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Properties of Co-Cr Dental Alloys Fabricated Using Additive Technologies

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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 asprinted patterns. Through the second one the metal framework is manufactured form 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

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 Cr_2O_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, γ phase in high temperatures, and with hexagonal close packed (hcp) lattice, ε phase in room temperature [4, 6]. The γ phase defines the ductility, while the ε 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 γ phase and carbides of the $M_{23}C_6$ type [4]. Therefore, the properties of Co-Cr dental alloys depend on the ratio between γ/ε 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 'threedimensional 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 µm 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 µm 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 µm, 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 µm 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 µm layer's thickness), is relatively high with average arithmetic deviation of the surface roughness $Ra = 3.24 \mu m$. Decreasing the layer's thickness to 35 μm leads to the lower surface roughness of $Ra = 2.18 \mu m$. 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 ($Ra = 3.39 \, \mu m$ and $Ra = 1.11 \, \mu m$, 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 γ phase, while the inter-dendritic regions consist of microeutectic (Co solid solution with intermetallic precipitations) and carbides of the (Cr, Mo)₂₃C₆ 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 ± 20 MPa, mean percent elongation 10 ± 2 and Young's modulus 260 ± 20 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 J/mm³ and porous, in input energy less than 150 J/mm³. 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 densed 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 γ and ε phases. The ε phase is formed by athermal martensitic transformation, and it is distributed as network of thin lamellae inside the γ phase. The higher hardness (47 HRC) is attributed to the presence of the ε -lamellae grown on the $\{111\}_{\nu}$ planes that restricts the dislocation movement in the γ 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 γ and ϵ phases in the microstructure and nearly the same hardness, 570 HV for lineformed alloy and 564 HV for island-formed alloy. Their research shows that the results of tensile strength (1158.22 ± 21 MPa for line scheme and 1115.56 ± 19 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 γ 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 μ m were observed in the SLM samples parallel to the building

direction, while in directions, perpendicular or inclined at 45° to the building direction, fine columnar structures with diameter about $0.5~\mu m$, 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 μ 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 ± 50 MPa and $R_{0.2}$ = 540 ± 20 MPa, respectively), while Young's modulus was lower (200 ± 10 GPa for SLM and 260 ± 20 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 widespan 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 ± 14 HV10 and 462 ± 22 HV0.05, 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 ε phase. The investigation of Dikova et al. [50] established similar hardness of Co-Cr four-part dental bridges, produced by SLM (407–460 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 ($R_{0.2} = 720$ MPa and $R_{0.2} = 410$ 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 $\it Ra$ varies between 6–18 $\it \mu m$ for 20 $\it \mu m$ layer's thickness and 13–33 $\it \mu m$ for 50 $\it \mu m$ layer's thickness. The higher values concern to the lower sloping angle to the basis of 8°, while the lower values for the larger angle of 70°. 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,

 $Ra = 10.22~\mu m$, followed by that of the samples, inclined at 45° with $Ra = 13.67~\mu m$, and the highest in the samples, parallel to the building direction, $Ra = 18.17~\mu m$. 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 ($Ra = 4.24~\mu m$ and $Ra = 1.11~\mu m$, respectively) and 25% higher compared to that cast with 3D-printed patterns ($Ra = 4.24~\mu m$ and $Ra = 3.39~\mu m$, 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 adhesioncohesion 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 ± 6.5 MPa, 43.3 ± 9.2 MPa and 46.8 ± 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 $Ra = 15 \mu m$ of as-received SLM Co-Cr samples to $Ra = 8 \mu m$ of glass blasted and to Ra-5 µm 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, Vandenbroucke and Kruth [60] established the process accuracy below 40 µm, 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 µm [75], as values, greater than 120 µm, 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 µm for 20-µm-thick layer and 128.8 µm for 30-µm-thick layer) is larger than the cast crowns (65.3–70.4 µm). 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 metalceramic 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 $86.64~\mu m$ for milling, $96.23~\mu m$ for DMLS, and $75.92~\mu m$ 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 γ and ϵ 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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