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

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4 G. Barucca ^{a,*}, E. Santecchia ^a, G. Majni ^a, E. Girardin ^b, E. Bassoli ^c, L. Denti ^c, A. Gatto ^c,
5 L. Iuliano ^d, T. Moskalewicz ^e, P. Mengucci ^a
6

7 ^a SIMAU, Università Politecnica delle Marche, via Brecce Bianche, 60131 Ancona, Italy.

8 ^b DISCO, Università Politecnica delle Marche, via Brecce Bianche, 60131 Ancona, Italy.

9 ^c DIMeC, University of Modena and Reggio Emilia, via Vignolese 905/B, Modena 41125, Italy.

10 ^d DISPEA, Politecnico di Torino, C.so Duca degli Abruzzi 24, 10129 Torino, Italy.

11 ^e Faculty of Metals Engineering and Industrial Computer Science, AGH University of Science
12 and Technology, Al. Mickiewicza 30, 30-059 Kraków, Poland.

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14
15 * Corresponding author: SIMAU, Università Politecnica delle Marche, via Brecce Bianche,
16 60131 Ancona, Italy. Tel.: +39 071 2204754; fax: +39 071 2204729.

17 E-mail address: g.barucca@univpm.it (G. Barucca).

18 **ABSTRACT**

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

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

33

34

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

37

38 1. INTRODUCTION

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

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

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

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

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

62 Cast alloys with a Cr content ranging from 19 wt% to 30 wt% and a Mo content in the range 5-
63 10 wt% were considered for biomedical applications and for many years these compositions
64 were used to produce medical implants such as hips, knees, ankles and bone plates [15].

65 Although in the past few years, several AM techniques were applied to produce biocompatible
66 Co-based alloys, only in few cases a deep microstructural characterisation of the sintered
67 components were performed. In particular, Gaytan et al. reported on the microstructure and the
68 mechanical properties of Co-based prototypes produced by electron beam melting. In this study,
69 they found high hardness values attributed to the formation of an ordinate array of metal carbides
70 [16]. Meacock et al. investigated the microstructure and the mechanical properties of a
71 biomedical Co-Cr-Mo alloy produced by laser powder microdeposition [17]. They observed a
72 homogenous microstructure comprised of fine cellular dendrites and measured an average
73 hardness value of 460 $\text{HV}_{0.02}$, well higher than the typical values obtained by other fabrication
74 processes. From these results, they concluded that the fine morphology is responsible of the
75 significantly increased hardness value.

76 Few other papers deal with the possibility of realizing medical parts of a Co-Cr-Mo alloy by the
77 DMLS technique, but it is worth to note that none of them reports on the correlation of the
78 samples microstructure to the mechanical properties of the final components as well as detailed
79 transmission electron microscopy analyses [19-21].

80 The mechanical properties of the sintered components are strictly linked to the samples
81 microstructure and are one of the major aspects connected to the practical applications of the AM
82 procedures. Usually, objects produced by metal powder sintering show poorer mechanical

83 properties than those produced by conventional procedures. This behaviour is mainly due to the
84 fact that DMLS, depending on the laser energy density employed, involves a partial or total
85 melting of the powder. Therefore, the products made by DMLS could show high surface
86 roughness, porosity (in certain cases even lack of densification), heterogeneous microstructure
87 and thermal residual stresses that may give rise to poor mechanical properties [22].

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

97

98 **2. MATERIALS AND METHODS**

99 2.1 Material composition and sintering parameters

100 Specimens were prepared by direct metal laser sintering using a Yb (ytterbium) fiber laser
101 system (EOSINT-M270) operating with the standard deposition parameters reported in Table 1.

102 **Table 1**

103 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

104

105 A Co-Cr-Mo alloy powder (EOS Cobalt/Chrome SP2) with the nominal composition (in wt%)
106 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
107 and Cd according to EN ISO 22674. The nominal composition was provided by the manufacturer
108 (EOS GmbH Electro Optical Systems). The powder is the EOS Cobalt/Chrome SP2 cobalt based
109 metal ceramic alloy intended for production of Porcelain-Fused to Metal (PFM) dental
110 restorations (crowns, bridges, etc.) in EOSINT M 270 Standard installation mode. The powder is
111 class IIa medical device in accordance with annex IX rule 8 of the MDD 93/42/EEC.
112 Composition corresponds to “type 4” CoCr dental material according to EN ISO 22674.
113 Rectangular parallelepipeds with size 250 mm x 4 mm and a thickness of 6 mm were sintered by
114 using the parameters reported in Table 1. In order to minimize anisotropy, each layer was built
115 with the laser scanning along a specific direction. Layer-by-layer the scanning direction was
116 rotated by 25° with respect to the previous one.

117

118 2.2 Hardness measurements

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

123

124 2.3 Structural characterisation

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

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

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

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

140

141 **3. RESULTS**

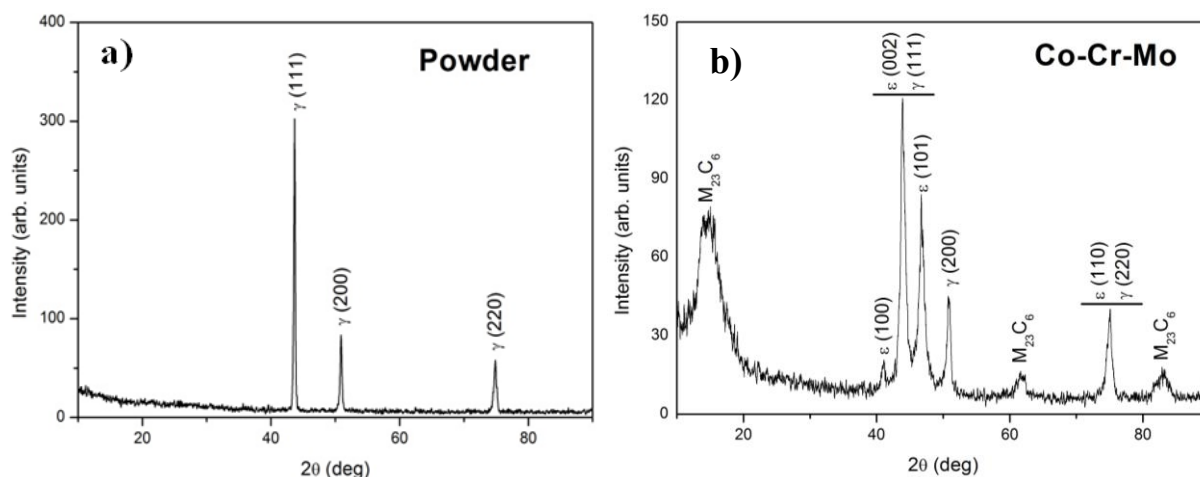
142 3.1 Hardness

143 The average Rockwell C hardness (HRC) value measured for the laser sintered samples is 47
144 HRC, a very high value considering that the usual range for cast Co-Cr-Mo alloys is from 25 to
145 35 HRC.

146

147 3.2 X-ray diffraction (XRD)

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



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

151

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

158 The XRD pattern of the sintered sample is shown in Fig. 1b. The most intense and well-defined
159 peaks are a result of the simultaneous presence of both γ and ϵ cobalt phases, as indicated in Fig.
160 1b where each diffraction peak is indexed with the name of the corresponding Co phase. A
161 double indexation is reported for the most intense peak at $2\theta=43.94^\circ$ and the peak at $2\theta=75.09^\circ$
162 because of the superposition of the reflections due to the ϵ and γ phases. The ϵ phase has a
163 hexagonal close packed (hcp) lattice with nominal parameters $a=0.25031$ nm and $c=0.40605$ nm
164 (ICDD card n. 5-727). By using the ϵ (100) and ϵ (101) peaks of the XRD pattern shown in Fig.
165 1b, the lattice parameters of the hexagonal ϵ phase formed in our alloy were determined to be
166 $a=0.2539$ nm and $c=0.4122$ nm with a c/a ratio of 1.623. The lattice parameter of the fcc γ phase
167 formed in the sintered sample evaluated by the γ (200) peak of Fig. 1b is $a=0.3589$ nm. Also in
168 this case, the calculated lattice parameters for the ϵ and γ phases formed in our alloy are in close
169 agreement with those reported in literature for similar compositions [23].

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

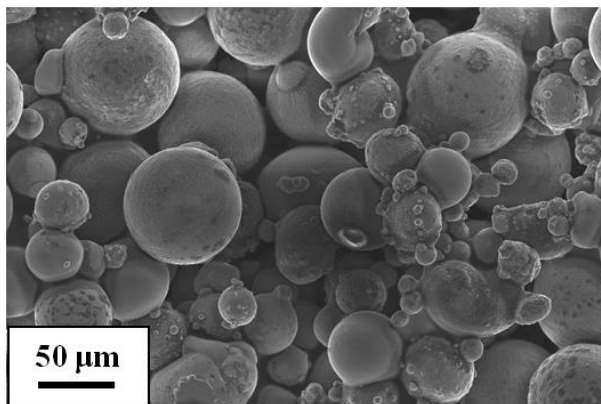
174 In addition to the ϵ and γ peaks in Fig. 1b, three broad peaks attributable to metals carbides are
175 also visible. These latter peaks generically indexed as $M_{23}C_6$ ($M=\text{Cr, Co, Mo, W}$) are due to
176 metal carbides having the cubic structure of the Cr_{23}C_6 compound (ICDD card n. 35-783).

177

178 3.3 Scanning electron microscopy (SEM) and microanalysis (EDX)

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

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



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

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

188

189 **Table 2**

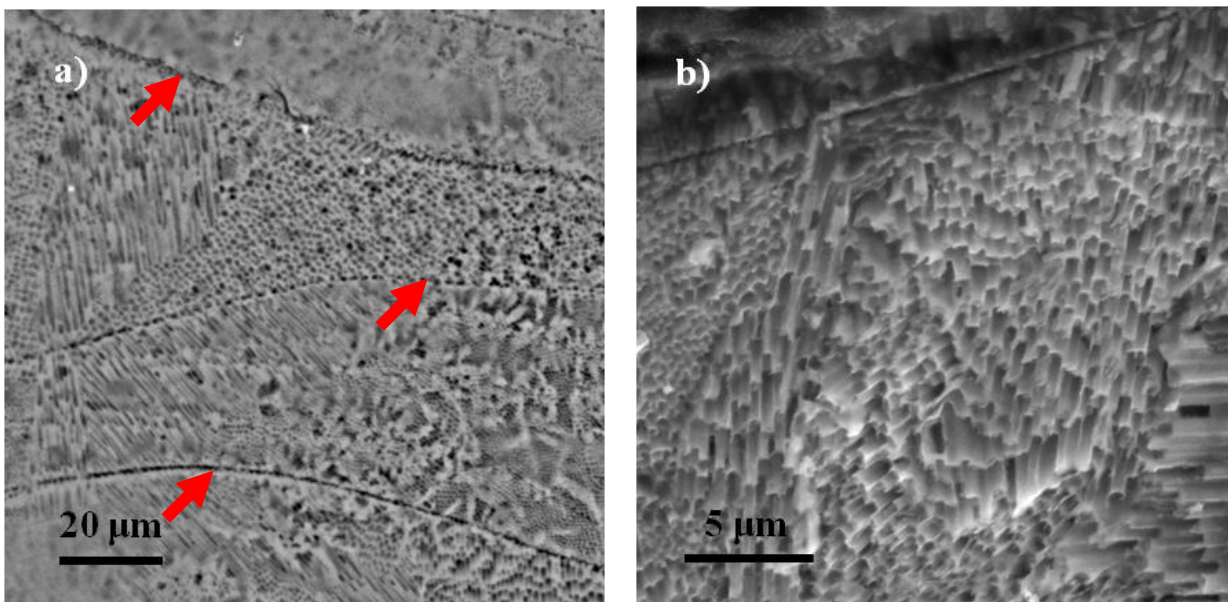
190 Experimental results of the EDX microanalysis performed on both the powder and the sintered
191 sample.

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

192

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

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



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

202
203 Observations performed at higher magnification allow to evidence the presence of an extremely
204 fine microstructure inside a single pool, Fig. 3b. Columnar structures, with diameters ranging
205 from 300 to 400 nm and heights from 4 to 8 μm , grow inside the matrix in form of domains. The
206 orientation of the columns is the same inside a single domain while it changes from one domain
207 to the other. In order to estimate the area fraction occupied by the columnar structures relative to

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

211

212 3.4 Transmission electron microscopy (TEM) and microanalysis (EDX)

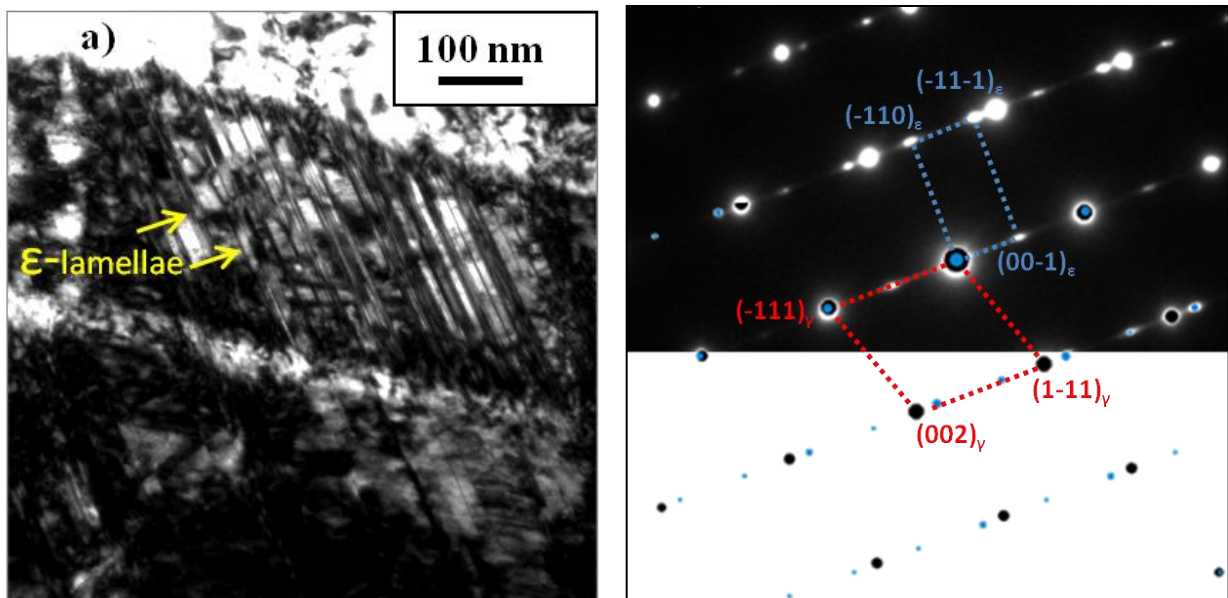
213 TEM observations of the sintered samples confirm the presence of the two ϵ and γ cobalt phases.

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

215 1-2 nm, but in some cases, they tend to aggregate in the same region of the sample forming

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

217



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

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

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

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

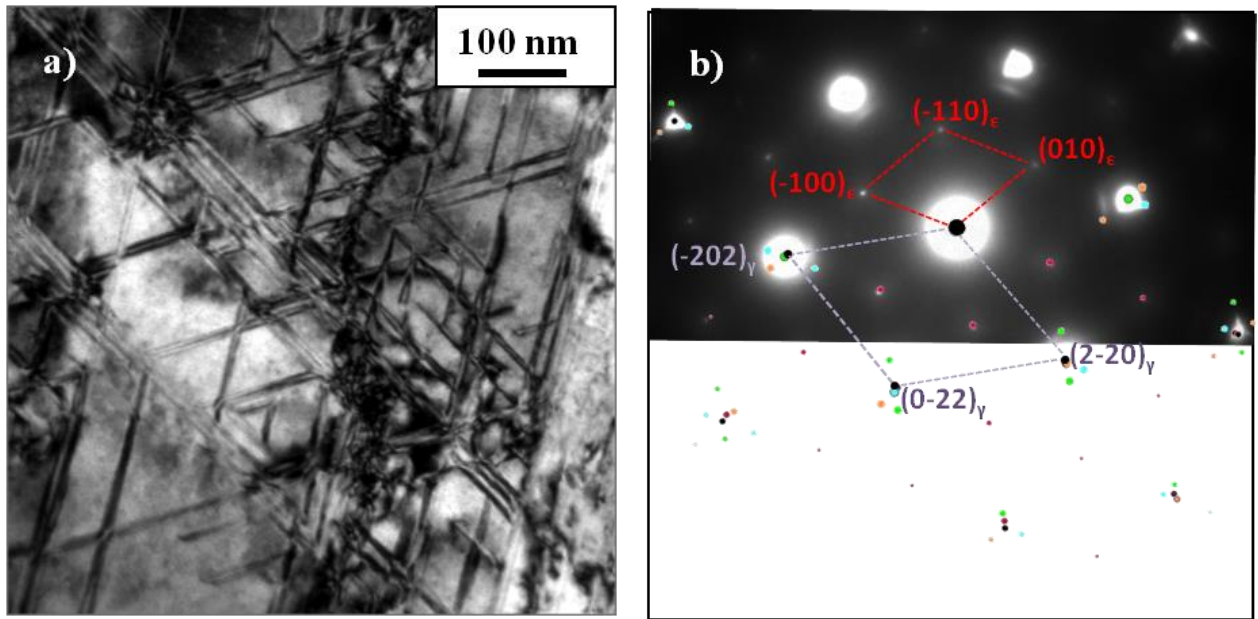
222

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

$$\begin{aligned} 233 & \{001\}_\varepsilon // \{111\}_\gamma \\ 234 & \langle 100 \rangle_\varepsilon // \langle 1-10 \rangle_\gamma \end{aligned}$$

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

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



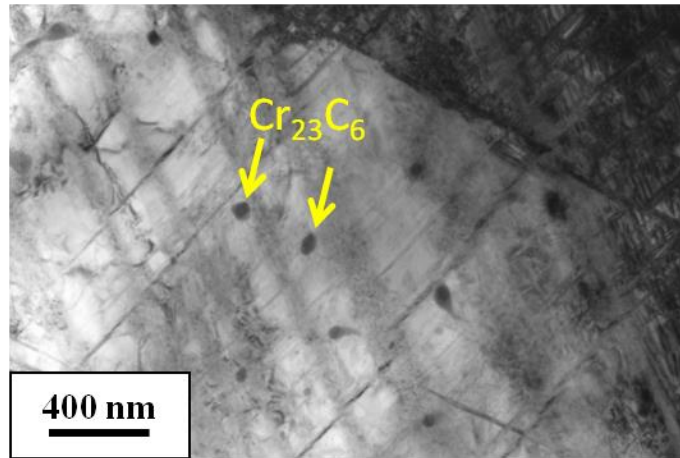
240 **Fig. 5.** Sintered sample: a) bright field TEM image taken in $\langle 111 \rangle_\gamma$ zone axis orientation; b)
 241 corresponding SAD pattern (upper part) and software simulation (lower part). In red is
 242 indicated the cell of the ϵ -Cobalt phase in one of the four possible orientations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

244

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

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

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



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

260

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

267 **Table 3**

268 Experimental results of the EDX measurements performed on both the matrix and the
269 precipitates.

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

270

271 **4. DISCUSSION**

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

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

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

303 SEM observations of the DLMS samples, reveal a complex microstructure. Parallel columnar
304 structures form different domains inside the same melted pool produced by the laser beam. This
305 morphology is very different from the cellular dendritic morphology observed by Meacock et al
306 [17]. They reported on the microstructure and properties of a typical Co-Cr-Mo biomedical alloy

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

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

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

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

336 Generally, for a conventional Co-Cr-Mo alloy, the percentage of athermal ϵ -martensite ranges
337 from 10 vol.% to 15vol.% depending on the chemical composition of the alloy, the solution
338 temperature and time, and the cooling rate [28]. Using only conventionally [31] or laser sintered
339 [17] Co-Cr-Mo powders, amounts of athermal ϵ -martensite ranging from 30 vol.% to 70 vol.%
340 were produced. The reason for these large amounts was mainly attributed to a large nucleation of
341 ϵ -embryos promoted by the free surfaces and grain development at powder contact surfaces
342 combined with recrystallization and grain growth within the powder particles, or promoted by
343 the cell grain boundary between the dendritic and interdendritic zone. In our samples, the cellular
344 dendritic morphology was not observed, and the powder particles completely melted during the
345 laser treatment. Thus, it is not possible to invoke in our samples the same mechanisms of
346 nucleation promotion. Furthermore, in the two above-mentioned works, TEM analyses were not
347 performed, therefore it is not possible to compare the distribution and morphology of the ϵ -
348 phase. Comparisons can be performed with the athermal ϵ -martensite present in conventional
349 Co-Cr-Mo alloys [32]. In such case, the ϵ -phase forms thick bands inside the fcc-phase. To our
350 knowledge, the formation of an intricate network of thin ϵ -lamellae, comparable to that of our
351 samples, was never observed before. All this suggests that in the DLMS procedure the cooling
352 rates of the melted powder are so rapid that a lot of lattice defects are formed during

353 solidification, and these defects exactly represent the ϵ -embryos promoting the martensitic
354 transformation.

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

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

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

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

377 The increased hardening manifested in the sintered samples along with the microstructure
378 homogeneity observed could make the direct metal laser sintering technique a very useful and
379 powerful procedure to produce surgical implants from Co-Cr-Mo alloys. In this framework, it
380 must be stressed that high hardness values are particularly desirable in the field of prosthesis
381 applications to reduce the debris due to the friction action in the polyethylene-on-metal artificial
382 joints. As shown by Gonzalez-Mora et al. [34], that studied the role of hardness and roughness
383 on the wear of polyethylene in the polyethylene-on-metal artificial joints, hard surfaces are more
384 resistant against scratching and consequently produces less polyethylene wear, the roughness
385 being not the main parameter.

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

390

391 **5. CONCLUSIONS**

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

- 397 1) The laser treatment melts the metallic Co-Cr-Mo powder and induces a phase transformation
398 from the γ (fcc) to the ϵ (hcp) phase;
- 399 2) The phase transformation is an athermal martensitic transformation and produces an intricate
400 network of thin ϵ -lamellae distributed inside the γ phase. This microstructure was never observed
401 before;
- 402 3) The large amount of ϵ -lamellae could be attributed to a large nucleation of ϵ -embryos
403 promoted by lattice defects formation during the rapid cooling of the melted powder;
- 404 4) Carbides are present inside the grains of the alloy and are probably formed on solidification;
- 405 5) The hardness values of the samples, higher than those reported in parts fabricated by different
406 processes, are due to the presence of ϵ -lamellae grown on the $\{111\}_{\gamma}$ planes that restricts the
407 dislocations slip in the γ (fcc) phase. Furthermore, slip in the ϵ -lamellae is inhibited by the
408 intersection of these hcp lamellae with other hcp lamellae or with fcc regions.
- 409 6) The DMLS technique could be used to realize surgical implants, where a high degree of
410 personalisation is required, saving money and time with respect to conventional procedures.

411

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414

415 **REFERENCES**

416 [1] A. Mazzoldi. Selective laser sintering in biomedical engineering. *Med Biol Eng Comput*
417 2013;51:245-256.

418 [2] Lantada AD, Morgado PL. Rapid prototyping for biomedical engineering: current capabilities
419 and challenges. *Annual Review of Biomedical Engineering* 2012;14:73-96.

420 [3] Rosochowski A, Matuszak A. Rapid tooling: the state of the art. *J Mater Process Technol*
421 2000;106:191-198.

422 [4] Hunt JA, Callaghan JT, Sutcliffe CJ, Morgan RH, Halford B, Black RA. The design and
423 production of Co-Cr alloy implants with controlled surface topography by CAD-CAM method
424 and their effects on osseointegration. *Biomaterials* 2005;26:5890-5897.

425 [5] Simchi A. Direct laser sintering of metal powders: Mechanism, kinetics and microstructural
426 features. *Mater Sci Eng A* 2006;428:148-158.

427 [6] Bassoli E, Gatto A, Iuliano L. Joining mechanisms and mechanical properties of PA
428 composites obtained by selective laser sintering. *Rapid Prototyp J* 2012;18:100-108.

429 [7] Gibson I, Cheung LK, Chow SP, Cheung WL, Beh SL, Savalani M, Lee SH. The use of rapid
430 prototyping to assist medical applications. *Rapid Prototyp J* 2006;12:53-58.

431 [8] Wang X, Yan Y, Zhang R. Rapid prototyping as a tool for manufacturing bioartificial livers.
432 *Trends in Biotechnology* 2007;25:505-513.

433 [9] Butscher A, Bohner M, Hofmann S, Gauckler L, Muller R. Structural and material
434 approaches to bone tissue engineering in powder-based three dimensional printing. *Acta*
435 *Biomaterialia* 2011;7:907-920.

436 [10] Atzeni E, Iuliano L, Minetola P, Salmi A. Proposal of an innovative benchmark for
437 accuracy evaluation of dental crown manufacturing. *Computers in Biology and Medicine*
438 2012;42:548-555.

439 [11] Davis JR. *Nickel, Cobalt and Their Alloys* Materials Park (OH): ASM
440 INTERNATIONAL;2000.

441 [12] Nasab MB, Hassan MR, Sahari BB. Metallic biomaterials of knee and hip - a review.
442 *Trends Biomater. Artif. Organs* 2010;24(2):69-82.

443 [13] Malayoglu U, Neville A. Mo and W as alloying elements in Co-based alloy – their effects
444 on erosion – corrosion resistance. *Wear* 2005;259:219-229.

445 [14] Shin J, Doh J, Kim J. Effect of molybdenum on the microstructure and wear resistance of
446 cobalt-base Stellite hardfacing alloys. *Surf Coat Technol* 2003;166:117-126.

447 [15] Davis JR, *Handbook of Materials for Medical Devices: ASM International; 2003:21-50*
448 DOI: 10.1361/hmmd2003p013.

449 [16] Gaytan SM, Murr LE, Martinez E, Martinez JL, Machado BI, Ramirez DA, Medina F,
450 Collins S, Wicher RB. Comparison of Microstructures and Mechanical Properties of Solid and
451 Mesh Cobalt-base Alloy Prototypes Fabricated by Electron Beam Melting. *Metall Mater Trans*
452 *A* 2010;41:3216-3227.

453 [17] Meacock CG, Vilar R. Structure and properties of a biomedical Co-Cr-Mo alloy produced
454 by laser powder microdeposition. *J Laser Appl* 2009;21:88-95.

455 [18] Vandenbroucke B, Kruth JP. Selective laser melting of biocompatible metals for rapid
456 manufacturing of medical parts. *Rapid Prototyp J* 2007;13:196-203.

457 [19] Averyanova M, Bertrand P, Verquin B. Manufacture of Co-Cr dental crowns and bridges by
458 selective laser Melting technology. *Virtual Phys Prototyp* 2011;16:179-185.

459 [20] Reclaru L, Ardelean L, Rusu L, Sinescu C. Co-Cr material selection in prosthetic
460 restoration: laser sintering technology. *Solid state phenomena* 2012;188:412-415.

461 [21] Cotrut CM, Ciucă S, Miculescu F, Antoniac I, Târcolea M, Vrânceanu DM. The influence
462 of classical and modern manufacturing technologies on the properties of metal dental bridge.
463 *Key engineering materials* 2014;583:163-168.

464 [22] Sanz C, Navas VG. Structural integrity of direct metal laser sintered parts subjected to
465 thermal and finishing treatments. *Journal of materials processing technology* 2013;213:2126-
466 2136.

467 [23] Saldivar-Garcia AJ, Lopez HF. Temperature effects on the lattice constants and crystal
468 structure of a Co-27Cr-5Mo low-carbon alloy. *Metall Mater Trans A* 2004;35:2517-2523.

469 [24] Garcia JS, Medrano MA, Rodriguez AS. Formation of hcp martensite during the isothermal
470 aging of an fcc Co-27Cr-5Mo-0.05C orthopedic implant alloy. *Metall Mater Trans A*
471 1999;30:1177-1184.

472 [25] Rasband WS. ImageJ, U. S. National Institutes of Health, Bethesda, Maryland, USA,
473 <http://imagej.nih.gov/ij/> 1997-2012.

474 [26] CrystalKitX version 1.9.1. Total Resolution LLC.

475 [27] Murr LE, Amato KN, Li SJ, Tian YX, Cheng XY, Gaytan SM, Martinez E, Shindo PW,
476 Medina F, Wicker RB. Microstructure and mechanical properties of open-cellular biomaterials
477 prototypes for total knee replacement implants fabricated by electron beam melting. *J Mech*
478 *Behav Biomed Mater* 2011;4:1396-1411.

479 [28] Saldivar-Garcia AJ, Manì MA, Salinas RA. Effect of solution treatments on the fcc/hcp
480 isothermal martensitic transformation in Co-27Cr-5Mo-0.05C aged at 800°C. *Scr Mater*
481 1999;40:717-722.

482 [29] Lopez HF. Alloy developments in biomedical Co-base alloys for HIP implant applications.
483 *Materials science forum* 2013;736:133-146.

484 [30] Vander Sande JB, Coke JR, Wulff J. A Transmission Electron Microscopy Study of the
485 Mechanisms of Strengthening in Heat-Treated Co-Cr-Mo-C Alloys. *Metall Trans A*
486 1976;7A:389-397.

- 487 [31] Song CB, Park HB, Seong HG, Lòpez HF. Development of a thermal ϵ -martensite in
488 atomized Co-Cr-Mo-C implant alloy powders. *Acta Biomaterialia* 2006;2:685-691.
- 489 [32] Lee SH, Nomura N, Chiba A. Significant improvement in mechanical properties of
490 biomedical Co-Cr-Mo alloys with combination of N addition and Cr-enrichment. *Mater Trans*
491 2008;49:260-264.
- 492 [33] Rajan K, Vander Sande JB. Room temperature strengthening mechanisms in a Co-Cr-Mo-C
493 alloy. *J Mater Sci* 1982;17:769-778.
- 494 [34] Gonzalez-Mora VA, Hoffmann M, Stroosnijder R, Gil FJ. The role of hardness and
495 roughness on the wear of different CoCrMo counterfaces on UHMWPE for artificial joints. *J*
496 *Biomedical Science and Engineering* 2011;4:651-656.