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CoCrMo-base Alloys for Dental Applications Obtained by Selective laser melting (SLM) and CAD/CAM Milling

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In this work, CoCrMo-base alloys specimens were produced by additive manufacturing using selective laser melting (SLM) as well as CAD/CAM milling. For SLM specimens, spherical particles were laser processed at 1320°C under argon atmosphere and submitted to thermal stress relieving at 750°C–45min. Specimens from CoCrMo blocks were milled by CAD/CAM machining and sintered at 1300°C–60min. The materials from both techniques were characterized by relative density, dilatometry, SEM/BSE, OM and XRD analysis. The mechanical properties were determined by Vickers hardness and tensile tests. The specimens from both techniques exhibited single phase γCo (FCC) and CTE of 14 $x10^{-6}$ $°C^{-1}$. Relative density of 95.4%/ 85.6%, hardness values near 400HV/ 350HV and UTS of 905MPa/ 780MPa were measured for SLM and CAD/CAM specimens, respectively. Higher relative density is the main factor for increased mechanical properties of SLM specimens. On the other hand, both SLM and CAD/CAM specimens present properties in accordance with ISO-22674 recommendations, compatible with dental applications such as bridges containing four or more elements as well as fully dense pontics.

Keywords: *Dental alloys, CoCrMo metal system, additive manufacturing, selective laser melting, CAD/CAM milling, microstructural characterization, mechanical properties.*

1. Introduction

CoCrMo alloys are commonly used for dental restorations due to their high corrosion resistance, good mechanical properties and biocompatibility[1-3]. Dental components have been produced from these alloys by prototyping techniques, classified in two groups: additive manufacturing, such as Selective Laser Melting (SLM) technique and subtractive manufacturing, such as the milling of pre-manufactured materials assisted by CAD/CAM (Computer Aided Design/Computer-Aided Manufacturing)[4-7].

Selective laser melting (SLM) or Selective laser sintering (SLS) are prototyping techniques where the components designed in a 3D software are manufactured by depositing thin layers of powders with simultaneous *in situ* melting/sintering of the material. The heat source is usually a laser beam which heat up the material to a suitable temperature, allowing either diffusion in solid state or melting, producing components of any format with accuracy in the micrometer-scale[8-11]. The manufacture speed is similar to that via CAD/CAM and the main advantages are: dimensional accuracy; the possibility to form complex geometries; no use of machining tools and better metallic yield, as the raw material is fully converted to the final product. One of the main disadvantages of this technique is the development of temperature gradients during fabrication of the component, leading to residual thermal stresses which may reduce its mechanical properties[9,11-13].

Previous investigations using SLM prototyping technique have been published targeting to understand the microstructural features of the CoCrMo alloys aiming to produce biomedical devices[14,15]. Barucca et al.[16] evaluated the microstructural evolution of CrCoMo dental restorations made by direct metal laser sintering and confirmed the phase transformation from γCo (FCC) to ε γCo (HCP). Zhou et al.[17] found 72 vol% of structured γCo (FCC) phase after SLM process and subsequent heat treatments at 1150 °C for 1 h. Furthermore,

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Qian et al.[18] detailed microstructure changes, particular those related to the welding pool boundaries, grain and sub-grain boundaries, their results showing that rapid cooling keeps the high-temperature γCo (FCC) phase and promotes a cellular sub-grain structure characterized by Mo fluctuation and inhibits carbide formation.

In this work, CoCrMo-base specimens were manufactured by SLM and evaluated in terms of their microstructures and mechanical properties (hardness and tensile tests). A commercial CoCrMo block used to produce dental metallic restorations by CAD/CAM was conventionally sintered to obtain data for comparison with the SLM produced specimens.

2. Experimental Procedure

2.1. Materials

Table 1 shows the chemical composition determined by X-ray fluorescence spectroscopy (XRF) (PANalytical – Axios advanced) of the CoCrMoW powder used for SLM experiments in this work as well as that of the Ceramill Sintron® block (Amman Girrbach AG – Austria) which was machined and conventionally sintered to be compared with the SLM product.

2.2. Processing

The CoCrMoW powder was laser processed at 1320 °C to initially manufacture cylindrical specimens of Ø 3 mm x 6 mm under argon atmosphere, using an EOSINT M280-EOS equipment with a Yb-fiber laser of 200W, STL CAD interface, scan speed of 700 mm/s and layer thickness of 20µm. The specimens were then heat treated at 750°C – 45 min. under argon atmosphere for stress relieve, using a Maitec F1150 Furnace. These cylindrical specimens were used for microstructural characterization as well as for hardness measurements. Following the same procedure above, tensile specimens were manufactured by SLM with dimensions shown in Figure 1a. Figure 1b illustrates the relative orientation of the tensile specimens with respect to the powder deposition direction.

Specimens of 5 x 5 x 10 mm dimensions were removed from CoCrMo Ceramill Sintron block (AmannGirrbach; Austria) and sintered at 1300°C – 60 min under argon atmosphere. These specimens were used for microstructural characterization as well as for hardness measurements. In addition, tensile specimens with the same dimensions of the SLM tensile specimens were removed by CAD/CAM from the Ceramill Sintron block, as indicated in Figure 1c, and also sintered at 1300°C – 60 min.

All the tensile specimens were grounded with SiC paper (#1200) before tests to minimize surface effects on the tensile tests data.

2.3. Microstructural and mechanical characterization of raw materials and sintered specimens

The raw materials (CoCrMoW powder and CoCrMo Ceramill Sintron block) and the processed materials were characterized via X-ray diffraction (XRD) and scanning electron microscopy (SEM) in the back-scattered electrons image mode (BSE).

The XRD experiments were carried out in a Shimadzu XRD6100 equipment using Cu-Kα radiation; scanning between 20° and 80°, step size of 0.05° and counting time of 3s/point. The phases present in the specimens were identified from Crystalographica Search-Match software (Oxford Cryosystems)[19].

SEM/BSE images from the raw-materials were obtained from a Hitachi TM 3000 SEM at 15 kV and 8.5 mm working distance. The processed materials were characterized by optical microscopy (Leica DM IRM) from flat and polished samples,

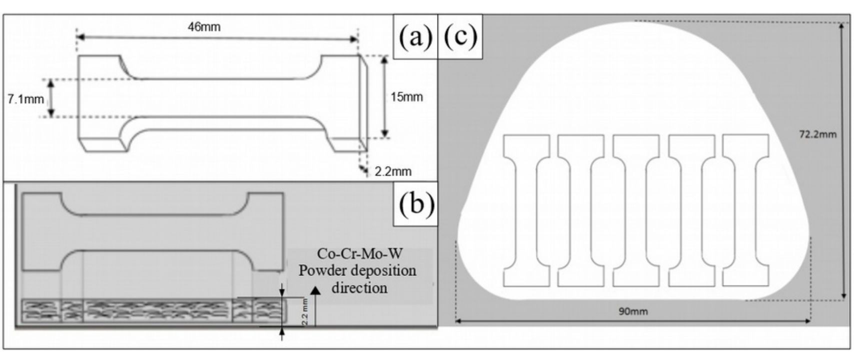

Figure 1. (a) Dimensions of the tensile tests specimens (b) Relative orientation of the SLM tensile specimens with respect to the powder deposition direction (c) Schematic top view of the CoCrMo block with indication of the tensile specimens removed by CAD/CAM.

Table 1. Chemical composition of the alloys used in the present study (wt.%)

Material	Processing	Co	Cr	Mo	W	Si	Mn	Fe	Others
CoCrMoW EOS SP2™ - Germany (Atomized powder)	Selective laser melting (SLM)	61.6	25.6	6.2	5.5	0.5	0.1	0.2	0.3
CoCrMo Ceramill Sintron block, AmmanGirrbach – Austria	Solid state sintering	64.4	28.4	5.6	-	0.2	0.9	0.2	0.3

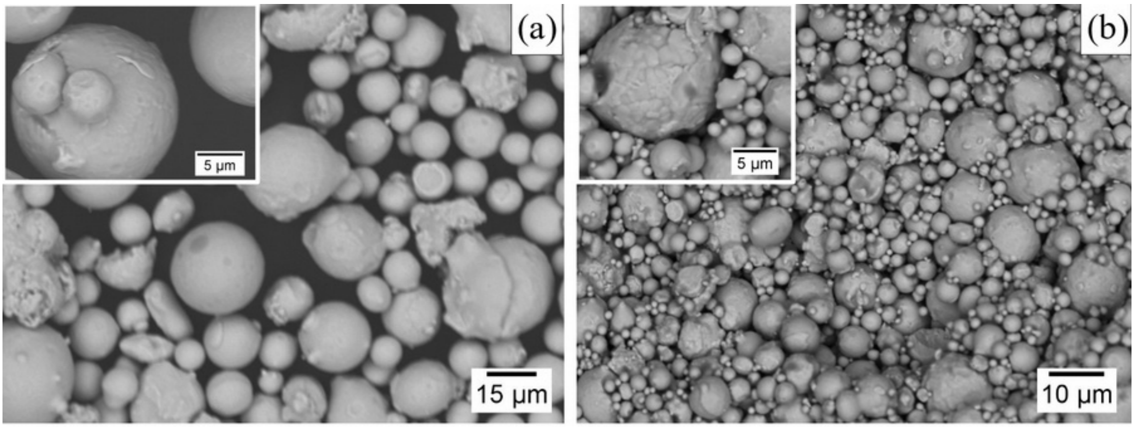

Figure 2. SEM/BSE micrographs of (a) CoCrMoW powder and (b) CoCrMo block.

etched electrolytically with a solution consisting of 100 mL distilled water and 4 mL of HCl under an applied voltage of 5V for 3 seconds. The grain size of processed materials were estimated using optical microscopy micrographs and *ImageJ* software[20], according to ASTM E112-14[21].

SLM and conventionally sintered specimens (CS) from Ceramill Sintron block had their relative density determined using Archimedes principle from 3 x 3 x 6 mm and 5 x 5 x 10 mm specimens, respectively, according to ASTM B962-14. The theoretical density used for SLM and CS materials were 8.5 and 7.9 g/cm^3 respectively.

The coefficient of thermal expansion (CTE) of SLM specimens were determined from Ø8 x 4 mm specimens using a Netzsch DML402C dilatometer, adopting 20°C/min heating rate under argon.

Microhardness measurements (n=20) were performed from SLM and CS specimens using a TIME-Group-China equipment, load of 300gf for 15s, from randomly measurements on the surface of each material. Average Vickers hardness values for each material and their respective standard deviations were determined. Tensile tests were performed at room temperature from three specimens for each material (SLM; CS) using an EMIC DL-10000 machine, displacement speed of 0.05 mm/min to determine the ultimate tensile strength of both SLM and CS materials.

3. Results and Discussion

Figure 2 shows micrographs of the CoCrMoW powder (Figure 2a) and CoCrMo Ceramill Sintron block (Figure 2b) obtained by SEM/BSE. It can be observed the presence of near spherical particles of different diameters in both materials, which is a characteristic of atomized powder from the liquid. Qualitatively, the average diameter size of the CoCrMoW powder is larger than that used to produce the CoCrMo CAD/CAM block.

Figure 3 shows XRD results (Cu-Kα radiation) from CoCrMoW powder, CoCrMo Ceramill Sintron block, SLM and CS specimens. All specimens are single phase materials composed of γCo(FCC). This γCo(FCC) is stable at high temperatures based on phase diagram data[22] and is retained at low temperature due to rapid cooling associated to all processing conditions which produced the materials reported

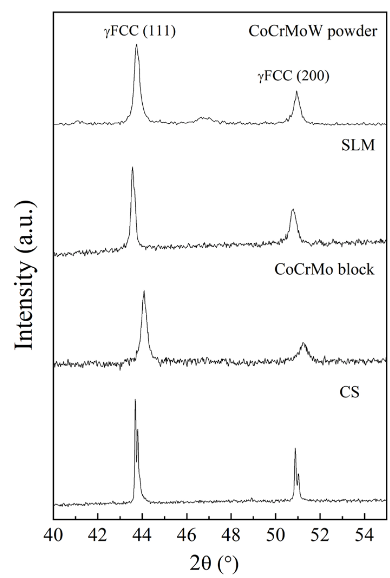

Figure 3. XRD patterns of (a) CoCrMoW powder, (b) SLM specimen, (c) CoCrMo Ceramill Sintron block and (d) CS specimen.

in Figure 3. It should be mentioned that under equilibrium cooling conditions at least some εCo (HCP) should be present at low temperatures.

The SLM specimens reached 95% of the theoretical density against 85.6% for the CS specimens, indicating that the sintering parameters used in the solid-state sintering of compacted CoCrMo block were not suitable for complete elimination of the pores presents in the block.

Metal-ceramic bond is based on a combination of mechanical, chemical and van der Waals forces, and a small CTE mismatch is needed to well attach the veneering ceramic to the CoCrMo alloy surface[23]. The SLM specimens exhibited a CTE of 14.0 x10^{-6} °C^{-1} which is close to results reported for similar alloys[23] and suggests good conditions for the application of veneering ceramics.

Figure 4 shows optical micrographs (OM) of a SLM specimen. Figure 4a, b shows the top view of the specimen where columnar grains morphology is observed, similar to that from Hedberg et al.[24] Figure 4 c,d depicts cross section layered

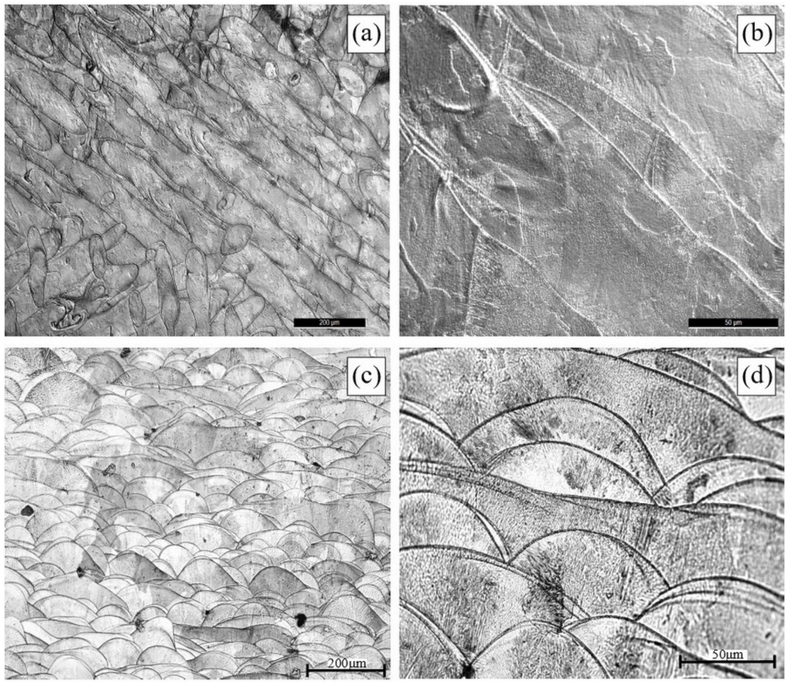

Figure 4. Optical micrographs of a SLM specimen under different magnifications: (a,b) top view; (c,d) cross section view.

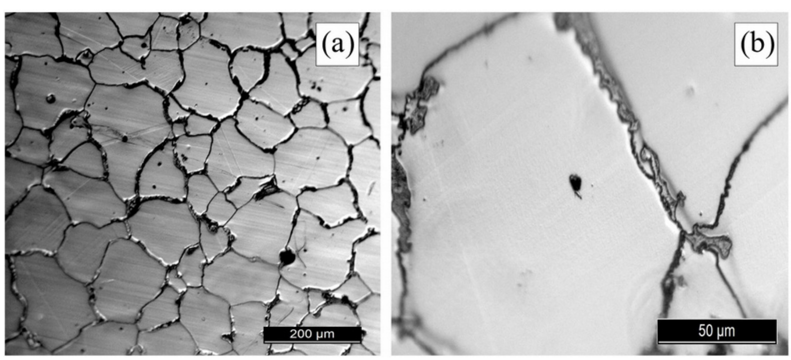

Figure 5. Optical micrographs of a CS specimen (1300°C-1h) under different magnifications.

structure of the SLM specimen with average grain size of 55μm (length) by 22μm (height), formed by melting/solidification of the powder during the passage of the laser beam. Similar morphology was found for SLM specimens of CoCrMoW alloys from Girardin et al.[25]. Based on these results, some anisotropy in terms of mechanical properties should be expected for the SLM material. As expected, CS specimens presented equiaxial grains with an average grain size of 150 μm, in addition to some porosity, as shown in Figure 5.

Figure 6 shows hardness values of approximately 400 HV for the SLM specimen, the CS specimen presenting lower values, near 375 HV. The difference in hardness values between SLM and CS is associated to differences in chemical composition; morphology; grain size as well as porosity between the two materials. Data from the literature is also included in Figure 6 for comparisons purposes. The hardness values of the SLM specimen are higher than those reported for the ASTM F1537 material as well as the material from

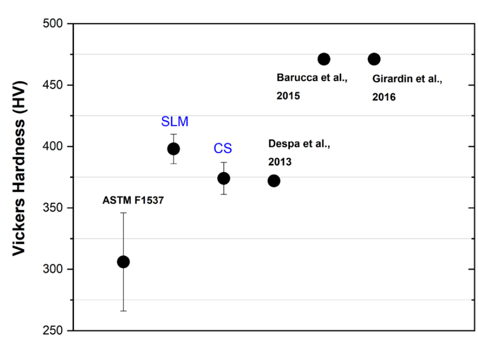

Figure 6. Vickers hardness values of the SLM and CS specimens as well as data from the literature.

Despa et al. work[26]. However, they are lower than those from the investigations of Barucca et al.[16] and Girardin et al.[25].

The average UTS values for the SLM and CS specimens were 905MPa and 780MPa, respectively, the lower values from the CS specimens being likely associated to the important porosity level found in this material. Data from SLM specimens in this work are lower than those reported by Despa et al.[26] (~1000 MPa), Girardin et al.[25] (~1290 MPa), and Qian et al.[18] (~1160 MPa), and close to that of Takaichi et al.[27] (~950 MPa). However, the SLM specimens exhibited average values compatible with the requirements of ISO 22674[28], which determines a minimum value of 500 MPa for applications such as fixed and removable restorations.

4. Conclusions

In both investigated manufacturing techniques (CAD/CAM milling or SLM), the major crystalline phase observed is a γCo solid solution. CAD/CAM samples present relative density close to 86%, with homogeneous equiaxial grains, in addition to some porosity (> 14%). As a result of this porosity, the values of hardness and tensile strength (UTS) obtained are of the order of 350 HV and 780 MPa, respectively. Comparatively, the samples obtained by SLM show higher densification (95.4%) and better mechanical properties, with hardness and UTS values of 400 HV and 905 MPa, respectively. The properties of the developed CoCrMo alloys enable the materials to have properties in agreement with the requirements of ISO 22674 standard ("dentistry - metallic restorations"). On the other hand, the microstructural characteristics (anisotropy) of SLM samples and the residual porosity of the CAD/CAM samples are important parameters that can be limiting for new applications, depending on the final requirements for the use of these materials, and might be improved.

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