milled from Co-Cr alloy show, however, a brittle fracture, only with the local presence of a ductile fracture (**Figure 15d**).

In the case of all the examined metallic materials, and independently from the applied manufacturing technology, a fracture of samples occurs most often on a root of the abutments linking successive teeth, while in the case of bridges made of ZrO<sub>2</sub>, such bridges undergo brittle cracking in different places (**Figure 16**).

## **6. Suitability of application of additive manufacturing methods of prosthetic restorations of the dental system as compared to machining methods**

Comparative investigations are presented in this chapter of the structure and properties of selected engineering materials used for dental prosthetic restorations manufactured alternatively by the machining method by milling on computerised numerical control (CNC) milling machines and by the additive selective laser sintering (SLS) method of solid and porous elements using CAD/CAM techniques; moreover, an original technology was presented of manufacturing the elements used in prosthodontics, produced with titanium and Ti6Al4V alloy powders with the SLS technique. The suitability was confirmed of applying the manufacturing technologies used in prosthodontics from powders by the SLS technique. The results of the executed tests of strength micro-samples and of the selected prosthetic bridges were compared. The bending strength of the titanium sintered selectively by laser, of the milled Ti6Al4V alloy and of the milled Co-Cr alloy is within the range of 1739–1959 MPa and tensile strength is within 739 and 858 MPa. It points out that the materials can be employed as prosthetic restorations, similarly as a selectively laser sintered Ti6Al4V alloy with the bending strength of approx. 2374 MPa and tensile strength of approx. 1312 MPa and pristine Ti with the bending strength of approx. 1682 MPa and tensile strength of 739 MPa. The SLS technology for titanium, and even more for Ti6Al4V alloy, ensures the achievement of mechanical properties comparable or better than a reference Co-Cr alloy which is commonly used for prosthetic restorations, including prosthetic bridges fabricated by milling solid discs with CNC milling machines. For all the examined engineering materials, the milled and then sintered ZrO<sub>2</sub> material exhibits the lowest strength properties. The average tensile strength of this material is approx. 47 MPa, that is, it is nearly 20 times smaller than of Co-Cr alloy, and the average bending strength is smaller nearly 3 times than this of Co-Cr alloy and is approx. 605 MPa. The maximum elongation does not exceed, respectively, 6%, and maximum bending is approx. 0.3%, and the both values are much smaller than such appropriate for Co-Cr alloy. The microscopic examinations of the surface of prosthetic bridges fabricated from this material by the machining method of disc milling and then sintering show more advantageous roughness than bridges produced from Co-Cr alloy, and their fracture after bending is decisively brittle, and cracking takes place in different places, not as in the case of Co-Cr alloy. Prosthetic restorations on a substructure of sintered ZrO<sub>2</sub> are, however, used more and more often, especially because it is necessary to ensure the best aesthetic values of the solution employed.

As a zirconium oxide substructure can be completely white, but also after colouring with special paints before sintering, it can have a colour consistent with the VITA colour palette, a fully natural aesthetic effect can be achieved of a ready prosthetic restoration. It is also noteworthy that a translucence effect can be achieved, especially on secant edges of such a prosthetic restoration, responding to the most demanding patients' needs. Such effects can be attained on a substructure made of Co-Cr alloy. On the other hand, it is practically impossible to use titanium as a substructure for prosthetic crowns and bridges because the material tends to change the shade of porcelain to darker and colder; hence it is very difficult to ensure the manufacturing repeatability of prosthetic restorations and their quality. A solution ensuring the best possible aesthetic values is to use zirconium oxide as a substructure. Due to a substantial technological and therapeutic risk, a solution with the lowest strength properties is most expensive, though. Therefore, a dental engineer needs to be aware of the limitations of this material and has to design prosthetic restorations on a zirconium oxide substructure differently than when metallic materials are used. The author of this work prepares in his daily engineering practice all kinds of bridges with  $\frac{3}{4}$  crowns, that is, such which are made on all the walls, except for the vestibular wall and the chewing surface, with a full structure, as so-called full contoured. Such a crown is coated from the vestibular part with veneering porcelain to ensure the best aesthetic values, and special paints and glaze are applied onto the other surfaces. The so-designed bridge, in the example shown in this work, would have walls with a thickness of approx. 2.5 mm instead of 0.6 mm, and a section area of abutments would be approx. 20–22 mm<sup>2</sup> instead of 10–12 mm<sup>2</sup>, as for the designs presented in this work and essentially relating to metallic materials. A much greater active section will allow to transfer higher loads, accordingly. The designer also has to keep in mind to support bridge spans on the periodontal tissue, never using the saddleback-like gum shape, but using an elliptic support with subgingival correction in each case. The so-designed prosthetic restoration will surely feature much higher strength properties than a prosthetic restoration with a reduced structure, being a reference point used in this work. Unfortunately, prosthetic restorations made on a zirconium oxide substructure with a simplified structure, as so-called caps with simple abutments, are still commonly used by dentists and dental technicians. The test results obtained seem not to confirm the applicability of the bridges, made of this material, designed this way. This puts into question a potential application of ZrO<sub>2</sub> sinter bridges in dental practice without using a special design method of such dental restorations. This fact can be confirmed by cases, known from medical practice, when such bridges are damaged during normal use by patients. The results presented in this chapter can be directly applied in dental practice to remove consequences of teeth lost due to tooth decay.

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# Properties of Co-Cr Dental Alloys Fabricated Using Additive Technologies

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Additional information is available at the end of the chapter

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## Abstract

The aim of the present paper is to make a review of the properties of dental alloys, fabricated using Additive Technologies (AT). The microstructure and mechanical properties of Co-Cr alloys as well as the accuracy and surface roughness of dental constructions are discussed. In dentistry two different approaches can be applied for production of metal frameworks using AT. According to the first one the wax/polymeric cast patterns are fabricated by 3D printing, than the constructions are cast from dental alloy with as-printed patterns. Through the second one the metal framework is manufactured from powder alloy directly from 3D virtual model by Selective Electron Beam Melting (SEBM) or Selective Laser Melting (SLM). The microstructure and mechanical properties of Co-Cr dental alloys, cast using 3D printed patterns, are typical for cast alloys. Their dimensional and adjustment accuracy is higher comparing to constructions, produced by traditional lost-wax casting or by SLM. The surface roughness is higher than that of the samples, cast by conventional technology, but lower comparing to the SLM objects. The microstructure of SLM Co-Cr dental alloys is fine grained and more homogeneous comparing that of the cast alloys, which defines higher hardness and mechanical properties, higher wear and corrosion resistance.

**Keywords:** materials science and engineering, biomaterials, regenerative stomatology, additive technologies, Co-Cr dental alloys, microstructure and properties

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## 1. Introduction

Dental alloys on the basis of cobalt and chromium are one of the most preferred for production of metal frameworks of dental constructions because of their high strength, high corrosion and wear resistance, high biocompatibility, and a relatively low cost [1, 2]. The chemical composition of Co-Cr dental alloys consists of 53–67% of Co, 25–32% of Cr, 2–6% of Mo, and small

quantities of W, Si, Al, and others [3]. Cr, Mo, and W are added for strengthening of the solid solution. Due to the relatively large amount of Cr, dense passive layer of  $\text{Cr}_2\text{O}_3$  with 1–4 nm thickness on the surface as well as carbides in the microstructure of the details is formed, determining the high hardness, high corrosion, and wear resistance [4, 5]. According to the phase diagram, Co-Cr dental alloys are characterized with face-centered cubic (fcc) lattice,  $\gamma$  phase in high temperatures, and with hexagonal close packed (hcp) lattice,  $\epsilon$  phase in room temperature [4, 6]. The  $\gamma$  phase defines the ductility, while the  $\epsilon$  phase defines the corrosion and wear resistance of the alloy [7]. In proper alloying, the microstructure of the Co-Cr dental alloys consists mainly of  $\gamma$  phase and carbides of the  $\text{M}_{23}\text{C}_6$  type [4]. Therefore, the properties of Co-Cr dental alloys depend on the ratio between  $\gamma/\epsilon$  phases and the type, quantity and distribution of the carbide phase in the microstructure.

The microstructure and properties of dental alloys depend on the manufacturing process and the technological regimes. Since the beginning of the last century, casting is the most common technology for production of metal constructions in dentistry. During this conventional technology, the metal frameworks are fabricated by centrifugal casting using hand-built wax patterns. The technological process is characterized with large amount of manual work, and although it is performed by a qualified dental technician, it can lead to low accuracy and satisfactory quality. The advent of the modern CAD/CAM systems and the additive technologies in the last 30 years of the last century allow to decrease the amount of manual work and production time, to improve the quality of dental constructions and as a consequence to reduce their price [8, 9].

The additive technologies (AT) are developed in the late 1980s as an alternative of the subtractive technologies. They are characterized with building of one layer at a time from a powder or liquid that is bonded by means of melting, fusing, or polymerization. The American Society for Testing and Materials (ASTM) defined additive manufacturing as ‘the process of joining materials to make objects from 3D model data, usually layer upon layer, as opposed to subtractive manufacturing methodologies’ [8–10]. These processes are also known as ‘three-dimensional printing’, ‘layered manufacturing’, ‘free-form fabrication’, ‘rapid prototyping’ and ‘rapid manufacturing’ [9–11]. The ASTM international committee, intended for specification of standards for additive manufacturing – ASTM F42 – created a categorization of all 3D printing technologies into seven major groups [11]. According to it, the following 3D printing technologies are used in work with biomaterials: 3D plotting/direct ink writing, laser-assisted bioprinting, selective laser sintering, stereolithography, fused deposition modeling, and robot-assisted deposition/robocasting. The stereolithography (SLA), fused deposition modeling (FDM), selective electron beam melting (SEBM), selective laser sintering (SLS), selective laser melting (SLM), and ink-jet printing (IJP) are among the AT, mostly used in the dental medicine [8, 9, 12–15].

During the SLA process, a concentrated beam of UV light is focused on the surface of a tank filled with liquid photopolymer. As the light beam draws the object on the surface of the liquid, each time a layer of resin is polymerized or cross-linked until the real object is obtained [8, 9, 12, 14, 16]. The FDM characterizes with extruding the thermoplastic materials through heated nozzle, or the material is fed from a reservoir through a syringe [9, 12, 16]. By SEBM,

the parts are manufactured by melting metal powder layer per layer with an electron beam in a high vacuum [8, 9, 14, 16]. In SLS/SLM technology, layers of particular powder material (mainly polymers and porcelains in SLS and pure metals or alloys in SLM) are fused into a real detail by a computer-directed laser [8, 9, 12, 17]. During IJP process, an extremely small ink droplet is ejected toward the substrate. Different substances can be used as ink aqueous solution of colouring agents and binders to a ceramic suspension to produce zirconia dental restorations [8, 9, 12, 18]. Another variant of the IJP is by depositing droplets of a polymer, and each formed layer is cured by UV light, which allows polymer material with characteristics similar to the technical wax to be used [8, 9, 13].

The main advantages of AT include production of complex objects from different materials—polymers, composites, metals and alloys; manufacturing of parts with dense/porous structure and predetermined surface roughness and controllable, is an easy and relatively quick process [9]. Due to the various materials used and the great variety of additive manufacturing processes, AT can be successfully applied in many fields of dentistry for the production of different types of dental constructions. AT give even opportunities to fabricate structures of hard-to-handle materials such as cobalt and chromium alloys [19]. Polymeric study models instead of dental plaster casts, surgical guides for placement of dental implants, temporary crowns and bridges as well as resin models for lost-wax casting can be fabricated by SLA and FDM [8, 9, 12, 20–22]. SEBM and SLM are used for manufacturing of customized implants for maxillofacial surgery, dense or porous dental implants, dental crowns and bridges as well as partial denture frameworks [23–31]. IJP is suitable for printing of zirconia dental restorations, polymeric dental models, orthodontic bracket guides, wax patterns of complete dentures, or wax models for casting [8, 9, 32, 33].

There are two main approaches for the production of metal constructions from Co-Cr dental alloys using AT. The first one concerns to the fabrication of wax/polymeric cast patterns by 3D printing, and the second one is casting of the framework from dental alloy. Through the second one, the metal object is manufactured directly from the 3D virtual model by SEBM or SLM. As the additive technologies are relatively new, develop extremely fast and with their indisputable advantages enter in many areas, so their implementation into the dentistry is faster than the research and data about the quality of the details produced by them. The aim of the present chapter is to make a review of the properties of dental alloys, fabricated using additive technologies. The microstructure and mechanical properties of Co-Cr alloys as well as the accuracy and surface roughness of dental constructions are discussed.

## **2. Properties of Co-Cr dental alloys cast with 3D-printed patterns**

The wax/polymeric cast patterns can be produced from generated 3D virtual models by laser-assisted or digital light projection (DLP) stereolithography, fused deposition modeling, and ink-jet printing. The type of the additive manufacturing process, the parameters of its technological regimes, and the properties of the used materials influence mainly on the geometrical characteristics, adjustment accuracy, and surface roughness of the cast patterns [33–36], thus defining the accuracy and surface quality of the cast dental constructions. As with any AT,

the layer's thickness, the position of the object toward the print direction, and the optical properties of the polymers (in SLA) have a decisive effect on the object's accuracy. The thinner the layer, the lower the angle to the print direction, and the lower the surface roughness, the higher the resolution and the dimensional accuracy, but the longer the production time [37].

The accuracy of dental constructions, produced by the modern CAD/CAM systems, is defined in the standard ISO 12836:2015 'Dentistry—Digitizing devices for CAD/CAM systems for indirect dental restorations—Test methods for assessing accuracy' [38]. Three standardized geometrical figures for accuracy evaluation are described in its Annexes A, B, and C [38]. Braian et al. [39] used the figures in the Annexes A and C, specifying the measurement of an inlay-shaped object and a multiunit specimen to simulate a four-unit bridge, for determining the production tolerances of four commercially available additive manufacturing systems, working on the SLS, multi-jet, or poly-jet principles. The samples were printed with different layer's thicknesses, optimal for each system, and ensuring the highest product's accuracy (as per the equipment manufacturer). According to the ISO/IEC GUIDE 99:2007(E/F) [40], the 'accuracy' is the closeness of agreement between a measured quantity value and a true quantity value of a measured object. The authors [39] defined the terms 'resolution' and 'repeatability'. The resolution refers to the smallest feature that the system can produce, while the reproducibility is described as the system ability to produce consistent output time after time. The researchers established that the accuracy of both types of samples, produced with four printers, is different in the three directions. The multi-jet printing ensures the highest accuracy of the linear as well as angular dimensions, followed by poly-jet process and SLS. It was concluded that the suitable type of printer should be chosen according to the intended dental application.

In evaluation of restorations, fabricated by digital technologies, subtractive (milling of wax and zirconia) and additive (SLA of photopolymer and SLS of Co-Cr alloy), Bae et al. [41] found out that the dimensions of the samples of all four groups are smaller than the reference data. Concerning to the repeatability of AT, they established the smallest difference from the reference data in the specimens, fabricated using SLA, and no significant differences between the SLA and SLS methods. Therefore, they concluded that the accuracy of additive manufacturing methods is better than the subtractive ones, as the mean accuracy discrepancies are the smallest for SLA, followed by the SLS, wax, and zirconia milling. But they pointed out the following as disadvantages: the print layers, clearly seen on the surface of the SLA sample, and circular, sunken forms of approximately 80  $\mu\text{m}$  in diameter on the SLS specimen surface. The investigations of Mai et al. [42] proved that the crowns fabricated by CAD/CAM systems (milling and polymer-jet 3D printing) have higher fitting accuracy than that of the molded ones. Among them, the polymer-jet 3D printing significantly enhanced the fit of the interim crowns, particularly in the occlusal region. According to Kim et al. [43], the fitting accuracy of dental crowns is affected by the number of copings fabricated by micro-stereolithography. Based on the marginal discrepancy, the most precise copings are printed when three arrays are used on a single-built platform. Therefore, there are limitations concerning to the reproducibility and accuracy of polymeric dental constructions, manufactured by 3D printing.

Ishida and Miyasaka [44] investigated the accuracy of the patterns for casting of all metal crowns, manufactured by four 3D printers, using different manufacturing processes: laser-assisted SLA, SLA with concentrated UV beam, FDM, and IJP. They established that in all types of manufacturing process, the outer and the inner diameters of the crowns are smaller than that of the virtual 3D model, which could be compensated with 3–5% increasing the dimensions of the virtual model. The FDM-printed crowns are characterized with the highest surface roughness, while the lowest is typical for the crowns, fabricated by laser-assisted SLA. Additionally, the difference of the roughness values along the 3D axes exists. They established that the roughness along the tooth axis of the crown created by laser-assisted SLA was the smallest, while that along the horizontal direction of the crown printed by multi-jet modeling (MJM) was the smallest. This can be explained with the specific features of the additive manufacturing process [8, 12, 45].

The higher roughness of the surfaces, parallel, or inclined to the print direction (Z axes), compared to that along X and Y axes is also established in the research of Dikova et al. [46]. Their investigations of cubic samples, printed with different polymers by DLP SLA, show that the roughness of the surfaces of the cubes with horizontal position toward the basis is less than those of the cubes, printed inclined in almost all types of polymers. All sizes of the cubes in both positions are larger than the size of the virtual model. In their subsequent investigations [47], it is observed that the decrease of the layer's thickness from 50 (recommended by the equipment manufacturer) to 35  $\mu\text{m}$  leads to nearly twice decrease of the surface roughness of the samples, made of resin NextDent Cast (developed especially for manufacturing of cast patterns), in both printing positions. It also leads to the highest dimensional accuracy and the least interval of deviation. The research team has shown that the dimensions, parallel to the basis, axes X and Y, are the most precise, while those, parallel or inclined to the printing direction, axis Z, are the most deviating. The dimensional and adjustment accuracy as well as the surface roughness of four-part dental bridges, made of polymers NextDent Cast and NextDent C+B (for temporary crowns and bridges) by DLP SLA, are investigated in the work of Dikova et al. [48]. They established that the dimensions in both directions of the bridges from both polymers, fabricated with less layer's thickness of 35  $\mu\text{m}$ , are smaller with 0.29–1.10%, compared to those of the virtual model, while the sizes of the bridges with larger layer's thickness of 50  $\mu\text{m}$  are 1.51–3.45% more than the virtual model. Dimensions of the samples of both polymers, situated in the building direction, are larger with 1.51–3.45%, and those, which are not in the print direction, are 0.49–0.53% smaller than those of the virtual 3D model. The inaccuracy in the geometrical dimensions causes inaccuracy of adjusting and absence of gap between the bridge constructions and the gypsum model. The surface roughness of the cast patterns, manufactured with regime, recommended by the producer (50  $\mu\text{m}$  layer's thickness), is relatively high with average arithmetic deviation of the surface roughness  $R_a = 3.24 \mu\text{m}$ . Decreasing the layer's thickness to 35  $\mu\text{m}$  leads to the lower surface roughness of  $R_a = 2.18 \mu\text{m}$ . The surface observations with optical microscopy proved the layered structure, which is a specific feature of the objects built up via stereolithography. The higher roughness of the 3D-printed cast patterns can complicate the cast process and cause higher roughness of the cast itself.

The geometrical accuracy of fixed dental prostheses, manufactured by additive technologies, is investigated in Ref. [49]. Four-part dental bridges are produced of Co-Cr alloy by three technological processes: conventional lost-wax casting with wax models, manufactured in silicon mold; lost-wax casting with 3D-printed (multi-jet modeling (MJM)) cast patterns, and direct fabricating by SLM. It was established that the surface roughness of Co-Cr fixed partial dentures, cast with 3D-printed wax patterns, is more than three times higher than the roughness of dentures, cast by conventional lost-wax technology ( $Ra = 3.39 \mu\text{m}$  and  $Ra = 1.11 \mu\text{m}$ , respectively). The surface observation of Co-Cr dental bridges proves the higher roughness as well as the traces of the layered manufacturing of the cast patterns, left even after sandblasting. The fixed partial dentures, cast with 3D-printed cast patterns, possess higher accuracy of the shape, sizes, and adjustment compared to the dentures, produced by conventional lost-wax casting. This is mainly due to the minimal manual work, because 3D-printed cast patterns are produced directly from the virtual model.

The microstructure of Co-Cr sample, cast with 3D-printed pattern (MJM), is a typical cast microstructure—inhomogeneous, consisting of large grains with dendrite morphology [50]. A large amount of lamellar and blocky carbides of different sizes are located mainly along the grain boundaries. The dendrites consist of  $\gamma$  phase, while the inter-dendritic regions consist of microeutectic (Co solid solution with intermetallic precipitations) and carbides of the  $(\text{Cr}, \text{Mo})_{23}\text{C}_6$  type. The hardness of the Co-Cr samples, cast with 3D-printed patterns, is in the range 327HV–343HV with uneven distribution due to the inhomogeneous microstructure. The dendritic grains with intermetallic phases, precipitated along the grain boundaries, were observed in the microstructure of the samples, cast with 3D-printed patterns from Co-Cr alloy remanium star CL by Kim et al. [51]. They characterized with yield strength  $540 \pm 20 \text{ MPa}$ , mean percent elongation  $10 \pm 2$  and Young's modulus  $260 \pm 20 \text{ GPa}$ .

The microstructure and strength properties of Co-Cr dental alloys, cast with 3D-printed patterns, are typical for castings. Their dimensional and fitting accuracy is higher than that of the constructions, manufactured by conventional casting, while their surface roughness is more than three times higher. Therefore, the dimensional and fitting accuracy and the surface roughness of Co-Cr dental substructures are strongly influenced by the quality of the cast patterns fabricated via AT. The data about the dimensional accuracy of wax/polymeric dental constructions, produced by different additive manufacturing processes, are contrary. In some cases, the dimensions of the printed objects are smaller than the virtual model; in another case, they are larger. It depends not only on the type of the manufacturing process but also on the scale factor—the sizes of the printed object. As a consequence of the low dimensional accuracy, the fitting accuracy is lower. The strategy of printing should be chosen very carefully, because too much objects in the same built platform can cause lower dimensional and fitting accuracy. Due to the features of the 3D printing processes, the sizes of the detail can be different in the three directions  $X$ ,  $Y$ , and  $Z$ ; therefore, it should be paid attention to the position of the object, especially toward the print direction. This will influence the surface roughness, too. The parameters of the technological regimes also influence the dimensional accuracy. Decreasing the layer's thickness leads to smaller sizes and lower roughness, which in some cases defines the higher accuracy. The special requirements to the materials, used for 3D printing of cast patterns, exist—to have no burned out residue and null or minimal thermal expansion—otherwise, the casting with low quality will be the result.

For fabricating the high-quality castings from Co-Cr dental alloys using 3D-printed patterns, some steps concerning to the processes of 3D printing and casting should be observed. In 3D printing (1) the printer, ensuring the cast pattern with high dimensional and fitting accuracy and satisfactory surface roughness, has to be chosen. The present review shows that the systems, working on the principle of the laser-assisted SLA, DLP SLA, MJM, and polymer-jet printing, are good candidates; (2) As each printer works with its specific materials, the right material, meeting the requirements for manufacturing the cast patterns, should be used; (3) The optimal technological regime has to be chosen, including the layer's thickness; (4) The strategy of printing has to be developed—positions, and the number of the objects; (5) Preliminary tests, calibration on the three axes  $X$ ,  $Y$ , and  $Z$  of the printer and compensation (if needed), have to be done to guarantee dimensions with high accuracy; and (6) 3D printing, post-curing (in some processes), and final surface treatment to enhance the smoothness. In the second part, the casting processes are (1) selection of the investment material, relevant to the material of the 3D-printed cast pattern, should be done for manufacturing casting mold; (2) heating of the casting mold with temperature regime concerning to the material of the 3D-printed cast pattern and the Co-Cr alloy and (3) casting with the given Co-Cr alloy, keeping the manufacturer's requirement.

### 3. Properties of Co-Cr dental alloys fabricated via SLM

The properties of the Co-Cr dental alloys depend on the microstructure, its morphology, and composition, which are defined by the manufacturing process and the technological regimes. The SLM is a complex thermophysical process, depending on a number of important parameters. During SLM, layers of metal powder are fused into a real object by a computer-directed laser. The process characterizes with high heating and cooling rates, leading to fine-grained microstructure of the solidified layer. As the heat is led away through the solid body, phase transformations run in the underneath layers heated above the transition temperatures [50]. Due to the high-temperature gradients during the SLM process, high residual stresses are generated in the details, which can cause subsequent deformations [17, 52–54]. These characteristics determine the specific microstructure and properties of the objects, produced by SLM as compared with that, manufactured by casting. The main technological parameters that are crucial for the production of high-quality construction are the laser power, scanning speed, laser beam diameter and distance between the traces, layer's thickness, and the working area [55–58]. In the development of any process for production of an object by SLM, it is necessary to evaluate the density, accuracy, surface roughness, hardness, and strength properties.

In SLM process, the volume of the molten metal depends on the volume energy density  $E_v$ , which is directly proportional to the power density  $N_s$  and inversely proportional to the scanning speed  $V$ . If the volume energy density  $E_v$  is insufficient, the incomplete melting of the deposited layer will occur. Therefore, the lower volume energy density  $E_v$  is the main reason for the porous structure [50]. This can be avoided by optimization of the technological parameters—increasing the laser power or decreasing the scanning speed. Varying with the input energy and scan spaces, Takaichi et al. [59] established that dense structure of SLM Co-29Cr-6Mo alloy can be obtained when the input energy of the laser scan increased more

than  $400 \text{ J/mm}^3$  and porous, in input energy less than  $150 \text{ J/mm}^3$ . Vandenbroucke and Kruth [60] ensured 99.9% density of the SLM Co-Cr-Mo alloy, working with optimized technological regime. In the investigation of the possibility for manufacturing of three-part dental bridge from Co-Cr alloy by SLM, Averyanova et al. [29] stated that all samples are densified with porosity less than 1%.

The specific features of the SLM process, characterizing with high heating and cooling rates, define unique microstructure of Co-Cr dental alloys and mechanical properties higher than that of the cast alloys. Meacock and Vilar [61] reported that the microstructure of biomedical Co-Cr-Mo alloy, produced by laser powder micro-deposition, is homogeneously composed of fine cellular dendrites. The average hardness was 460 HV0.2, which is higher than the values obtained by the other fabrication process. In investigation of Co-Cr-Mo parts, produced by direct metal laser sintering, Barucca et al. [62] established that the microstructure consists of  $\gamma$  and  $\epsilon$  phases. The  $\epsilon$  phase is formed by athermal martensitic transformation, and it is distributed as network of thin lamellae inside the  $\gamma$  phase. The higher hardness (47 HRC) is attributed to the presence of the  $\epsilon$ -lamellae grown on the  $\{111\}_\gamma$  planes that restricts the dislocation movement in the  $\gamma$  phase. Lu et al. [63] investigated the microstructure, hardness, mechanical properties, electrochemical behaviour, and metal release of Co-Cr-W alloy fabricated by SLM in two different scanning strategies—line and island. They established the coexistence of the  $\gamma$  and  $\epsilon$  phases in the microstructure and nearly the same hardness, 570 HV for line-formed alloy and 564 HV for island-formed alloy. Their research shows that the results of tensile strength ( $1158.22 \pm 21 \text{ MPa}$  for line scheme and  $1115.56 \pm 19 \text{ MPa}$  for island scheme), hardness, density, electrochemical, and metal release tests are independent of the scanning strategy, and the yield strength of both samples meets the ISO 22764:2006 standard for dental restorations. The tensile strength of two Co-Cr dental alloys—cast remanium GM and SLM F75— was investigated in the work of Jevremovic et al. [64]. They established more than 1.5 times higher tensile strength of the SLM samples compared to the cast ones (1363–1472 MPa and 900 MPa, respectively). Vandenbroucke and Kruth [60] did complex investigation of SLM titanium and Co-Cr-Mo alloys. The mechanical tests proved that the SLM Co-Cr details fulfil the requirements for hardness, strength, and stiffness. Concerning to the corrosion—the SLM Co-Cr samples showed lower emission than the cast ones due to the more homogeneous and finer microstructure of the laser molten material.

In investigation of the influence of the object's position to the building direction, some researchers established anisotropy of the mechanical properties and especially of fatigue strength. The microstructure and mechanical properties of SLM Co-29Cr-6Mo alloy were studied out in the work of Takaichi et al. [59]. Unique microstructure was formed, consisting of the fine cellular dendrites in the elongated grains, parallel to the building direction. The cellular boundaries were enriched with Cr and Mo, and the  $\gamma$  phase was dominant in the SLM building. Due to the unique microstructure, the mechanical anisotropy was confirmed in the samples, but the yield strength, Ultimate Tensile Strength (UTS), and elongation were higher than that of the cast alloy. The research of Kajima et al. [65] shows that the microstructure of SLM specimens of Co-Cr-Mo alloys is quite different from those of the cast samples, which consists of coarse dendrites with visible precipitates in the inter-dendritic regions. The fine cellular dendrites with diameter about  $0.5 \mu\text{m}$  were observed in the SLM samples parallel to the building

direction, while in directions, perpendicular or inclined at  $45^\circ$  to the building direction, fine columnar structures with diameter about  $0.5 \mu\text{m}$ , elongated along the building direction, were found. In lower magnification, gradual arch-shaped molten pool boundaries, typical for the SLM process, were observed. The tensile strength of the three groups of specimens is in the range 1170–1274 MPa, which is higher than that of the cast samples. Concerning to the fatigue strength, the results confirmed the anisotropy of the SLM alloy. The samples, parallel to the building direction, exhibit significantly longer fatigue life than the cast specimens, while the fatigue life of the two groups is significantly shorter than that of the cast specimens.

The research of Kim et al. [51] shows that the SLM Co-Cr alloy remanium star CL clearly exhibits the laser scan traces, as in higher magnification, the presence of fine grains with sizes about  $35 \mu\text{m}$  can be recognized. The SLM samples showed the highest mean ultimate tensile strength, followed by milled/post-sintered, cast, and milled samples. The yield strength and mean percent elongation of SLM alloy were higher than the cast alloy ( $R_{0.2} = 580 \pm 50 \text{ MPa}$  and  $R_{0.2} = 540 \pm 20 \text{ MPa}$ , respectively), while Young's modulus was lower ( $200 \pm 10 \text{ GPa}$  for SLM and  $260 \pm 20 \text{ GPa}$  for cast). A high yield strength and relatively low but sufficient modulus of elasticity of the SLM samples allow this technology to be used for manufacturing dental constructions, such as removable partial dentures, clasps, thin-veneered crowns, and wide-span bridges.

Averyanova et al. [29] investigated three-part dental bridge of Co-Cr alloy, manufactured by SLM. The hardness of the SLM Co-Cr alloy is in the range of  $400 \pm 14 \text{ HV}_{10}$  and  $462 \pm 22 \text{ HV}_{0.05}$ , while the average tensile strength is 1157 MPa, which is equal to that of the wrought alloy and about twice higher than the cast Co-Cr alloy (655 MPa). The microstructure of SLM dental bridges is nonequilibrium, consisting mainly of  $98.7 \pm 1.8\%$  fcc Co-rich solid solution and  $1.3 \pm 0.5\%$  of hcp  $\epsilon$  phase. The investigation of Dikova et al. [50] established similar hardness of Co-Cr four-part dental bridges, produced by SLM ( $407\text{--}460 \text{ HV}$ ), which is higher than the cast alloy and has nearly even distribution along the depth of each crown. Their subsequent investigations [66] show that the tensile strength and the yield strength of the SLM Co-Cr alloy are higher than the cast alloy ( $R_{0.2} = 720 \text{ MPa}$  and  $R_{0.2} = 410 \text{ MPa}$ , respectively), while the elastic modulus is comparable (213 and 209 GPa, accordingly). The higher hardness and more homogeneous microstructure of SLM Co-Cr dental alloys determine their higher wear and corrosion resistance [67].

The specific features of the SLM process and the parameters of the powder materials used determine the high surface roughness of the SLM Co-Cr dental alloys. The object position and orientation to the building direction as well as the choice and modeling of the supports are also of great importance [58]. The accuracy and the relation between the surface roughness and the sloping angle were researched in Ref. [60] using special benchmark models. It was proven that the surface roughness depends on the layer's thickness and sloping angle to the basis. The average arithmetic deviation of the surface roughness  $R_a$  varies between 6–18  $\mu\text{m}$  for 20  $\mu\text{m}$  layer's thickness and 13–33  $\mu\text{m}$  for 50  $\mu\text{m}$  layer's thickness. The higher values concern to the lower sloping angle to the basis of  $8^\circ$ , while the lower values for the larger angle of  $70^\circ$ . The research of Kajima et al. [65] confirmed that the surface roughness depends on the building direction. It is the lowest in the samples, perpendicular to the building direction,

$Ra = 10.22 \mu\text{m}$ , followed by that of the samples, inclined at  $45^\circ$  with  $Ra = 13.67 \mu\text{m}$ , and the highest in the samples, parallel to the building direction,  $Ra = 18.17 \mu\text{m}$ . It was established in Ref. [49] that the roughness of the vestibular surface of the second premolar of four-part dental bridge, manufactured by SLM, is nearly four times higher than the roughness of the conventional cast bridge ( $Ra = 4.24 \mu\text{m}$  and  $Ra = 1.11 \mu\text{m}$ , respectively) and 25% higher compared to that cast with 3D-printed patterns ( $Ra = 4.24 \mu\text{m}$  and  $Ra = 3.39 \mu\text{m}$ , respectively). It is proposed that the considerably higher roughness and partially melted powder on the surface of the SLM samples could lead to the increase of the mechanical as well as the chemical components of the adhesion of the porcelain to the Co-Cr alloys, thus promoting higher adhesion strength of the porcelain coating.

Concerning to the standard ISO 9693-1:2012 [68], the minimum acceptable bond strength of metal-ceramic is 25 MPa. Kaleli and Sarac [69] compared porcelain bond strength of Co-Cr frameworks manufactured by conventional lost-wax technique, milling, direct metal laser sintering (DMLS), and direct process powder-bed method. There was no significant difference between the values of porcelain bond strength to the samples, produced by different methods. The mean bond strength was 38.08 MPa for cast samples, while that of the DMLS samples was 40.73 MPa. The type of failure of the cast samples was adhesive/mixed, while that of the DMLS samples was cohesive/mixed. Li et al. [70] confirmed that there are no significant differences between the bond strength of the cast, milled, and SLM Co-Cr alloys. The milled and SLM groups showed significantly more porcelain adherence than the cast group. Akova et al. [71] also revealed no statistically significant difference of the shear bond strength of porcelain to the cast and SLM Co-Cr dental alloys (72.9 and 67.0 MPa, respectively). The failure type of the porcelain of the cast samples was of the mixed adhesion-cohesion type, while the failure of the SLM samples was of the mixed/adhesive type. The similar porcelain bond strength to the cast and SLM Co-Cr dental alloys was confirmed in the work of Wu et al. [72]—54.17 and 55.78 MPa accordingly. They established that the SLM alloy had an intermediate layer with elemental interpretation between the alloy and the porcelain, resulting in an improved bonding strength. Xiang et al. [73] established no significant difference for the mean bond strength of the SLM (44 MPa) and traditional cast (43 MPa) Co-Cr samples. A mixed fracture mode on the debonding interface of both the SLM and the cast groups was observed, but the SLM group showed significantly more porcelain adherence. Only Wang et al. [74] stated that there are statistically significant differences of the porcelain bond strength to the cast, CNC milled and SLM Co-Cr samples ( $37.7 \pm 6.5$  MPa,  $43.3 \pm 9.2$  MPa and  $46.8 \pm 5.1$  MPa, respectively), as the debonding surface of the all samples was of the cohesive failure mode. It should be noticed out that the surface roughness of the SLM samples decreases two–three times after sandblasting before porcelain firing (from  $Ra = 15 \mu\text{m}$  of as-received SLM Co-Cr samples to  $Ra = 8 \mu\text{m}$  of glass blasted and to  $Ra = 5 \mu\text{m}$  in ultrasonic ceramic field) [60]; as in the most cases, the physical appearance and the surface quality are similar to the conventionally manufactured by investment casting [58]. Current investigations show that the SLM metal-ceramic system exhibits a bonding strength that exceeds the requirement of ISO 9691: 1:2012. It even shows a better behaviour in porcelain adherence comparable to the traditional cast methods.

The higher roughness of SLM Co-Cr alloys can cause lower dimensional accuracy and comparatively satisfactory adjustment accuracy in comparison to the objects, cast by conventional technology or with 3D-printed patterns. In SLM of Co-Cr-Mo alloy, Vandembroucke and Kruth [60] established the process accuracy below 40  $\mu\text{m}$ , which fulfil requirements of most medical and dental applications. According to Bibb et al. [30], SLM-manufactured Co-Cr frameworks for removable partial denture possess accuracy and quality of fit comparable to the existing traditional methods used in the dental laboratories. Averyanova et al. [29] confirmed that the geometrical accuracy of three-part dental bridge of Co-Cr alloy, produced by SLM, is comparable to that of the substructures, produced by conventional technology. The good repeatability of the SLM process in manufacturing Co-Cr four-part dental bridges was reported by Dzhendov et al. [49]. The maximal deviations of the dimensions of SLM bridges were the lowest compared to the conventional casting and casting with 3D-printed patterns. But the dimensions of the SLM dentures were lower than that of the base model with  $-0.07/-0.23$  mm. The adjustment accuracy of the SLM bridges is comparable to that of the bridges, cast with 3D-printed patterns, and is higher than that of the conventionally cast dentures.

There is no consensus regarding the clinically acceptable limits of marginal fit of dental restorations. Most researchers agree on an acceptable marginal discrepancy (distance from the abutment margin to the metal coping in a straight line) below the range of 100–120  $\mu\text{m}$  [75], as values, greater than 120  $\mu\text{m}$ , are considered not clinically acceptable [76–78]. The research of Kim et al. [75] stated that the marginal fit values of the Co-Cr alloy greatly depended on the fabrication methods and, occasionally, on the alloy systems. They found out that the marginal discrepancy of the SLM crowns (98.7  $\mu\text{m}$  for 20- $\mu\text{m}$ -thick layer and 128.8  $\mu\text{m}$  for 30- $\mu\text{m}$ -thick layer) is larger than the cast crowns (65.3–70.4  $\mu\text{m}$ ). In SLM samples, the marginal discrepancy increases with the increase of the layer's thickness. Kaleli and Sarac [76] compared the marginal adaptation after fabrication of the framework, porcelain application, and cementation of metal-ceramic restorations prepared by conventional lost-wax technique, milling, DMLS, and a direct powder-bed process. They observed the lowest marginal discrepancy values in the crowns, prepared by direct process powder-bed method, followed by the DMLS, milling, and casting. The research of Pompa et al. [77] concerns to the differences of marginal fit of laser-fused and conventional technologies for production of fixed dental prostheses. They established that the copings, manufactured by SLM, have better marginal adaptation within an acceptable range. But the cement gap characterized with irregular distribution was wider in the region of the shoulder than at the point of closure. The marginal discrepancy increased after porcelain application and cementation. In comparison of the marginal fit of metal laser sintered (MLS) Co-Cr alloy copings and conventional cast Ni-Cr alloy copings, Sundar et al. [79] concluded that the MLS copings had a better marginal fit and a decrease in micro-leakage compared to the copings, manufactured by conventional lost-wax technique. Huang et al. [80] compared the marginal and internal fit of SLM metal-ceramic crowns with lost-wax cast ones. They established that the SLM Co-Cr metal-ceramic crowns were better in marginal fit, not significantly different in axial fit and less accurate in occlusal fit than that of the cast samples. Concerning to the gap distribution, Tamac et al. [81] reported nearly the same results in comparing the clinical marginal and internal adaptation of metal-ceramic crowns, fabricated by CAD/CAM milling, DMLS, and

traditional casting. They established that mean marginal gap values were 86.64  $\mu\text{m}$  for milling, 96.23  $\mu\text{m}$  for DMLS, and 75.92  $\mu\text{m}$  for casting. The gap values in the axial wall region were the higher for the three groups of samples, followed by the gap values of axio-occlusal and occlusal surface regions. The cement film thickness at the occlusal region and axio-occlusal region was higher for the DMLS crowns. Consequently, the laser-assisted technologies for direct production of metal dental restorations, such as SLM, SLS, and DMLS, ensure improved or at least clinically acceptable fitting values compared with that of the conventional casting.

The Co-Cr dental alloys, fabricated by SLM, characterize with homogeneous fine-grained microstructure, consisting mainly of  $\gamma$  and  $\epsilon$  phases in different ratios. Their unique microstructure defines higher mechanical properties,—hardness, yield and tensile strength, fatigue strength as well as higher wear and corrosion resistance—compared to the cast alloys. As a consequence of the peculiarities of the SLM manufacturing and the position of the object toward the building direction, anisotropy in mechanical properties, especially in the fatigue life, can be observed. The work with optimized technological regimes can guarantee the constructions with density higher than 99% and comparatively low roughness. But as a whole, the surface roughness of the SLM Co-Cr alloys is higher than the alloys, cast conventionally or with 3D-printed patterns, due to the specific features of the manufacturing process and the use of metal powder as raw material. It was expected that the higher surface roughness could decrease the dimensional and fitting accuracy and promote the higher adhesion strength of the porcelain coating. But the current review shows that the dimensional accuracy of the SLM details is higher than the cast samples and the fitting accuracy is improved or clinically accepted, most probably due to the CAD/CAM nature of the manufacturing process, which additionally enables high repeatability. Concerning to the adhesion strength of the porcelain to the SLM dental alloys, more authors reported that it is comparable with the adhesion strength to the cast alloys, which may be due to the decreased roughness of the SLM samples after sandblasting before porcelain firing. The Co-Cr dental alloys, fabricated by SLM, comply with the standards and requirements concerning the dimensional and fitting accuracy as well as strength properties and can be successfully used in production of dental constructions.

#### 4. Conclusion

In dentistry, two different approaches can be applied for the production of metal frameworks using AT. According to the first one, the wax/polymeric cast patterns are fabricated by 3D printing, and the constructions are cast from dental alloy with as-printed patterns. Through the second one, the metal framework is a manufactured form of powder alloy directly from the 3D virtual model by SEBM or SLM.

The specific features of the manufacturing processes, the parameters of the technological regimes, and the properties of the materials influence on the accuracy and properties of Co-Cr dental constructions.

The microstructure and mechanical properties of Co-Cr dental alloys, cast using 3D-printed patterns, are typical for cast alloys. Their dimensional and adjustment accuracy is higher

compared to the constructions, produced by traditional lost-wax casting or by SLM. The surface roughness is higher than that of the samples, cast by conventional technology, but lower compared to the SLM objects.

The microstructure of SLM Co-Cr dental alloys is fine grained and more homogeneous comparing to that of the cast alloys, which defines higher hardness and mechanical properties, higher wear and corrosion resistance. The surface roughness of SLM Co-Cr dental alloys is higher than that of the alloys, cast conventionally or with 3D-printed patterns. The dimensional accuracy of SLM Co-Cr details is higher than the cast samples, while the fitting accuracy is improved or clinically accepted.

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