Original Article

Sintering behaviour of Co-28%Cr-6%Mo compacted blocks for dental prosthesis

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In this work, the sintering behaviour of compacted CoCrMo blocks was investigated. The material was characterized in the as-received and sintered conditions through X-ray fluorescence, X-ray diffraction, density and scanning electron microscopy (SEM). The materials sinterability was evaluated by means of dilatometry and isothermal sintering at 800, 1000, 1200 and 1300 °C for different isothermal holding times. The particles of the as-received compacted blocks exhibited spherical shape with sizes ranging from 2 μm to 16 μm with a monomodal distribution. The as-received blocks presented a relative density of 57% and γCoFeCo single-phase microstructure. After sintering, the specimens presented a γCoFeCo + εCo26 (HCP) two-phase microstructure. Dilatometry data has indicated that the compacted blocks present discrete shrinkage anisotropy. Sintering starts close to 815 °C and a high shrinkage rate occurs near 1150 °C. The microstructure of the specimens sintered at 1200 °C has shown equiaxed grains and was highly dependent on the sintering time, with mean grain size ranging from 4.9 ± 1.3 μm (1200 °C – 60 min) to 28.4 ± 11.3 μm (1200 °C – 240 min). The specimen sintered at 1200 °C – 240 min was in the final sintering stage and attained a densification near 90%. Sintering at 1300 °C – 60 min has led to exaggerated grain growth, with values of the order of 88.6 ± 16.7 μm and should be avoided because in addition it has not contributed to an increase in densification. The data from this work might be used to guide sintering cycles conditions for the manufacture of dental prostheses.

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1. Introduction

CoCrMo alloys are widely used as biomaterials for orthopaedic implants, especially in artificial hip and knee joints, as well as infrastructures of metaloceramic dental prosthesis, due to their high biocompatibility, wear and corrosion resistance [1–5].

For several years, CoCr alloy dental restorations were manufactured using traditional casting techniques. The advancement of manufacturing technologies using rapid prototyping allowed to produce these parts through two main paths using the computer-aided design/computer-aided manufacturing (CAD/CAM) process [6]. These manufacturing
techniques are usually classified as hard machining or soft machining. Hard machining of CoCr blocks has the advantage of minimizing the formation of defects and porosities induced by casting. However, the high hardness of the bulk blocks used in the machining, in addition to the increased wear of the tool and the machine (milling machine) as well as the high maintenance cost, present significant drawbacks [7]. On the other hand, the manufacture of CoCr dental restorations using soft machining, also called Milling Post-Sintering (MPS) [8], can be a technically and economically viable alternative.

MPS is a powder metallurgy (PM) manufacturing technique where a solid, blank body formed from atomized powders, compacted and/or pre-sintered, is milled and subsequently followed by a final sintered step. This is performed under inert atmosphere to avoid oxidation, until reaching high levels of densification [8,9]. This technique allows to produce CoCr alloys parts when refined grains microstructure and high mechanical properties are required. It has advantages such as short production times, versatility of use and ability to process materials with special characteristics, including porosity gradients or composite materials [10–13]. Kim et al. [14] points to the biological advantages of the manufacture of CoCr material using MPS over traditional cast alloys, including lower Co ions release and higher cell viability, indicating better biocompatibility than similar alloys developed by traditional casting. The characteristics of the microstructure of the MPS alloys being free of segregation and precipitated carbides are the key to their high biocompatibility.

Previous investigations on the sinterability of CoCrMo alloy obtained by PM have been published targeting to understand the sintering mechanisms and to define process parameters for solid state sintering [9,15–17]. Daud et al. [15] characterized a CoCrMo (ASTM F75) alloy produced by solid state sintering, the material has shown a low porosity when sintered at 1300 °C – 90 min, with Vickers hardness value of 293 HV. Rodrigues et al. [9] studied the production of a CoCrMo alloy for dental implants through PM routes and found that sintering at 1280 °C – 60 min produced a dense material with dimensional stability and the best passivation behaviour in Ringer’s solution. In addition, specimens sintered at 1300 °C – 60 min acquired the highest density and hardness values. Abdullah et al. [16] analyzed the effect of sintering temperature on physical properties and hardness of CoCrMo alloy in specimens sintered at 1300 °C – 1 h, obtaining 26% of shrinkage and a hardness near 245 HV. Zhou et al. [17] studied the mechanical properties of a CoCrMo block fabricated from spherical powders (particle size from 20 μm to 50 μm). Specimens acquired tensile strength near to 640 MPa, elongation of 11% and hardness of 325 HV.

Several studies report the pressure-assisted sintering and mechanical properties of CoCrMo alloys [4,18–20]. Henriques et al. [4] produced hot pressed blocks of Co31Cr4Mo (wt.%) using powders with particle size from 4.4 μm to 12.7 μm. The specimens sintered at 1000 °C – 1 h were considered fully dense with hardness of 490 HV and rupture strength near 2350 MPa.

In this work, compacted Co-28%Cr-6%Mo (wt.%) blocks used in MPS technique to produce dental restorations were characterized in the as-received and in the sintered state using different temperatures and time conditions to determine their sinterability. The characterization was carried out by means of chemical analysis; X-ray diffraction; optical microscopy, scanning electron microscopy; dilatometry and density.

2. Materials and methods

CoCrMo blocks with approximately 90 × 60 × 10 mm³ (Ceramill Sirona®, AmannGirrbach, Austria) for CAD/CAM system were used in this work.

2.1. Characterizations of CoCrMo blocks

The chemical composition of the CoCrMo blocks was determined using X-ray fluorescence spectroscopy (XRF) (PANalytical® – Axios Advanced), carbon content was measured by the combustion method using LECO® equipment and the results were compared to ASTM F1537-11 standard [21]. Phase identification was performed by X-ray diffractometry (XRD) (Shimadzu® XRD-6000) with Mo-Kα radiation, at 40 kV and 40 mA; 2θ ranging from 18° to 40°, step size of 0.05° and counting time of 5 s per step.

Relative density was evaluated using the Archimedes principle, according to ASTM B962-14 standard [22], considering a theoretical density (ρth) of 7.89 g/cm³. The porosity was calculated [23] by the following equation:

\[
P(\%) = \left[1 - \left(\frac{ρ}{ρ_{th}}\right)\right] \times 100
\]

Scanning electron microscopy (SEM) micrographs of the materials were obtained in backscattered electron image mode (BSE) (Hitachi® TM 3000). The particles size distribution of the compacted CoCrMo blocks was estimated using ImageJ software [24]. A total of approximately 6500 particles were evaluated from 250 randomly chosen areas.

2.2. Dilatometry and sintering of CoCrMo specimens

The sinterability of the CoCrMo specimens was evaluated by dilatometry using a Linseis-L75® Platinum Series dilometer under high purity argon (min. 99.995%) flow throughout the heating and cooling cycle, adopting an heating rate of 5 °C/min and then holding at 1200 °C for 120 min. Specimens of 5 × 5 × 10 mm³ were also mechanically removed from CoCrMo blocks in vertical and horizontal directions with respect to the compaction axis, aiming to determine a possible shrinkage anisotropy. The shrinkage was measured by linear variable differential transducer (LVDT) with sensitivity of 0.01 mm.

As-received specimens of 10 × 5 × 5 mm³ were also mechanically removed from the block and then isothermally sintered at different temperatures and times as shown in Table 1, using a MoSi₂ Lindberg/Blue-M® tubular furnace. To prevent oxidation, the specimens were sealed in quartz capsules under vacuum.

2.3. Characterizations of sintered specimens

The crystalline phases present in the sintered specimens as well as the apparent density and porosity of the specimens
Table 1 – Sintering parameters used in this study.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Sintering times (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>800</td>
<td>15 60 – – 240</td>
</tr>
<tr>
<td>1000</td>
<td>15 60 – – 240</td>
</tr>
<tr>
<td>1200</td>
<td>15 60 120 180 240</td>
</tr>
<tr>
<td>1300</td>
<td>– 60 – – –</td>
</tr>
</tbody>
</table>

were determined using the same methodology applied for the CoCrMo blocks specimens (item 2.1).

Microstructural evaluation was carried out on surfaces of intentionally fractured sintered specimens using a SEM/BSE (Hitachi TM 3000®). No metallographic preparation was carried out to avoid any deformation of the pore structure. The grain size of specimens sintered at 1200 °C and 1300 °C were estimated using optical microscopy micrographs and ImageJ software [24], according to ASTM E112-14 [25]. The images were obtained in a Leica DM IRM® optical microscopy from polished and electrochemically etched samples. The etching conditions were: electrolytic solution consisting of 100 ml distilled water and 4 ml of HCl; applied voltage of 5 V for 3 s.

3. Results and discussion

3.1. Characterizations of as-received CoCrMo blocks

The XRF chemical composition analysis of the CoCrMo blocks agreed to ASTM F1537-11 standard [21], as shown in Table 2. The small amounts of C, P and Ca identified have no effect on the final use of this product as dental material. In addition, the absence of Cd, Be and Ga, that are notably harmful to health, guarantee its use as biomaterial.

Table 2 – XRF chemical analysis of CoCrMo blocks compared to ASTM F1537-11 (elements content in weight percent).

<table>
<thead>
<tr>
<th></th>
<th>Cr</th>
<th>Mo</th>
<th>Mn</th>
<th>Si</th>
<th>P</th>
<th>Fe</th>
<th>Ca</th>
<th>Al</th>
<th>C</th>
<th>Co</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-received CoCrMo blocks</td>
<td>28.44</td>
<td>5.56</td>
<td>0.88</td>
<td>0.31</td>
<td>0.18</td>
<td>0.17</td>
<td>0.12</td>
<td>0.03</td>
<td>0.15</td>
<td></td>
</tr>
<tr>
<td>ASTM F1537-11</td>
<td>26.0–30.0</td>
<td>5.0–7.0</td>
<td>0–1.0</td>
<td>0–1.0</td>
<td>–</td>
<td>0–0.75</td>
<td>–</td>
<td>&lt;0.14</td>
<td>Balance</td>
<td></td>
</tr>
</tbody>
</table>

SEM/BSE micrographs from as-received CoCrMo compacted block (Fig. 1(a) and (b)) show near spherical particles of different diameters without indication of neck formation. The particle size distribution of the compacted block (Fig. 2) was found to be asymmetric and monomodal, with 61% of the particles having an average size smaller than 2 μm, 37% of the particles with a mean size between 2 μm and 6 μm and about 2% of the particles with a diameter greater than 6 μm, the latter responsible for most of the material’s volume.

The particle size distribution of the CoCrMo blocks used in CAD/CAM milling systems is an important parameter to be considered in the development of blocks for MPS. In general, small particle sizes reduce the final sintering temperature because there is an increase in the total specific surface area, increasing the reactivity of the powders and consequently their sintering [26]. The particle size distribution should privilege different particle sizes. In such a way that it is allowed the maximum filling of the voids in the interstices of the larger particles by small particles, in order to increase the packaging factor, and consequently the green density of the compact [27,28].

In this work, the compacted block presented a relative green density near 57 ± 1% of the theoretical density and the micrographs presented in Fig. 1 indicate that the particle size distribution allowed a high packaging of the block. Furthermore, a secondary gain associated with this high green density is a greater machinability in the manufacture of dental prostheses, in addition to lower wear of the milling cutters during manufacturing [29].

Fig. 3 shows XRD patterns of as-received compacted CoCrMo block and sintered specimens. The as-received material (Fig. 3(a)) is γCo(FCC) single phase, indicating formation of cobalt solid solution (Co_{m}), which contains Cr and Mo in substitutional solid solution. The presence of this phase is in agreement with the isothermal section of the Co-Cr-Mo system at 1300 °C [30], which proposes γCo(FCC) at high temperature for this composition. This phase should have been formed primarily during solidification of the liquid droplets from Spray Atomization Technique and it is present at room temperature in a metastable condition, because the phase transformation kinetics of γCo(FCC) ↔ εCo(HCP) is extremely sluggish [31,32].

![Fig. 1 – SEM/BSE micrographs of as-received CoCrMo compacted block.](image-url)
3.2. Dilatometry

Fig. 4 shows plots of shrinkage \((dL/L_0) \times \) temperature \(^{(\circ C)}\) and shrinkage rate \((dL/dt) \times \) temperature \(^{(\circ C)}\) from the experiments of dilatometry. As shown in Fig. 4(a), up to 815 \(^{\circ}\)C thermal expansion occurs for both specimens (vertical and horizontal). It is possible to observe a small variation in expansion of the specimens, which is evidenced by evaluating the shrinkage rate (Fig. 4(b)). This behaviour can be related to the initial characteristics of the CoCrMo particles that present spherical format with wide particle size distribution. Below 815 \(^{\circ}\)C the sintering process of the CoCrMo alloy should have exhibited only adhesion between particles. It is also possible to verify that at 815 \(^{\circ}\)C a small variation of the absolute values of linear shrinkage \((dL/L_0)\) is observed, which indicates that the compact presented some anisotropy, caused by the compacting process of the powders.

Starting at 815 \(^{\circ}\)C, the initial sintering stage begins with the formation and growth of necks. At this stage, considerable shrinkage is not observed because the neck formation process is governed initially by the evaporation/condensation mechanism on the surfaces of the particles, with subsequent mass transport by the surface. In addition, the chemical species of the alloy should present low diffusivities at these temperatures, not allowing high shrinkage rates. This initial sintering stage should occur up to approximately 940 \(^{\circ}\)C according to data in Fig. 4(a).

The intermediate sintering stage should start at 940 \(^{\circ}\)C and was characterized by the increase of the shrinkage rates \((dL/dt)\) due to the heterogeneous distribution of CoCrMo spherical particles. At this stage the necks between particles are elongated, the pores become spheroidal and the channels are closed. The open porosity should practically disappears. For higher temperatures, significant bulk mass transport takes place through plastic flow, grain boundary diffusion and volume diffusion in the solid-state sintering process [26]. The maximum shrinkage rates were observed at 1156 \(^{\circ}\)C and 1200 \(^{\circ}\)C for vertical and horizontal specimens, respectively (Fig. 4(b)).

3.3. Characterizations of sintered CoCrMo specimens

The XRD patterns of the CoCrMo specimens isothermally sintered at 800, 1000, 1200 and 1300 \(^{\circ}\)C (Fig. 3(b)-(e)) for 60 min show a small fraction of f-Co\((HCP)\), which should have been formed by martensitic \(\gamma\)Co\((FCC) \leftrightarrow f\)Co\((HCP)\) phase transformation [32-35]. Similar results were observed for the other specimens sintered at 800, 1000 and 1200 \(^{\circ}\)C for 15, 120 and 240 min. 

Fig. 5 exhibits the relative density of the specimens sintered in different temperatures and isothermal holding times. Sintering at 800 and 1000 \(^{\circ}\)C did not cause an important densification of the specimens, with a relative density of less than 70% regardless of the sintering time used. In agreement with the dilatometry results at 800 and 1000 \(^{\circ}\)C, the sintered specimens exhibited small shrinkage rates, indicating that the energy supplied to the specimens has activated mainly surface diffusion mechanisms.

However, sintering at 1200 and 1300 \(^{\circ}\)C promoted a high densification and a measurable linear shrinkage, evidencing the activation of mass diffusion mechanisms during sintering.
The specimen sintered at 1200 °C for 15 min. presented 70.2 ± 0.4% of theoretical density with 6.5 ± 0.7% of linear shrinkage while the specimen sintered at 1200 °C for 240 min. has shown 90.3 ± 0.5% of theoretical density and 10.8 ± 0.7% shrinkage. These results evidenced an important influence of sintering time on these properties, as shown in Fig. 6. Song et al. [32] have found approximately 79% and 81% of relative density for one hour sintering time at 1200 and 1300 °C, respectively, which are close to the results obtained in this study.

The results of porosity as a function of the sintering conditions indicate porosities values higher than 20% for all specimens sintered at 1200 °C for dwell times lower than 180 min as well as for the specimens sintered at 1300 °C – 60 min. Only the specimens sintered at 1200 °C – 240 min reached a porosity near 9.7%.

The tensile strength of CoCrMo alloys is significantly reduced by the presence of porosity in the sintered material, which reduces the effective load carrying capacity of the dental prosthesis. An analytical model proposed by Gibson and Ashby [36] describes the relationship between tensile strength and relative density as:

$$\frac{\sigma}{\sigma_0} = C \left( \frac{\rho}{\rho_0} \right)^n$$  \hspace{1cm} (2)

where $\sigma$ and $\sigma_0$ are the tensile strength of a sintered specimen and a fully dense alloy, respectively, $(1 - \rho/\rho_0)$ is the porosity, C and n are constant characteristics of the material that depend on its structure.

Fig. 3 – X-ray diffraction patterns of: (a) as-received CoCrMo compacted block; sintered specimens at (b) 800 °C/60 min, (c) 1000 °C/60 min, (d) 1200 °C/60 min, (e) 1300 °C/60 min.
The requirements of mechanical strength of ceramic materials used in the coating of metal-ceramic prosthesis indicate that a strength of more than 300 MPa is required for the use of this alloy in the manufacture of single-piece prostheses and 500 MPa for the preparation of multicomponents prostheses of up to 3 elements involving molars [37]. Considering that the tensile strength indicated by manufacturers of fully dense CoCrMo alloys is of the order of 900 MPa, the porosity values can serve as a guide for the prediction of the tensile strength of the sintered parts under different sintering
conditions, allowing the identification of possible use for the prosthesis obtained by MPS. However, it should be pointed out that some porosity is important for a better adhesion of the ceramic veneering.

Fig. 5 – Relative density of CoCrMo as function of sintering temperature and isothermal holding time.

Fig. 6 – Linear shrinkage (%) x sintering times of the specimens sintered at 1200 °C.

Fig. 7(a) presents the microstructure of all specimens sintered at 800 °C, evidencing an initial stage of solid-state sintering by neck formation, specially involving the smaller particles. As expected, the number of necks formed increased for longer sintering times (240 min). As informed above, the

Fig. 7 – SEM/BSE micrographs illustrating the stages of solid-state sintering of the specimens: (a) 800 °C – 240 min, (b) 1000 °C – 240 min, (c) 1200 °C – 240 min and (d) 1300 °C – 60 min.
block particles had different diameters, the energy associated with the particles curvature is higher for the smaller particles, producing a flow of atoms from the smaller to the larger particles, which leads to neck formation. As the necks are small compared to the particles size, the main mass transport mechanism should have been through surface diffusion instead of evaporation and condensation. The particles lose the spherical shape when the material is sintered at 1000 °C, as shown in Fig. 7(b) for the specimen sintered at 1000 °C for 240 min. It was also noted that all particles were interconnected through necks that are larger than those formed in the specimens sintered at 800 °C, suggesting that some bulk

Fig. 8 – Optical and SEM/BSE micrographs (inserts) from flat polished specimens sintered at 1200 °C: (a) 60 min, (b) 120 min, (c) 180 min and (d) 240 min, (e) 240 min; 1300 °C: (f) 60 min.
mass transportation mechanism has taken place, even though no measurable macroscopic shrinkage has been detected. At even higher sintering temperatures, no indication of the initial block microstructure could be observed, as depicted in Fig. 7(c) and (d) for the specimens sintered at 1200 and 1300 °C. The important shrinkage of these specimens, as discussed previously, is explained by the activation of mass transport mechanisms (bulk transport) promoting atom migration from the particles interior towards the necks, in addition to the movement of vacancies in the opposite direction. The vacancies are then eliminated at the surface, resulting in the shrinkage of the material.

Optical micrographs from flat polished specimens sintered at 1200 and 1300 °C, are shown in Fig. 8. They suggest an important densification with well-defined grain boundaries in most of them. Notice in Fig. 8(d) and (e) the presence of bands consisting of either twins or $\gamma$Co$_{6}$[$\text{NiCr}$] phase [38]. The black spots correspond to carbides formed during solidification, pores or regions corroded by etching.

SEM/BSE micrographs from flat polished are also given in Fig. 8, they suggest a matrix of $\gamma$Co$_{9}$[$\text{Cr}$] with carbides distributed throughout for all specimens sintered at 1200 °C up to 4 h. It should be noticed a trend for complete carbide dissolution for longer times. For the specimen heat-treated at 1300 °C for 1 h, no indication of carbides is noted. These results are in agreement with thermodynamic calculation using ThermoCalc and data from Kaplan et al. [39]. These authors propose the possible formation of $\text{M}_{23}\text{C}_{6}$ and $\text{M}_{7}\text{C}_{3}$ carbide during solidification and $\text{M}_{7}\text{C}_{3}$ during heat treatments in the temperature range of 800 – 1160 °C, based on thermodynamic data from the Co-Cr-C system. However, several studies [40–42] show that Mo addition promotes the formation of the $\text{M}_{6}\text{C}$ type carbide in addition to $\text{M}_{23}\text{C}_{6}$ and $\text{M}_{7}\text{C}_{3}$.

Fig. 9 shows the grain growth behaviour from specimens sintered at 1200 and 1300 °C as function of isothermal sintering time. As expected, longer sintering times and higher temperatures lead to larger grain size [33,34,43]. The specimen sintered at 1200 °C for 60 min had a grain size of 4.9 ± 1.3 µm and the one sintered for 240 min had a grain size of 28.4 ± 11.3 µm. Specimens sintered at 1300 °C display the highest grain size (88.6 ± 16.7 µm), as shown in Fig. 8(f).

4. Conclusions

This work investigated the sinterability of compacted commercial CoCrMo blocks of composition Co-28%Cr-6%Mo for dental prosthesis. The particles in the as-received condition presented spherical shape with 98% of them below 6 µm.

From the dilatometric experiments, it was observed that the shrinkage of the materials starts at 815 °C, however, no significant densification was observed up to 1000 °C. The highest densification condition (90%) was observed for the specimens sintered at 1200 °C for 240 min, the only one exhibiting characteristics of final stage of solid-state sintering.

Conflicts of interest

The authors declare no conflicts of interest.

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