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Title: Structural characterization of biomedical Co-Cr-Mo components produced by Direct Metal Laser Sintering

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Keywords: metals and alloys; laser processing; sintering; transmission electron microscopy, TEM; scanning electron microscopy, SEM; X-ray diffraction.

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Abstract: Direct Metal Laser Sintering (DMLS) is a technique to manufacture complex functional mechanical parts from a computer-aided design (CAD) model. Usually, the mechanical components produced by this procedure show higher residual porosity and poorer mechanical properties than those obtained by conventional manufacturing techniques.

In this work, a Co-Cr-Mo alloy produced by DMLS with a composition suitable for biomedical applications was submitted to hardness measurements and structural characterisation. The alloy showed a hardness value remarkably higher than those commonly obtained for the same cast or wrought alloys. In order to clarify the origin of this unexpected result, the samples microstructure was investigated by X-ray diffraction (XRD), electron microscopy (SEM and TEM) and energy dispersive microanalysis (EDX). For the first time, a homogeneous microstructure comprised of an intricate network of thin ϵ (hcp)-lamellae distributed inside a γ (fcc) phase was observed. The ϵ -lamellae grown on the $\{111\}\gamma$ planes limit the dislocation slip inside the γ (fcc) phase, causing the measured hardness increase. The results suggest possible innovative applications of the DMLS technique to the production of mechanical parts in the medical and dental fields.

Highlights

- Samples of a Co-Cr-Mo biomedical alloy were produced by direct metal laser sintering.
- Samples show hardness values unexpectedly high.
- Samples were investigated by X-ray diffraction and electron microscopy techniques.
- A fine structure composed of ϵ -phase lamellae formed inside the γ -phase was observed.
- The correlation between microstructure and mechanical properties was identified.
- Results suggest important applicative potential of the production technique in the medical field.

1 **Structural characterization of biomedical Co-Cr-Mo**
2 **components produced by Direct Metal Laser Sintering**

3
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18

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- 24 • Results suggest important applicative potential of the production technique in the medical
- 25 field.

26 **ABSTRACT**

27 Direct Metal Laser Sintering (DMLS) is a technique to manufacture complex functional
28 mechanical parts from a computer-aided design (CAD) model. Usually, the mechanical
29 components produced by this procedure show higher residual porosity and poorer mechanical
30 properties than those obtained by conventional manufacturing techniques.

31 In this work, a Co-Cr-Mo alloy produced by DMLS with a composition suitable for biomedical
32 applications was submitted to hardness measurements and structural characterisation. The alloy
33 showed a hardness value remarkably higher than those commonly obtained for the same cast or
34 wrought alloys. In order to clarify the origin of this unexpected result, the samples microstructure
35 was investigated by X-ray diffraction (XRD), electron microscopy (SEM and TEM) and energy
36 dispersive microanalysis (EDX). For the first time, a homogeneous microstructure comprised of
37 an intricate network of thin ϵ (hcp)-lamellae distributed inside a γ (fcc) phase was observed. The
38 ϵ -lamellae grown on the $\{111\}_{\gamma}$ planes limit the dislocation slip inside the γ (fcc) phase, causing
39 the measured hardness increase. The results suggest possible innovative applications of the
40 DMLS technique to the production of mechanical parts in the medical and dental fields.

41

42

43 **KEYWORDS:** metals and alloys; laser processing; sintering; transmission electron
44 microscopy, TEM; scanning electron microscopy, SEM; X-ray diffraction.

45

46 **1. INTRODUCTION**

47 Nowadays, a new class of manufacturing methods are becoming increasingly important for the
48 production of biomedical devices. Among them, novel methods based on additive manufacturing
49 (AM), assisted by computer-aided design/computer-aided manufacturing (CAD/CAM), allow the
50 production of intricate mechanical parts [1-4].

51 Direct metal laser sintering (DMLS) is an AM process that uses the heat of a solid state laser to
52 sinter metal powder particles [5]. In this case, a distribution mechanism pre-places successive
53 layers of powder on a suitable substrate, while a laser beam controlled by a scanning system
54 locally sinters the powder in accordance with the CAD model [6]. This technology, like other
55 AM procedures, is highly rewarding in medicine where a high degree of personalization is
56 required [7-9]. Prosthetic applications are particularly well suited for processing by means of
57 DMLS due to their complex geometry, low volume and strong individualization [10].
58 Furthermore, the manufacturing of multiple unique parts in a single production run enables
59 extensive customization with a strong reduction of manual operation leading to higher
60 repeatability and good savings in money and delivery times.

61 Cobalt-based alloys were extensively used in cast and hard facing forms over the past twenty
62 years because of their corrosion and wear resistance, biocompatibility and excellent strength and
63 toughness at high temperature [11]. Typical applications of the Co-based alloys involved both
64 the biomedical and the metallurgical fields [12, 13].

65 From a structural point of view, cobalt is characterized by a ϵ (hcp) low temperature phase and a
66 γ (fcc) phase at higher temperature. The addition of chromium improves the corrosion and the
67 oxidation resistance of the alloy, as well as its hardness, ductility and wear resistance through

68 carbide formation. Molybdenum improves the corrosion resistance and acts as a solid-solution
69 strengthener by forming the Co_3Mo (hcp) intermetallic compound [14].

70 Cast alloys with a Cr content ranging from 19 wt% to 30 wt% and a Mo content in the range 5-
71 10 wt% were considered for biomedical applications and for many years these compositions
72 were used to produce medical implants such as hips, knees, ankles and bone plates [15].

73 Although in the past few years, several AM techniques were applied to produce biocompatible
74 Co-based alloys, only in few cases a deep microstructural characterisation of the sintered
75 components were performed. In particular, Gaytan et al. reported on the microstructure and the
76 mechanical properties of Co-based prototypes produced by electron beam melting. In this study,
77 they found high hardness values attributed to the formation of an ordinate array of metal carbides
78 [16]. Meacock et al. investigated the microstructure and the mechanical properties of a
79 biomedical Co-Cr-Mo alloy produced by laser powder microdeposition [17]. They observed a
80 homogenous microstructure comprised of fine cellular dendrites and measured an average
81 hardness value of 460 $\text{HV}_{0.02}$, well higher than the typical values obtained by other fabrication
82 processes. From these results, they concluded that the fine morphology is responsible of the
83 significantly increased hardness value.

84 Few other papers deal with the possibility of realizing medical parts of a Co-Cr-Mo alloy by
85 DMLS, but it is worth to note that none of them reports the correlation of the samples
86 microstructure to the mechanical properties of the final components [19-21].

87 The mechanical properties of the sintered components are strictly linked to the samples
88 microstructure and are one of the major aspects connected to the practical applications of the AM
89 procedures. Usually, objects produced by metal powder sintering show poorer mechanical
90 properties than those produced by conventional procedures. This behaviour is mainly due to the

91 fact that DMLS, depending on the laser energy density employed, involves a partial or total
92 melting of the powder. Therefore, the products made by DMLS could show high surface
93 roughness, porosity (in certain cases even lack of densification), heterogeneous microstructure
94 and thermal residual stresses, that may give rise to poor mechanical properties [22].

95 In this paper, metallic components of a biocompatible Co-Cr-Mo alloy produced by the DMLS
96 technique were deeply investigated in order to correlate their mechanical properties to the
97 corresponding microstructure. To this aim, hardness measurements, X ray diffraction (XRD)
98 analysis, electron microscopy (SEM, TEM) observations and energy dispersive microanalysis
99 (EDX) were performed on the samples. Results evidenced a surprisingly high hardness value of
100 the investigated Co-Cr-Mo alloy in comparison of the hardness values commonly reported in
101 literature for similar compositions. This unexpected result was attributed to the peculiar
102 microstructure observed in the analysed samples, that, to our knowledge, was never reported
103 before.

104

105 **2. MATERIALS AND METHODS**

106 2.1 Material composition and sintering parameters

107 Specimens were prepared by direct metal laser sintering using a Yb (ytterbium) fiber laser
108 system (EOSINT-M270) operating with the standard deposition parameters reported in Table1.

109

Table 1. *Parameters used for DMLS*

laser power	200W
laser spot diameter	0.200 mm
Scan speed	up to 7.0 m/s
Building speed	2-20 mm ³ /s
Layer thickness	0.020 mm
Protective atmosphere	max 1.5% oxygen

110

111 A Co-Cr-Mo alloy powder (EOS Cobalt/Chrome SP2) with the nominal composition (in wt%)
112 Co 63.8, Cr 24.7, Mo 5.1, W 5.4 , Si 1.0, was used as raw material. The powder is free of Ni, Be
113 and Cd according to EN ISO 22674. The nominal composition was provided by the manufacturer
114 (EOS GmbH Electro Optical Systems). The powder is the EOS Cobalt/Chrome SP2 cobalt based
115 metal ceramic alloy intended for production of Porcelain-Fused to Metal (PFM) dental
116 restorations (crowns, bridges, etc.) in EOSINT M 270 Standard installation mode. The powder is
117 class IIa medical device in accordance with annex IX rule 8 of the MDD 93/42/EEC.
118 Composition corresponds to “type 4” CoCr dental material according to EN ISO 22674.

119 Rectangular parallelepipeds with size 250 mm x 4 mm and a thickness of 6 mm were sintered by
120 using the parameters reported in Table 1. In order to minimize anisotropy, each layer was built
121 with the laser scanning along a specific direction. Layer-by-layer the scanning direction was
122 rotated by 25° with respect to the previous one.

123

124 2.2 Hardness measurements

125 Hardness tests were performed on the sintered samples using the Rockwell scale C
126 (specifications ISO 4498 : Sintered metal materials, excluding hard metals - Determination of
127 apparent hardness and microhardness). Measurements were obtained averaging five indentations
128 following ISO 6508: Rockwell hardness test.

129

130 2.3 Structural characterisation

131 Structural and microstructural characterizations were carried out by X-ray diffraction (XRD),
132 scanning (SEM) and transmission (TEM) electron microscopy techniques.

133 XRD measurements were performed by a Bruker D8 Advance diffractometer operating with a
134 Cu-K α radiation source at V= 40kV and I= 40 mA in the angular range $2\theta=10 - 90^\circ$.

135 SEM analyses were carried out by a ZEISS SUPRA 40 microscope equipped with a Bruker
136 Quantax energy dispersive X-ray microanalysis (EDX). Observations were performed on both
137 the as-received metallic powder and cross-sectioned sintered samples. Before observations,
138 samples surfaces were prepared using a conventional metallographic procedure and
139 electrochemically etched in the following conditions: HCl 0.1 M, 2V, 2 min.

140 TEM analyses were carried out by a Philips CM200 electron microscope operating at 200 kV
141 and by a JEOL JEM-2010 ARP microscope equipped with an Oxford Inca energy dispersive X-
142 ray microanalysis (EDX). For TEM observations, samples were prepared by the conventional
143 thinning procedure consisting of mechanical polishing by grinding papers, diamond pastes and a
144 dimple grinder. Final thinning was carried out by an ion beam system (Gatan PIPS) using Ar
145 ions at 5 kV.

146

147 **3. RESULTS**

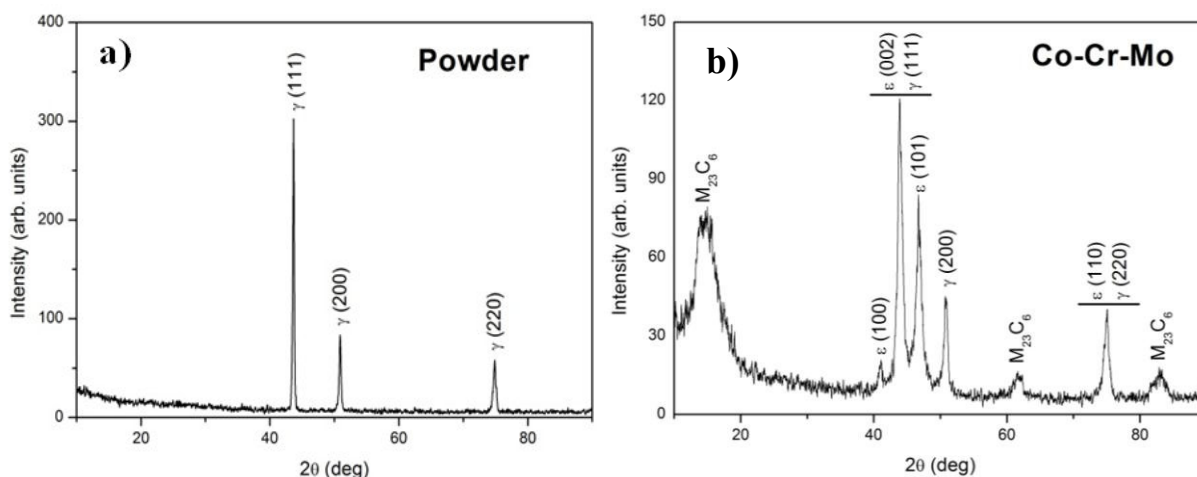
148 3.1 Hardness

149 The average Rockwell C hardness (HRC) value measured for the laser sintered samples is 47
150 HRC, a very high value considering that the usual range for cast Co-Cr-Mo alloys is from 25 to
151 35 HRC.

152

153 3.2 X-ray diffraction (XRD)

154 X-ray diffraction measurements were performed on both the Co-Cr-Mo powder used as raw
155 material for the DMLS process and on the different regions of the sintered samples (Fig. 1).



156 **Fig. 1.** X-ray diffraction patterns: a) as-received metallic powder; b) sintered sample.

157

158 Fig. 1a reports the XRD pattern of the as-received metallic powder. All the visible peaks can be
159 attributed to the cubic cobalt phase, commonly referred to as γ phase. The γ phase has a face
160 centred cubic (fcc) lattice with a nominal parameter $a=0.35447$ nm (ICDD card n. 15-806). For
161 the alloy under study, the best fit performed by using the three diffraction peaks of Fig. 1a
162 provides a lattice parameter value $a=0.3586$ nm, in close agreement with the values reported in
163 literature for alloys of similar composition [23].

164 The XRD pattern of the sintered sample is shown in Fig. 1b. The most intense and well-defined
165 peaks are a result of the simultaneous presence of both γ and ϵ cobalt phases, as indicated in Fig.
166 1b where each diffraction peak is indexed with the name of the corresponding Co phase. A
167 double indexation is reported for the most intense peak at $2\theta=43.94^\circ$ and the peak at $2\theta=75.09^\circ$
168 because of the superposition of the reflections due to the ϵ and γ phases. The ϵ phase has a
169 hexagonal close packed (hcp) lattice with nominal parameters $a=0.25031$ nm and $c=0.40605$ nm
170 (ICDD card n. 5-727). By using the ϵ (100) and ϵ (101) peaks of the XRD pattern shown in Fig.
171 1b, the lattice parameters of the hexagonal ϵ phase formed in our alloy were determined to be
172 $a=0.2539$ nm and $c=0.4122$ nm with a c/a ratio of 1.623. The lattice parameter of the fcc γ phase
173 formed in the sintered sample evaluated by the γ (200) peak of Fig. 1b is $a=0.3589$ nm. Also in
174 this case, the calculated lattice parameters for the ϵ and γ phases formed in our alloy are in close
175 agreement with those reported in literature for similar compositions [23].

176 In order to estimate the volume fraction of the hcp and fcc cobalt phases in the sintered sample,
177 the integrated intensities of the γ (200) and ϵ (101) peaks were used. The quantitative
178 determination, performed by using the method of Sage and Gillaud [24], resulted in an ϵ -phase
179 volume fraction $f_{\text{hcp}}=0.49\pm 0.03$.

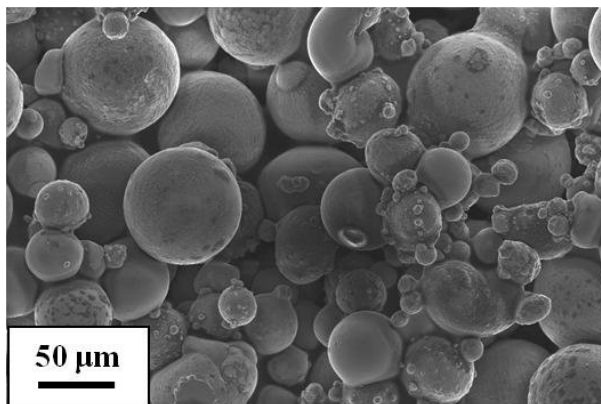
180 In addition to the ϵ and γ peaks in Fig. 1b, three broad peaks attributable to metals carbides are
181 also visible. These latter peaks generically indexed as M_2C_6 ($M=Cr, Co, Mo, W$) are due to
182 metal carbides having the cubic structure of the Cr_23C_6 compound (ICDD card n. 35-783).

183

184 3.3 Scanning electron microscopy (SEM) and microanalysis (EDX)

185 Scanning electron microscopy observations were performed on the as-received powder and on
186 the sintered samples. Particles forming the metallic powder are shown in Fig. 2.

187 From the SEM images the average size of the spherical particles were evaluated. Measurements
188 were performed by averaging the data obtained from different areas of the samples. Results
189 showed that the size of the particles ranges from 4 to 80 μm .



190 **Fig. 2.** SEM image of the as-received metallic powder.

191 EDX analysis performed on the powder showed a chemical composition in agreement with the
192 nominal composition of the alloy reported above. In Table 2 the experimental values obtained
193 from the EDX analyses performed on the powder and on the sintered sample are reported.

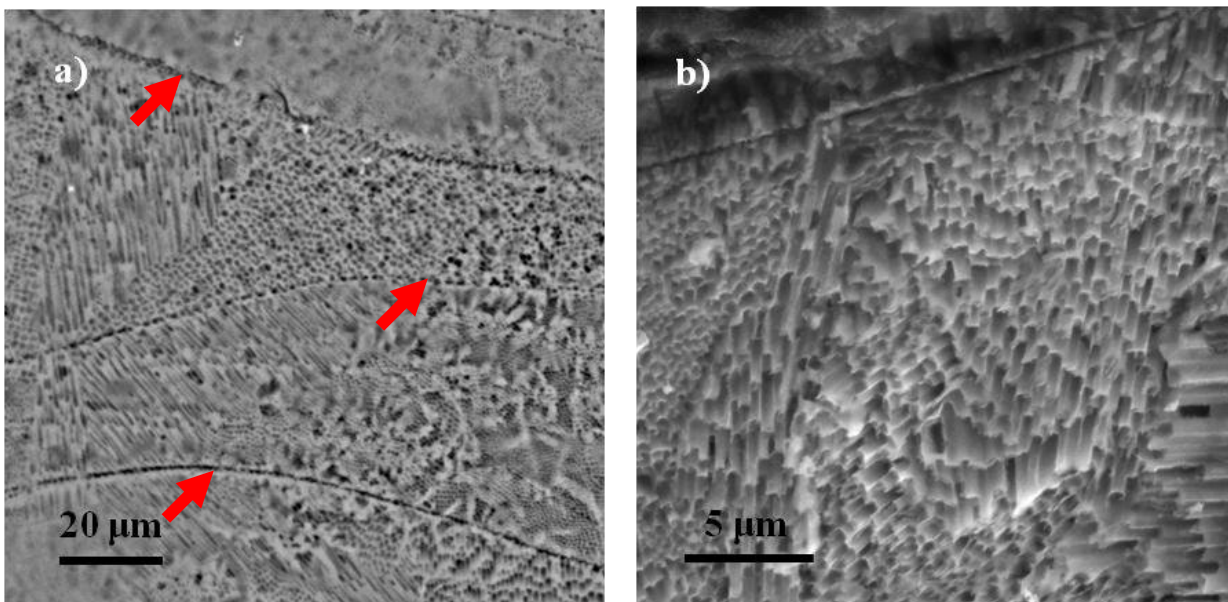
194
195 **Table 2.** Experimental results of the EDX microanalysis performed on both the powder and the
196 sintered sample.

Element	Powder (wt%)	Sintered sample (wt%)
Co	62	63
Cr	26	26
Mo	5	6
W	4	4
Si	1	1

197

198 It is worth to note that the average composition of the powder and the sintered sample is almost
199 the same, as can be inferred from Table 2.

200 The inner structure of the sintered samples, as observed by SEM, is shown in Fig. 3. Samples
201 were sectioned parallel to the laser beam direction, and SEM observations were performed after
202 a metallographic preparation of the surfaces followed by an electrochemical etching. The lines
203 separating the different weld pools produced by the laser scan on each layer are evidenced by
204 arrows in the image taken at low magnification, Fig. 3a.



205 **Fig. 3** SEM images of the sintered samples. a) low magnification: lines separating different weld
206 pools are arrowed; b) high magnification.

207
208 Observations performed at higher magnification allow to evidence the presence of an extremely
209 fine microstructure inside a single pool, Fig. 3b. Columnar structures, with diameters ranging
210 from 300 to 400 nm and heights from 4 to 8 μm , grow inside the matrix in form of domains. The
211 orientation of the columns is the same inside a single domain while it changes from one domain
212 to the other. In order to estimate the area fraction occupied by the columnar structures relative to

213 the matrix, several SEM images were processed by using an image analysis software [25]. An
214 area fraction of $45\pm 5\%$ was provided by software. This value, as a rough approximation, can be
215 considered as the volume fraction of the columnar structures relative to the rest of the sample.

216

217 3.4 Transmission electron microscopy (TEM) and microanalysis (EDX)

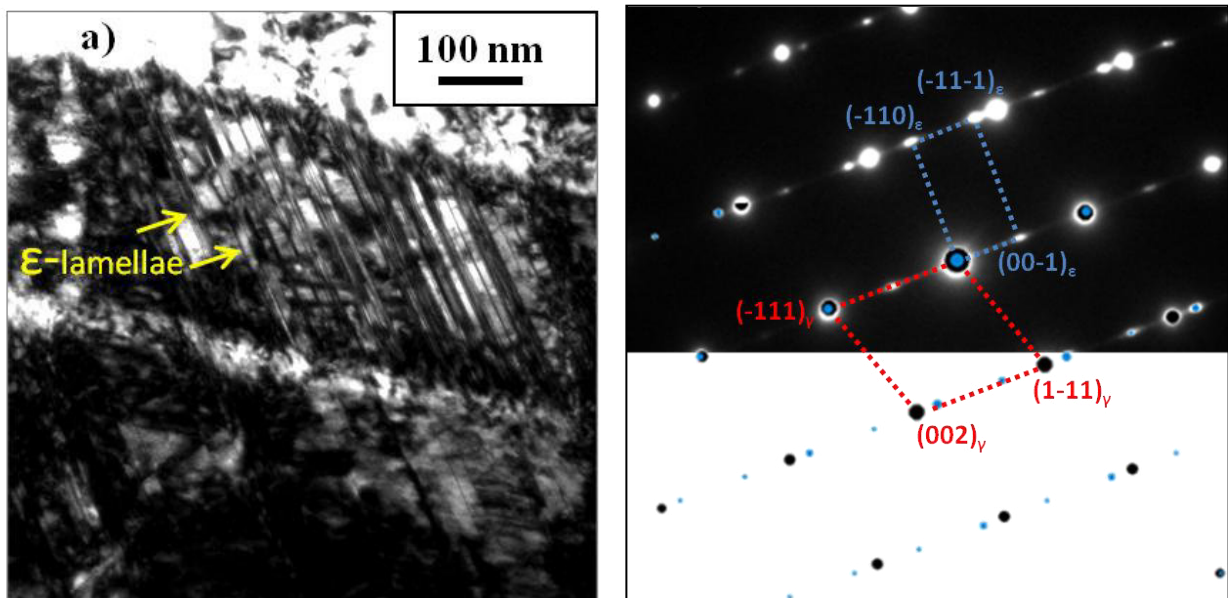
218 TEM observations of the sintered samples confirm the presence of the two ϵ and γ cobalt phases.

219 The ϵ phase forms as small lamellae inside the γ phase. The thickness of the ϵ phase lamellae is

220 1-2 nm, but in some cases, they tend to aggregate in the same region of the sample forming

221 alternate structures of ϵ and γ phases with lateral dimensions of up to 400 nm.

222



223 **Fig. 4.** Sintered sample: a) TEM bright field image of the ϵ lamellae inside the γ phase

224 (arrowed); b) SAD pattern taken in the same area in $\langle 110 \rangle_\gamma$ zone axis orientation (upper part)

225 and corresponding software simulation (lower part). In red is indicated the cell of the γ -Cobalt

226 phase and in blue the cell of the ϵ -Cobalt phase.

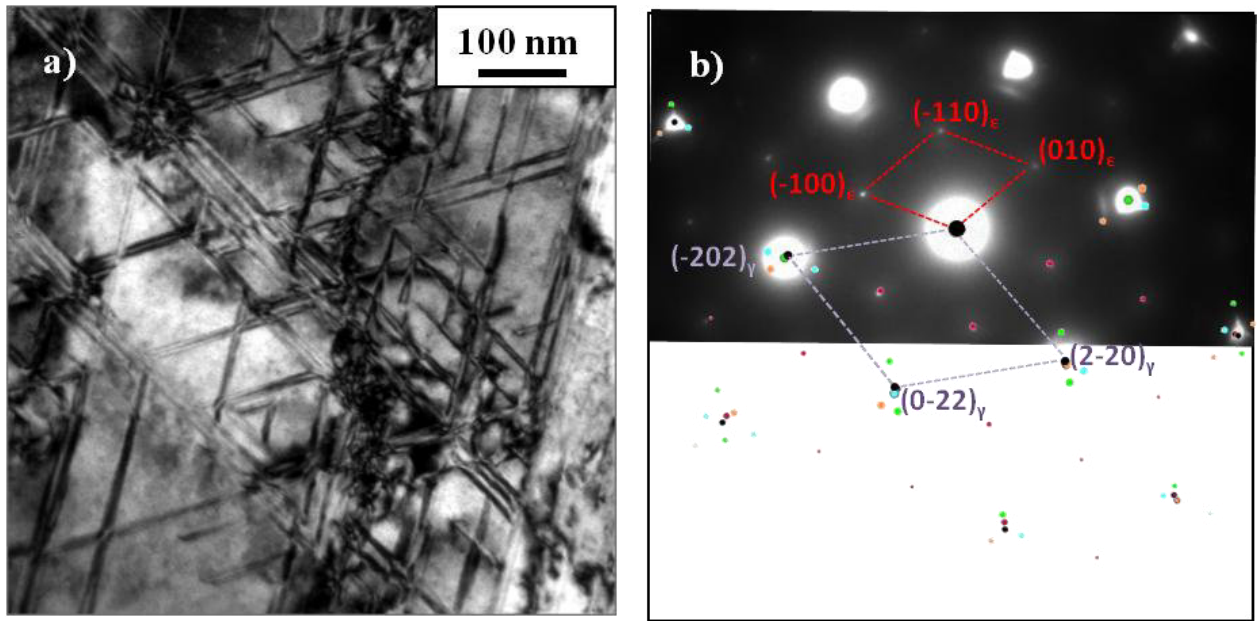
227

228 In Fig. 4a, taken in $\langle 110 \rangle_\gamma$ zone axis orientation, the lamellar structure is clearly visible. The
229 lamellae are parallel to each other, and the distance between them is not constant. Considering
230 the ensemble of these lamellae, it is possible to envisage one of the columnar structures visible in
231 the SEM images. The corresponding selected area diffraction (SAD) pattern is reported in the
232 upper part of Fig. 4b while its simulation performed with the CrystalKitX software [26] is shown
233 in the lower part of Fig. 4b. The remarkable agreement between the simulated pattern and the
234 experimental one is evident. The most intense spots visible in Fig. 4b (top) are a result of the fcc
235 γ -phase (red cell) while the smaller ones are a result of the hcp ε -phase (blue cell). The geometry
236 of the spot distribution in the SAD pattern of Fig. 4b (top) reveals that the ε lamellae form with
237 the following orientation relationships with the γ matrix:

$$\begin{aligned} 238 \quad & \{001\}_\varepsilon // \{111\}_\gamma \\ 239 \quad & \langle 100 \rangle_\varepsilon // \langle 1-10 \rangle_\gamma \end{aligned}$$

240 Furthermore, as can be observed in Fig. 4b (top), the spots of the ε phase are streaked in direction
241 of the $\{111\}_\gamma$ spots indicating that the lamellae grow on the $\{111\}_\gamma$ lattice planes and have a
242 small thickness in the $\langle 111 \rangle_\gamma$ lattice direction.

243 In order to investigate the spatial distribution of the hcp lamellae in greater details, TEM
244 observations were also performed in the $\langle 111 \rangle_\gamma$ zone axis orientation.



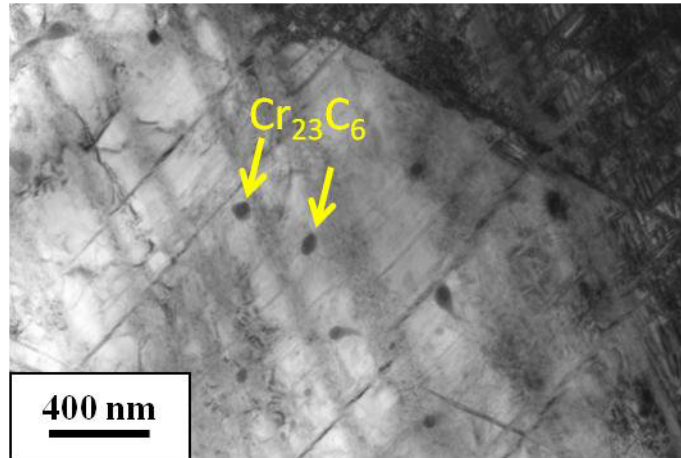
245 **Fig. 5.** Sintered sample: a) bright field TEM image taken in $\langle 111 \rangle_\gamma$ zone axis orientation; b)
 246 corresponding SAD pattern (upper part) and software simulation (lower part). In red is
 247 indicated the cell of the ϵ -Cobalt phase in one of the four possible orientations on the $\{111\}_\gamma$
 248 lattice planes, and in violet the cell of the γ -Cobalt phase.

249

250 A bright field image of the sample in this orientation is shown in Fig. 5a. Lamellae and stacking
 251 faults lying on different $\{111\}_\gamma$ lattice planes are visible and form an intricate network. The
 252 corresponding SAD pattern, with the simulation performed by the CrystalKitX software, are
 253 shown in the upper and lower part of Fig. 5b, respectively. The SAD pattern was simulated
 254 considering the four possible orientations of the ϵ phase on the $\{111\}_\gamma$ lattice planes. Different
 255 colours correspond to different orientations. In particular the diffraction spots corresponding to
 256 the $(001)_\epsilon // (111)_\gamma$ orientation were indexed in Fig. 5b and indicated with the red cell.

257 It must be stressed that all the SAD patterns, taken even in other orientations, never showed the
 258 presence of twins reflections ($1/3 \langle hkl \rangle$), although at a first glance the ϵ lamellae could be
 259 confused with microtwins.

260 TEM observations performed on the sintered samples also revealed the presence of small
261 quantities of precipitates uniformly distributed. Precipitates, visible as dark dots inside the matrix
262 in Fig. 6, have a spherical or elliptical shape with size ranging from 50 to 300 nm.



263 **Fig. 6.** TEM bright field image of the sintered sample showing the presence of some metal
264 carbides (arrowed).

265
266 In order to investigate the chemical composition of these precipitates, EDX measurements were
267 performed. Results show an increase of the Cr, W and Mo content in the precipitates with respect
268 to the matrix, while the precipitates composition remains almost the same independently of their
269 shape, Table 3. The crystallographic nature of the precipitates was investigated by the SAD
270 technique. Results are compatible with the presence of a phase having the $Cr_{23}C_6$ lattice
271 structure.

272 **Table 3.** *Experimental results of the EDX measurements performed on both the matrix and the*
273 *precipitates.*

Element	Matrix (wt%)	Precipitates (wt%)
Co	63	52
Cr	24	26
Mo	5	11
W	6	10
Si	1	1

274

275 **4. DISCUSSION**

276 The hardness values of the laser sintered samples are surprisingly high, considering the method
277 used for their realization. Generally, components produced by an additive manufacturing
278 technique, such as the Direct Laser Metal Sintering procedure used in this work, can be affected
279 by residual porosity and show poorer mechanical properties than those obtained by traditional
280 manufacturing techniques [22]. In our case, however, hardness results to be remarkably high,
281 even if compared to the same cast or wrought alloy. The explanation of this result is linked to the
282 inner structure of the samples, as will be discussed below. Furthermore, it must be stressed that
283 hardness is only one of the mechanical properties playing an important role in material selection
284 for application in the human body [12]. Other quantities such as tensile strength, Young's
285 modulus and elongation must be considered when the application range of a biomaterial is
286 involved. On the other hand, Murr et al. demonstrated the possibility to set the Young's modulus
287 of femoral component constituted of a Co-29Cr-6Mo alloy by opportunely developing mesh and

288 foam implant prototypes produced by an additive manufacturing technique [27]. This means that
289 the implant design influences also its final mechanical properties.

290 X-ray diffraction results show a phase transformation connected to the laser treatment. In
291 particular, while the powder is exclusively composed of the γ (fcc) cobalt phase, the sintered
292 sample contains both the γ (fcc) and ϵ (hcp) phases. Cobalt-based alloys undergo an fcc \leftrightarrow hcp
293 martensitic transformation. The equilibrium temperature between the high-temperature γ (fcc)
294 phase and the low-temperature ϵ (hcp) phase is around 970 °C. In pure Co the equilibrium
295 temperature between the two phases is around 427°C [28]. The fcc \rightarrow hcp transformation in Co
296 and its alloys is very sluggish due to the limited chemical driving forces available at the
297 transformation temperature. Thus, under normal cooling conditions, the fcc phase is retained
298 below the phase boundary in a metastable state. The metastable fcc phase can transform to hcp
299 by plastic deformation, by isothermal aging at temperatures between 650 and 950 °C, and
300 athermally, by rapid cooling from the annealing temperatures ($> 1100^\circ\text{C}$) [24,29]. In our
301 samples, the laser beam produces the local melting of the metal powder that rapidly solidifies
302 and cools down due to the high thermal conductivity of the metallic alloy and the smallness of
303 the heated area during the laser treatment. Thus, in the successive small areas treated with the
304 laser beam during the production process is possible to reach a condition very similar to that
305 responsible of the athermal martensitic transformation. Accordingly the athermal martensitic
306 transformation is the origin of the ϵ (hcp) phase in our sintered samples.

307 SEM observations of the DLMS samples, reveal a complex microstructure. Parallel columnar
308 structures form different domains inside the same melted pool produced by the laser beam. This
309 morphology is very different from the cellular dendritic morphology observed by Meacock et al
310 [17]. They reported on the microstructure and properties of a typical Co-Cr-Mo biomedical alloy

311 manufactured by laser powder microdeposition (LPMD). Although this latter technique,
312 similarly to the DLMS, involves melting of a small quantity of metal powder by a laser beam
313 followed by a rapid quenching, different microstructures are produced. It must be stressed that
314 the laser sintering process is very complex because it involves multiple modes of heat, mass and
315 momentum transfer, and chemical reactions [5]. As a consequence, it is not too surprising that
316 two different laser sintering techniques produce different final samples microstructure. Gaytan et
317 al. [16] reported on the microstructure and mechanical properties of parts fabricated by electron
318 beam melting (EBM) of a Co-26Cr-6Mo-0.2C powder. They observed hardness values similar to
319 the values experimentally obtained in our work, attributed to the formation of carbides lined up
320 to form columns perpendicular to the build direction. Although the columns of carbides look
321 similar to the columnar structures visible in our SEM images, XRD and TEM analyses show that
322 metal carbides are only present in small quantities and do not form columnar structures in our
323 samples. In particular, TEM observations reveal the formation of ϵ -martensite lamellae inside the
324 fcc-Co grains. These lamellae grow on the $\{111\}$ planes of the cubic γ -phase and tend to
325 aggregate forming the columnar structures visible in the SEM images. Therefore, the columnar
326 structures visible in our SEM images although similar to other structure reported in literature,
327 have a completely different nature, never observed before.

328 As known, the hcp stacking sequence can be produced by introducing an intrinsic stacking fault
329 on every second (111) plane of an fcc lattice. Furthermore, this can be accomplished by a
330 shearing process if the intrinsic faults are bounded by Shockley $a/6 \langle 112 \rangle$ partial dislocations.
331 This mechanism, invoked in the fcc \rightarrow hcp martensitic transformation [30], explains the
332 orientation relationship between the ϵ and the γ phases experimentally observed in the electron
333 diffraction patterns reported in Fig. 4b. Considering the different families of $\{111\}$ planes, the

334 presence of different orientations of the columnar structures inside a single melt pool is not
335 surprising.

336 The estimation of the area fraction occupied by the columnar structures with respect to the
337 matrix, obtained by SEM images elaboration, is comparable with the ϵ -phase volume fractions
338 obtained by XRD spectra analyses. This is in agreement with TEM observations revealing that
339 the columnar structures are due to the aggregation of ϵ -martensite lamellae.

340 Generally, for a conventional Co-Cr-Mo alloy, the percentage of athermal ϵ -martensite ranges
341 from 10 vol.% to 15vol.% depending on the chemical composition of the alloy, the solution
342 temperature and time, and the cooling rate [28]. Using only conventionally [31] or laser sintered
343 [17] Co-Cr-Mo powders, amounts of athermal ϵ -martensite ranging from 30 vol.% to 70 vol.%
344 were produced. The reason for these large amounts was mainly attributed to a large nucleation of
345 ϵ -embryos promoted by the free surfaces and grain development at powder contact surfaces
346 combined with recrystallization and grain growth within the powder particles, or promoted by
347 the cell grain boundary between the dendritic and interdendritic zone. In our samples, the cellular
348 dendritic morphology was not observed, and the powder particles completely melted during the
349 laser treatment. Thus, it is not possible to invoke in our samples the same mechanisms of
350 nucleation promotion. Furthermore, in the two above-mentioned works, TEM analyses were not
351 performed, therefore it is not possible to compare the distribution and morphology of the ϵ -
352 phase. Comparisons can be performed with the athermal ϵ -martensite present in conventional
353 Co-Cr-Mo alloys [32]. In such case, the ϵ -phase forms thick bands inside the fcc-phase. To our
354 knowledge, the formation of an intricate network of thin ϵ -lamellae, comparable to that of our
355 samples, was never observed before. All this suggests that in the DLMS procedure the cooling
356 rates of the melted powder are so rapid that a lot of lattice defects are formed during

357 solidification, and these defects exactly represent the ϵ -embryos promoting the martensitic
358 transformation.

359 For completeness, during the samples sintering, the deposited layers were heated as each
360 successive layer was deposited. These heating treatments could have induced isothermal
361 martensitic transformations in the alloy. However, it is reported in literature that the isothermal
362 martensitic formation is accompanied by the formation of discontinuous rows of carbides
363 connected to the negligible carbon solubility in the hcp phase [30,33]. The spherical carbides
364 present in our samples do not satisfy the features reported above, and they are probably formed
365 during the solidification process.

366 The HRC hardness values reported for the common cast Co-Cr-Mo alloys range from 25 to 35
367 HRC. These values are considerably lower than those measured in the part manufactured by
368 DLMS. Furthermore, it was found that the hardness value exhibits a linear increase at the
369 increasing of the ϵ phase content [24]. This latter result can be attributed to the growth of the ϵ -
370 phase on the $\{111\}_\gamma$ planes that restrict dislocation slip in the fcc lattice. Moreover, the
371 dislocation slip in the hcp lamellae is also inhibited by the intersection of these hcp lamellae with
372 other hcp ones or with fcc regions [30]. Therefore, all the aforementioned phenomena and the
373 peculiar intricate network of ϵ -lamellae experimentally observed in our samples, can explain the
374 high hardness values obtained. In fact, in our samples the ϵ lamellae grow on the slip plains of
375 the γ -(fcc) phase. The density and the spatial distribution of these ϵ lamellae enormously restrict
376 the dislocations slip, thus increasing the hardness values of our samples.

377 The presence of metal carbides could even play a role in the strengthening of the alloy by the
378 Orowan mechanism. However, considering the small quantity of carbides observed in our

379 samples, it is more probable that the main mechanism of strengthening is due to the martensitic
380 transformation induced in the alloy by the DLMS procedure.

381 The increased strengthening manifested in the sintered samples along with the microstructure
382 homogeneity observed could make the direct metal laser sintering technique a very useful and
383 powerful procedure to produce surgical implants from Co-Cr-Mo alloys.

384 Future work will involve studies on the correlation between the deposition parameters of the
385 DMLS production process, and the microstructure and the mechanical properties of the final
386 products. Furthermore, additional mechanical tests will be performed on the sintered Co-Cr-Mo
387 samples in order to investigate tensile strength, Young's modulus and elongation.

388

389 **5. CONCLUSIONS**

390 In the present paper, we reported on the structural and microstructural characterization of Co-Cr-
391 Mo parts produced by Direct Metal Laser Sintering. The composition of the alloy was chosen in
392 order to produce biocompatible parts. Sintered samples were characterized by X-ray diffraction,
393 scanning and transmission electron microscopy and EDS microanalysis. The main results
394 obtained can be listed as follows:

395 1) The laser treatment melts the metallic Co-Cr-Mo powder and induces a phase transformation
396 from the γ (fcc) to the ϵ (hcp) phase;

397 2) The phase transformation is an athermal martensitic transformation and produces an intricate
398 network of thin ϵ -lamellae distributed inside the γ phase. This microstructure was never observed
399 before;

400 3) The large amount of ϵ -lamellae could be attributed to a large nucleation of ϵ -embryos
401 promoted by lattice defects formation during the rapid cooling of the melted powder;

- 402 4) Carbides are present inside the grains of the alloy and are probably formed on solidification;
- 403 5) The hardness values of the samples, higher than those reported in parts fabricated by different
- 404 processes, are due to the presence of ϵ -lamellae grown on the $\{111\}_\gamma$ planes that restricts the
- 405 dislocations slip in the γ (fcc) phase. Furthermore, slip in the ϵ -lamellae is inhibited by the
- 406 intersection of these hcp lamellae with other hcp lamellae or with fcc regions.
- 407 6) The DMLS technique could be used to realize surgical implants, where an high degree of
- 408 personalisation is required, saving money and time with respect to conventional procedures.

409

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412

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Title: Structural characterization of biomedical Co-Cr-Mo components produced by Direct Metal Laser Sintering
Materials Science and Engineering C

Authors reply

The paper has been revised following the reviewers suggestions. In particular, Abstract and Introduction were deeply modified.

English was checked throughout the manuscript.

A Highlights session is added in the manuscript.

In the following, the reviewer comment is indicated by "R:" while the authors reply by "A:".

The position of the text added or modified in the manuscript is specified in parentheses in terms of page number (p.) and line number (l.).

Reviewer #1: The authors present a paper aiming to analyze the hardness and the microstructure of samples produced by direct metal laser sintering of a Co-Cr-Mo alloy. I would propose Major Revisions.

R: In general terms, more clarity about the purpose of the work, how it fits into previous work and a clear evaluation of the outcomes is required. The author must emphasize why the paper provides new insight and it is interesting for the scientific community. A better connexion with previous research is also required to support the obtained results and place them into the context of literature.

A: Introduction has been deeply modified following the reviewer suggestions. New and updated references have been added [20, 21]. The original results presented in the paper are summarised both in the Abstract (p. 3, l. 36-40) and in the Introduction (p. 6, l. 95-103).

R: A gap of research has been identified when it is said that the 'The study of the samples microstructure is fundamental to set the parameters used in the AM procedures and to choose the composition of the metal powders in order to meet the request for certain mechanical properties'. However, no correlation between the obtained results and the parameters of the process and composition of the metal powders has been established. In order to make a contribution to knowledge, more concise statements should be stated describing the influence of the process on the material properties (hardness and microstructure), and some ways to mitigate the associated problems.

A: This part was deleted because not strictly focused on the subject matter. More information on the influence of the deposition parameters on the properties of the obtained components can be found in ref [22].

R: The language and writing style should aim to be concise, with simple, easy to understand sentences. The English needs to be checked throughout. Some sections should be divided in different subsections, such as 'Section 2' and 'Results'. This will simplify and clarify the text, and it will solve readability issues.

A: Language and writing style have been checked and revised throughout the document. Section 2 "Materials and methods" and Section 3 "Results" have been divided in subsections, as suggested.

R: Further remarks to the paper:

- Abstract: it should only report on experimental details, results and main conclusions. Including background information, such as the description of the Direct Metal Laser Sintering Technique, should be avoided.

A: Abstract has been modified, as suggested (p.3).

R: - English needs to be checked to avoid some language issues such as: 'objects realized by sintering metal powder...'; 'founded' instead of found (line 3, page 5); '...the mechanical properties was identified...', instead of 'were identified'.

A: English checked throughout the manuscript.

R: - Introduction section: although the authors summarize some previous work in the area, the context needs to be more convincingly presented, placed into the context of the literature. Please, cite more references on the production of Cr-Co-Mo samples by laser sintering and improve the explanation on the applicability of the research results in the biomedical field.

A: Introduction revised and more references added, as reported above (p. 4-6).

R: - Page 4, first paragraph. The author states that 'Recently, they have been attracting strong interest for biomedical implants [13,15].' Please, describe why these two references have been cited here, and add the most important information to the introduction section. The correct way to cite previous work includes some description of what the authors did, and what the conclusion was - so the reader knows how seriously to take the information you claim from them.

A: Introduction completely revised, as stated above (p. 4-6).

R: - Page 4, end of the first paragraph, it is stated that 'Cast alloys containing 27-30 wt% Cr and 5-7wt% Mo are biocompatible and have been used for many years to produce medical implants'. Have these data been obtained from a previous study? If so, please, include the reference.

A: This result was obtained in a previous study and the reference to it is added as ref [15] of the manuscript.

R: - Page 4, paragraph two. Please, explain the reasons why '... objects realized by sintering metal powder show mechanical properties worse than those held by objects produced in a conventional way...'.
A: The explanation required and reference [22] are added (p. 5-6, l. 89-94).

R: - The purpose of the work has not been clearly defined. Even some results and conclusions are mixed when defining the purpose of the investigation.
A: The purpose of the work as well as the main results and the conclusions are rewritten in the Introduction (p. 6, l. 95-103)

R: - For clarity, characteristics of the raw materials should be stated in 'Section 2. Materials'. Information should be reordered for a better understanding: in page 8, SEM analyses of the raw material are mixed with XRD analysis of the samples developed by laser sintering.
A: Section 2 "Materials and methods" and Section 3 "Results" are divided in subsections. The results obtained by each different characterisation technique are reported separately (p. 6-17).

R: - Was the composition of the raw material provided by the manufacturer? If so, please, state it. How was it manufactured? Is the chemical composition in agreement with some specification for powders to be used for surgical and medical implant coatings?
A: The nominal composition of the raw material (powder) was provided by the manufacturer (EOS GmbH Electro Optical Systems). The powder is the EOS Cobalt/Chrome SP2 cobalt based metal ceramic alloy intended for production of Porcelain-Fused to Metal (PFM) dental restorations (crowns, bridges, etc.) in EOSINT M 270 Standard installation mode. The powder is class IIa medical device in accordance with annex IX rule 8 of the MDD 93/42/EEC. Composition corresponds to "type 4" CoCr dental material according to EN ISO 22674. Information added in manuscript (p. 7, l. 111-118).

R: - How was the average particle size determined?
A: The average particle size is determined from SEM images. A sentence on this specific issue is added in Section 3.3 "Scanning electron microscopy (SEM) and microanalysis (EDS)" (p. 11, l. 187-189).

R: - Page 5. Methods. Were the parameters selected for the Laser Melting Sintering Process based on previous results?
A: The deposition parameters adopted for the laser sintering are the standard parameters recommended by the manufacturer.

R: - Page 5, first line: Using the passive voice would be more appropriate than the Active form 'We investigated...'.
A: Modified as suggested (p. 6, l. 95-97).

R: - Section 2, page 6. Please complete the information on the working conditions of the XRD equipment, that is: kV, mV and the range of 2θ degrees in which the test was performed.

A: The required information is added (p. 8, l. 133-134).

R: - Page 14, section 4: 'The hardness values of the laser sintered samples are surprisingly good, considering the method used for their realization. Generally, components produced by an additive manufacturing technique, such as the Direct Laser Metal Sintering procedure used in this work, can be affected by residual porosity and show poorer mechanical properties than those obtained with traditional manufacturing techniques. In our case, however, hardness was found to be remarkably high...'

Are the high hardness values obtained good for biomedical applications? Is it associated to brittleness? Please, discuss it.

A: Section 4 "Discussion" is modified on the basis of the reviewer comments. Further comments on the mechanical parameters influencing the material behaviour are added (p. 17-18, l. 280-289).

R: If mechanical properties tend to be poorer in samples produced by Direct Metal Sintering, should the hardness values also diminish? If their increase is attributed to martensitic transformations, is there any way to reduce the hardness values of the obtained samples? Please, discuss these issues and place the obtained results into the context of literature.

A: Aim of this work is to correlate the hardness value measured on the samples to their microstructure. The complete determination of the mechanical behaviour of the samples is beyond the scope of the work. Future work on the same materials will take into consideration more mechanical aspects. Comments on this issue are added at the end of the "Discussion" (p. 22, l. 384-387).

R: - Are there other proposals that might usefully be tested in future work?

A: A list of possible issues to be explored is reported at the end of the "Discussion" (p. 22, line 379-382).

R: - References: some references date from year 1992, 1990, 1983, 1982, 1981, 1976, 1968 or even 1950. Even if correct, they may be hardly remarkable for a scientific paper. Please replace some of them with proper references from the open literature.

A: References were updated (p. 23-26).

Reviewer #3: In this paper, the authors used direct Metal Laser Sintering (DMLS) technique to sinter metal powder particles. During their processing, they found a homogeneous microstructure comprised of thin ϵ (hcp)-lamellae distributed inside a γ (fcc) phase. It's hoped that this structure would prevent the dislocation slip and increase the sample hardness. With this structure, DMLS is expected to fabricate a useful computer-aid-designed three dimensional object with proper mechanical property for medical applications. This is an interesting result. However, the paper should provide more details.

R: (1) Hardness only reflects one aspect of the material mechanical property. The main mechanical property considering for the medical metal implants is the compression or intension property. There are somewhat big differences between the hardness and compression/intension. The author implied in the paper the structure is useful to improve the hardness, but not mentioned if that is benefit to improve the compression or intension property.

A: Aim of this work is to correlate the hardness value measured on the samples to their microstructure. The complete determination of the mechanical behaviour of the samples is beyond the scope of the work. Future work on the same materials will take into consideration more mechanical parameters and the mechanical properties required for biomedical applications. Comments on this issue are added at the end of the "Discussion" (p. 22, l. 384-387).

R: (2) The introduction part should provide more information about the current progress on the topic of the material structure developed by the DMLS or related technique, but not the background of the rapid manufacture and cobalt based alloy.

A: Introduction has been deeply modified following the reviewer suggestions. New and updated references have been added [20, 21]. The original results presented in the paper are summarised both in the Abstract (p. 3, l. 36-40) and in the Introduction (p. 6, l. 95-103).

R: (3) If the powder was commercially brought, it is needed to provide the powder manufacture's name and the grades.

A: The raw material is a commercial powder provided by EOS GmbH Electro Optical Systems. The powder is the EOS Cobalt/Chrome SP2 cobalt based metal ceramic alloy intended for production of Porcelain-Fused to Metal (PFM) dental restorations (crowns, bridges, etc.) in EOSINT M 270 Standard installation mode. The powder is class IIa medical device in accordance with annex IX rule 8 of the MDD 93/42/EEC. Composition corresponds to "type 4" CoCr dental material according to EN ISO 22674. Information added in manuscript (p. 7, l. 111-118).

R: (4) Fig. 1b, ordinate values of Y axis should be presented. Fig 1 should put the XRD pattern of sample fabricated by the traditional method.

A: Figure 1b is modified, as suggested: the Y scale is added (p.9). Figure 1 reports the experimental results obtained in this study by XRD. We experimentally performed XRD measurements on the raw material (powder) and the sintered samples. So, we reported these results in the "Results"

section of the manuscript in Figure 1a and Figure 1b, respectively. The XRD patterns of samples fabricated by traditional methods can be found in literature.

R: (5) Fig. 2, the bar size is 50 μm , the biggest powder in the SEM image is about 60 μm . However, the author describe the "...They have a spherical shape and size range from 4 to 90 μm ...". It's look like the description and the image is inconsistent.

A: The average particle size is determined from SEM images by averaging the data obtained from several areas. Results show that the particle size is within the range 4-80 μm . A sentence on this specific issue is added in Section 3.3 "Scanning electron microscopy (SEM) and microanalysis (EDS)" (p. 11, l. 187-189).

R: (6) Page 9, "EDX measurements performed...", page 11 "EDX measurements performed...", page14 "EDX measurements were...", but, no EDX results are found in the paper.

A: The results of the EDX measurements are now added. Table 2, added in subsection 3.3 (p. 11), reports the EDX results obtained on the raw material (powder) and the sintered sample. Table 3, added in the subsection 3.4 (p.17), reports the EDX results obtained on the matrix (sintered sample) and the precipitates (metal carbides) visible in the TEM image reported in Figure 6.

R: (7) Page 8, "resulted in an ϵ -phase volume fraction $f_{\text{hcp}}=0.49\pm 0.03$ ", Page 11, " The ϵ phase forms lamellae inside the γ phase...". if the volume fraction of ϵ -phase is almost the main phase, the description in page 11 should be changed.

A: The experimental results show that the epsilon phase is not present in the raw material (powder) while it is largely present in the sintered samples (see XRD results reported in Figure 1 and TEM results reported in Figure 4 and Figure 5). It must be considered that epsilon is the stable phase at low temperature while gamma is the stable phase at high temperature. Therefore, since DMLS induces the melting of the powder, the epsilon phase forms as a consequence of the gamma-epsilon martensitic transformation. So, the epsilon phase forms inside the gamma phase, as reported in the "Discussion".

Reviewer #5: This research paper reported the structural and microstructural characterization of Co-Cr-Mo parts produced by Direct Metal Laser Sintering. The method used is quite conventional, however, the results are a little valuable. It is obvious that this paper is not that well organized. Some minor revision must be taken.

R: 1. Please include an "Highlights section"

A: The highlights session is added (p. 2).

R: 2. The "M&M" and "Results" parts should be organized in sub-units, each used technique has to be described separately and consequently numbered.

A: Section 2 "Materials and methods" and Section 3 "Results" are divided in subsections. The results obtained by each different characterisation technique are reported separately (p. 6-17).

R: 3. The authors show an increase in Cr and Mo concentrations with respect to the matrix and evidence that precipitates have the same composition independently of their shape. Crystallographic examination of the precipitate was done by SAD technique. How to prove the biocompatibility of such precipitates?

A: The formation of the metal carbides in alloys having a composition similar to the alloy investigated in this work is well known in literature. From a compositional point of view, the sintered samples obtained by DMLS in this study are very similar to alloys reported as biocompatible materials in literature. Furthermore, the dimension and density of the metal carbides in our samples are comparable and sometimes even lower than those reported in several papers in literature. Therefore, even though a specific study on the biocompatibility of our samples was not performed, it is reasonable to consider the sintered samples of our study as biocompatible materials.

R: 4. P15: "Generally, components produced by an additive manufacturing technique, such as the Direct Laser Metal Sintering procedure used in this work, can be affected by residual porosity and show poorer mechanical properties than those obtained with traditional manufacturing techniques." Please add any references.

A: On this specific issue ref [22] is added.