Structural and morphological approach of Co-Cr dental alloys processed by alternative manufacturing technologies

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Abstract. The integration of digitalized processing technologies in traditional dental restorations manufacturing is an emerging application. The objective of this study was to identify the different structural and morphological characteristics of Co-Cr dental alloys processed by alternative manufacturing techniques in order to understand the influence of microstructure on restorations properties and their clinical behavior. Metallic specimens made of Co-Cr dental alloys were prepared using traditional casting (CST), and computerized milling (MIL), selective laser sintering (SLS) and selective laser melting (SLM). The structural information of the samples was obtained by X-ray diffraction, the morphology and the topography of the samples were investigated by Scanning Electron Microscopy and Atomic Force Microscope. Given that the microstructure was significantly different, further differences in the clinical behavior of prosthetic restorations manufactured using additive techniques are anticipated.

1. Introduction
Cobalt-chromium (Co-Cr) alloys are widely used in the technology of fixed dental prosthesis because of their excellent mechanical properties and low production costs compared to high noble dental alloys. Continuous advancements in metallurgical technology have expanded the range of methods by which these restorations can be manufactured [1]. Main alternatives for the conventional melting-casting technology are digitalized processing technologies. The recent introduction of these techniques in the dental field has marked a turning point in the prosthesis production methodology, from the traditional hand made to the innovative automated approach. The integration of new technologies in traditional dental restorations manufacturing is an emerging application [2].
Digitized technologies can be classified as based on subtractive manufacturing (SM), such as the milling of pre-manufactured materials assisted by computer-aided design/computer-aided manufacturing (CAD/CAM) systems [3-8], or on additive manufacturing (AM), such as the more recently developed selective laser sintering (SLS) and selective laser melting (SLM) techniques [9-13].
Although CAD/CAM has long been directly associated with the milling procedure in dental literature, it should be mentioned that SLS and SLM are also classified as CAD/CAM technologies. Processing of Co-Cr dental alloys can markedly affect the mechanical properties of the resulting components; therefore it should be carefully controlled to obtain the desired quality [14,15]. Although casting remains the traditional processes used to manufacture CoCr alloy restorations [14], nowadays additive manufacturing (AM) is being accepted as the novel candidate for the fabrication of customized dental prostheses [16-18]. AM has attracted much attention over the past ten years due to its immanent advantages, such as design freedom and short working times. AM techniques have already been known for more than 20 years but were at first limited to the rapid manufacturing of porous structures and prototypes [19]. 

Given the large differences in the manufacturing process between casting, which uses the complete melting and overheating of casting materials, the milling of a prefabricated metal block and additive manufacturing using a fine metallic powder, large differences in microstructural characteristics are anticipated [3]. In terms of chemical composition, there is little difference between Co-Cr alloys used for different manufacturing technologies. Typical Co–Cr alloys contain between 55-63 wt% cobalt and 25-28 wt% chromium [20].

2. Objective
The objective of this study was to identify the different structural and morphological characteristics of Co-Cr dental alloys processed by alternative manufacturing techniques in order to understand the influence of microstructure on restorations properties and their clinical behavior.

3. Materials and methods
Metallic specimens made of Co-Cr dental alloys were prepared using traditional casting (CST), and computerized milling (MIL), selective laser sintering (SLS) and selective laser melting (SLM). For the experimental analyses round plates 20 mm diameter and 2 mm thick were fabricated using different technologies.

The cast alloy was manufactured by conventional lost wax technique with a phosphate-bonded investment. The mold was cast with Wirobond® SG alloy (Bego, Bremen, Germany) at 900°C using a vacuum pressure casting machines Nautilus (Bego, Bremen, Germany). The mold was left to cool down to room temperature and the specimens were then divested, sandblasted with alumina particles (200 μm) and finished with rotative instruments, burs suitable for Co-Cr alloys. Type 4 alloy Wirobond® SG fulfils all criteria of the ISO 22674 and ISO 9693-1 Standards. The composition is Co 63.8; Cr 24.8; W 5.3; Mo 5.1; other constituents Si, and Fe. Wirobond® SG allows normal cooling and provides effective, economic processing in the laboratory.

A prefabricated block of a commercial Co-Cr dental alloy CopraBond K (White Peaks Dental Systems GmbH & Co. KG, Essen, Germany), a non precious blank on Co-Cr base, type 4, was milled to fabricate the sample using Datron D5 5-axis dental milling machine (Datron, Mühlthal, Germany). A disc wax pattern was digitized and the specimens were cut to their final dimensions. The composition is: Co 61.0, Cr 28.0, W 8.5, Mn 0.25, Fe <0.5, Si 1.65, C <0.1. CopraBond K is a nickel- and beryllium free Co-Cr blank, specially designed for CAD/CAM applications. The material is very homogenous and lends itself to machining extremely well by milling.

The laser-sintered specimens were prepared from commercial Co-Cr powder ST2724G (SINT-TECH, ) using a dental laser sintering device (PXS Dental System, Phenix Systems, Clermont-Ferrand, France). For scanning the high accuracy D700 scanner (3Shape, Copenhagen, Denmark) and for design Dental System™ CAD Software (3Shape, Copenhagen, Denmark) were used. Chemical composition of Co-Cr alloy (wt.%): Co 54.31; Cr 23.08; Mo 11.12; W 7.85; Si 1.67; Mn 1.67; Fe<0.1. Cobalt-Chromium ST2724G is a type 5 alloy, certified ISO 9001 and ISO 13485. The layering function for the powder material is a fundamental part of the laser sintering process. A mechanism patented by Phenix Systems allows you to adapt to the shape and average size of the grains of powder. This function can be
programmed and adjusted to suit any type of ceramic or metal powder with a granulation equal to or greater than a micron. For SLM a Co-Cr bonding alloy for the manufacturing of removable and fixed restorations by SLM was used. The alloy is a type 4 alloy according to ISO 22674. Nominal values of alloy composition in mass percent: Co 59.0; Cr 25.0; W 9.5; Mo 3.5; Si max. 1; other constituents: C, Fe, Mn, N max. 1.5. The specimens resulted after CAD/CAM technologies were not additional prepared. The weights of the specimens were: 1.40 g for MIL; 1.35 g for SLS; 1.17 g for SLM and 1.06 for CST. The structural information of the samples was obtained by X-ray diffraction on a XRD, X’pert Powder X-ray diffractometer (PANalytical B.V., Almelo, Netherlands) using Cu Kα radiation, at room temperature. The morphology and the topography of the samples were investigated by Scanning Electron Microscopy with Energy Dispersive X-Ray Analysis SEM / EDAX Model INSPECT S (FEI, Oregon, USA) and atomic force microscope AFM Model Nanosurf® EasyScan 2 (Nanosurf AG, Liestal, Switzerland).

4. Results and discussions
Depending on the nature and chemical composition of the samples the morphology is different. The microstructure of Co–Cr dental alloys depends also on the manufacturing technique. The morphological aspect of the resulting powders was examined by SEM, as shown in Figure 1 a, b, c, d. The magnification used for SEM measurements was 6000 X. Depending on the nature and chemical composition of the samples the morphology is different.

![SEM images](image)

**Figure 1.** The SEM images of: a) MIL; b) SLS; c) SLM and d) CST.

In Figure 2 (a-d) the EDAX analyses of the samples are presented. The EDAX analysis certified initial molar ratios between material compositions.

![EDAX analyses](image)

**Figure 2.** EDAX analysis of: a) MIL; b) SLS; c) SLM and d) CST.

In Figure 3 are shown the AFM images of the surface for each of the studied materials, using a scan size of 2μm x 2μm. The contact mode cantilever was used to measure the samples.
Figure 3. 3D AFM images of: a) MIL; b) SLS; c) SLM and d) CST.

The average surface roughness $S_a$ and mean square root roughness $S_q$ were calculated and for the samples and are given in Table 1.

Table 1. The surface roughnesses.

| Samples | $S_a$ (nm) | $S_q$ (nm) |
|---------|-----------|------------|
| MIL     | 2.7       | 3.7        |
| SLS     | 3.8       | 5          |
| SLM     | 35        | 42         |
| CST     | 7.4       | 8.8        |

There is a strong correlation between the aspect of the samples (SEM images) and the rugosity. The more uniform samples reflect in the lowest value of rugosity and the non uniform architectures present the highest value of roughness. The roughness is reflected in porous structures, which can be correlated also with the weight of the samples (in descending order MIL, SLS, SLM and CST).

These findings regarding microstructural properties may have clinical implications. SLM and SLS technologies have recently been introduced in the dental field, and a vast spectrum of factors should be tested and/or optimized to increase its efficacy in the production of metallic dental restorations [3].

In the steadily increasing market for 3D printing technologies, SLS and SLM solutions are leading procedures for metal based additive manufacturing technology. These extremely reliable and economical methods enable the manufacturing of highly complex geometry restorations, which cannot be milled in such a way. The material science analysis of cross sectional images confirms the outstanding quality of our metal powders. In the manufacturing process of the SLM technology the components achieve even better metallurgical characteristics than using the conventional casting process with the same material [21]. Taking into account the many benefits of AM technologies, and the findings regarding the studied structural and morphological characteristics of Co-Cr dental alloys processed by alternative manufacturing techniques, more research is required in order to understand the influence of microstructure on restoration properties, further veneering procedures of the frameworks, and last but not least the clinical behavior.

5. Conclusions
1. Even if there is little difference between the chemical compositions of the Co-Cr alloys used for different manufacturing technologies, the structural and morphological characteristics of Co-Cr dental alloys processed by alternative manufacturing techniques are different.
2. Milling of pre-manufactured blocks assisted by CAD CAM technologies is associated with the best structural and morphological characteristics of the processed materials.
3. The immanent advantages of additive technologies are accompanied by porosities resulted after the deposition of the fine metallic powder, especially for the SLM method. The chemical compositions resulting after AM actually differ widely from those indicated by manufacturers for the powders.
4. Given that the microstructure was significantly different, further differences in the clinical behavior of prosthetic restorations manufactured using additive techniques are anticipated.
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