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CuCrZr alloy produced by Laser Powder Bed Fusion: microstructure, nanoscale strengthening mechanisms, electrical and mechanical properties

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Abstract

CuCrZr is a precipitation hardening alloy, used for its good electrical and thermal properties combined to high mechanical properties. Using additive manufacturing technologies, and more specifically the laser powder bed fusion (L-PBF) process, allows designing highly complex parts such as compact and efficient CuCrZr heat exchangers. Additional understanding of the specific CuCrZr metallurgy during this manufacturing process is still needed to fully take advantages of these possibilities. This work aimed (i) to clarify the impact of the L-PBF process and post-fabrication heat treatments on the microstructure of L-PBF CuCrZr alloy, (ii) to determine the corresponding mechanical and electrical properties and (iii) to quantify the contributions of the different nano-scale strengthening mechanisms (nano-precipitation, dislocations, solid solution, grain size refinement) depending on the different heat treatments. The microstructures of the CuCrZr samples are carefully analyzed at different scales thanks to scanning electron and transmission electron microscopy, highlighting the effect of the different heat treatments. In all heat-treated samples, Cr nano-precipitates are uniformly dispersed in the Cu matrix; few Zr nano-precipitates are observed either at grain boundaries, next to Cr nano-precipitates, or inside the Cu matrix. Moreover, the mean grain size, dislocation density, mean radius and volume fraction of the Chromium nano-precipitates are measured. These data are introduced in the identified hardening mechanisms to estimate the yield strengths (YS) of the

29 different analyzed CuCrZr microstructures. The results are compared to the experimental
30 values, including those of a reference wrought heat-treated CuCrZr, and discussed. A good
31 correlation is found between calculated and experimental values. For the first time, the main
32 hardening mechanisms of L-PBF CuCrZr are quantified and the interest of the “L-PBF+Direct
33 Age Hardening (DAH)” process route to get a high amount of Cr nano-precipitates is
34 confirmed. The DAH applied to L-PBF materials provides high mechanical properties (184
35 HV1 hardness, YS=527 MPa, UTS=585MPa) while keeping a good elongation (14%) and
36 electrical conductivity (42 MS.m^{-1}). These results are due to a combination between (i) a high
37 Cr nano-precipitates density, leading to a high precipitation hardening, and (ii) a high
38 dislocation density associated to the presence of remaining solidification cells.

39 **Keywords:** Laser Powder Bed Fusion, mechanical properties, electrical properties, CuCrZr
40 alloy, nanoscale strengthening mechanisms, heat treatments

41 **1. Introduction**

42 The Copper-Chromium-Zirconium (Cr: 0.5-1.2 wt.%; Zr: 0.03-0.3 wt.%) alloy is a
43 precipitation-hardening alloy, which offers high electrical, thermal and mechanical properties.
44 It is used, for example, in nuclear fusion reactor components as heat exchangers [1-2]. Laser
45 Powder Bed Fusion (L-PBF) is a metallic additive manufacturing process, which has multiple
46 advantages such as the ability to create easily complex shape components. It is used to build
47 heat exchangers with small internal channels, improving their thermal exchange properties [1].

48 L-PBF process involves depositing a thin layer of metal powder that is melted by a laser
49 according to a pattern defined by a *Computer Aided Design* (CAD) file. This operation is
50 repeated to create a three-dimensional object.

51 Due to high optical reflectivity of copper-rich powders at the laser wavelength (1070 nm),
52 several authors have studied the effect of coatings on Cu on CuCr powders, both for increasing

53 absorption and forming in-situ alloys [3-5]. Even if this approach is effective in decreasing laser
54 reflectivity, and thus the energy density required for melting the powder, neither Sn coating [3-
55 4], nor Ni coating [3] lead to a final alloy as mechanically resistant as CuCrZr. The formation
56 of a carburized layer at the surface of a CuCr powder, thanks to a nanometer carbon black
57 powder deposition followed by a 750°C heat treatment [5], allowed to get relatively high tensile
58 properties of L-PBF parts (Yield Strength YS = 347 MPa) after direct ageing, but this was only
59 reached with a laser power over 400W. Indeed, CuCrZr gas-atomized powder can be processed
60 efficiently in the 300-400W power range without costly additional powder modifications.

61 Despite the difficulties to process CuCr or CuCrZr alloy by L-PBF due to their high thermal
62 conductivity and high optical reflectivity at 1070 nm [6], several recent studies [1,7-11] showed
63 the ability to create dense CuCr and CuCrZr parts (relative density > 99%) in particular by using
64 laser power over 300 W. Zeng et al. [11] studied the evolution of the Cu lattice parameter by
65 X-rays diffraction (XRD) after heat treatments and the thermal properties of Cu-1.5Cr-0.5Zr
66 alloy. This short communication only addresses the thermal properties; microstructures and
67 mechanical properties were not deeply studied. The authors indicate that as-built L-PBF
68 CuCrZr is not stable when re-heated and must be stabilized at temperatures above 500°C to
69 form precipitates.

70 CuCr and CuCrZr wrought alloy needs to be heat-treated in order to induce the precipitation of
71 nano-phases responsible for the hardening of the alloy. The different stages of heat treatments
72 consist in a solution annealing (SA) of the Cr and Zr elements in the Cu matrix, followed by
73 water quenching (WQ) leading to a supersaturated matrix. Finally, an age hardening (AH)
74 treatment is necessary to precipitate (Cr, Zr) nano-phases in the matrix [12-13].

75 As the high cooling rate involved during the L-PBF process (of the order of 10^6 K/s) has the
76 effect of quenching the microstructure, a direct age hardening (DAH) heat treatment can be
77 applied to the as-built samples. Indeed, several studies [7,9,14] report that the L-PBF as-built

78 CuCr or CuCrZr alloys show no evidence of Cr or Zr precipitation at micrometric scale. More
79 interesting, such a heat treatment leads to an increase of the Vickers hardness [7,9], the ultimate
80 tensile stress (UTS) [7,14] and the electrical conductivity [7,14] with a thermal conductivity [9]
81 comparable to that of wrought samples subjected to a conventional SA+AH heat treatment.

82 Zhang et al. [10] compared the effect of several heat treatments (SA between 900°C and
83 1020°C; SA at 1020°C + AH at 480°C; DAH at 480°C) on the lattice parameter, microstructure,
84 mechanical properties, electrical properties and corrosion performances of Cu-0.5Cr alloy.
85 Nano-precipitates were identified as nano-Cr face centered cubic (FCC) or body centered cubic
86 (BCC) phases with specific orientation relationship as determined by Transmission Electron
87 Microscopy (TEM)/selected area electron diffraction pattern. Concentrations of alloying
88 elements in matrix range from 0.46 wt% in the as-built state, to 0.29 wt% in the SA+AH state
89 and 0.03 % in the DAH, showing the interest of this last heat-treatment on the precipitation.
90 The volume fraction of nano-precipitates varies from 0.05% in as-built state to 0.25 % in
91 SA+AH state and up to 0.58 % in the DAH state. The experimental yield strength reaches 377
92 MPa after DAH, the elongation being 19% and the electrical conductivity 98 %IACS. The
93 authors compared their YS experimental values to modelled ones using an addition of the
94 different hardening contributions and experimental data from electron backscattered diffraction
95 (EBSD) and TEM analyses; they found a good correlation.

96 Several studies dedicated to wrought CuCrZr alloy have shown that adding small amounts of
97 zirconium to the Cu-Cr alloy plays a role in the precipitation of Cr and significantly increases
98 the mechanical properties of the alloy [15-17]. With a small addition of Zr in a Cu-0.5Cr alloy,
99 increases of 10 % on the yield strength and 6 % on the Vickers hardness are observed [17]. So,
100 in a similar way as it was done by [10] for L-PBF Cu-Cr, there is an important interest to
101 determine the contribution of each strengthening mechanisms in the case of a L-PBF CuCrZr
102 alloy.

103 The main objective of the present work is to clarify the impact of the L-PBF process and post-
104 fabrication heat treatments on the nano-scale microstructure of L-PBF CuCrZr alloy and the
105 different strengthening mechanisms (related to nano-precipitation, dislocation strengthening,
106 solid solution strengthening, grain size refinement). The understanding of these mechanisms
107 are essential to be able to tailor the mechanical and electrical properties of the alloy to the
108 targeted application. For this purpose, a study was performed to select the process parameters
109 leading to the highest density. Then, scanning electron microscopy (SEM) associated to electron
110 backscattered diffraction (EBSD) and transmission electron microscopy (TEM) associated to
111 energy-dispersive X-rays spectroscopy (X-EDS) were used to characterize the samples
112 microstructures. Vickers hardness and tensile tests were used to compare the mechanical
113 properties, whereas eddy current measurements allowed determining the electrical properties.
114 Based on EBSD and TEM analyses, mean grain size, dislocation density, mean radius and
115 volume fraction of nano-precipitates were measured on the different heat-treated samples.
116 Those measurements were used to calculate the yield strengths and compare them to the
117 experimental YS values. The results obtained on L-PBF samples (As-built, SA+AH and DAH)
118 were compared to those of a reference wrought SA+AH material. For the first time, the main
119 hardening mechanisms of L-PBF CuCrZr are quantified and the interest of the “L-PBF+DAH”
120 process route to get a high amount of chromium nano-precipitates is shown.

121 **2. Materials and methods**

122 **2.1. Materials**

123 L-PBF CuCrZr specimens were produced using a spherical 10-45 μm nitrogen-atomized
124 powder (TLS Technik GmbH & Co). Chemical compositions of the powder, the L-PBF samples
125 and the wrought CuCrZr plate, used as a reference, were measured by Instrumental
126 Gas Analysis (IGA) and Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-

127 OES) (Table 1). Chromium and zirconium contents in all samples are conform to the
 128 EN12420:2014 standard [18]. The iron content in the powder and the L-PBF samples is a bit
 129 higher than the minimum value expected by the standard.

130 Table 1: Chemical compositions of CuCrZr powder upon receipt, L-PBF CuCrZr and wrought
 131 CuCrZr samples compared to standard (values correspond to the average of three
 132 measurements).

Element [wt.%]	Cr	Zr	Fe	Si	O	Others	Cu
CuCrZr - EN12420:2014 standard	0.5-1.2	0.03-0.3	< 0.008	< 0.1	< 0.2		<i>Bal.</i>
Wrought CuCrZr (reference)	0.596 ± 0.014	0.071 ± 0.001	0.004 ± 0.001	<0.002	0.005 ± 0.001	-	<i>Bal.</i>
Powder upon receipt	0.751 ± 0.01	0.086 ± 0.002	0.020 ± 0.001	0.005 ± 0.002	0.018 ± 0.002	0.02	<i>Bal.</i>
L-PBF CuCrZr (studied material)	0.781 ± 0.012	0.088 ± 0.003	0.029 ± 0.001	0.008 ± 0.005	0.012 ± 0.001	-	<i>Bal.</i>

133 2.2. L-PBF specimens

134 All specimens were produced on a FS271 L-PBF device (Farsoon, China). The device is
 135 equipped with a 480 W fiber laser with a wavelength of 1070 nm and a 130 μm Gaussian spot
 136 diameter. The powder was handled in a glovebox, dried before L-PBF and the oxygen level was
 137 maintained below 250 ppm during the whole fabrication process. During the process, the
 138 powder was spread using a silicon blade, and the specimens were produced on a 270 mm x 270
 139 mm C45 steel platform. The layer thickness was set to 30 μm. A zigzag laser strategy on 10
 140 mm wide stripes, forming a 45° angle with the cubes or pieces edge, with a 90° rotation between
 141 layers was used. The chamber was filled with argon gas. Cubes (10x10x10 mm³, Figure 1.b)
 142 were built with a different set of parameters and the resulting density was measured. Their base
 143 was rotated 45° with respect to the blade path. The laser power (P) varied from 360 to 480 W,
 144 the scan speed (v) from 200 to 700 mm.s⁻¹ and the hatch (h) from 100 to 120 μm. The optimized
 145 parameters, i.e. the parameters that lead to the highest density (99.4%), are a power of 480 W,
 146 a scan speed of 700 mm.s⁻¹ and a hatch of 100 μm (Figure 1.a). Those parameters were then
 147 used to fabricate mechanical and electrical samples (Figure 1.c). 55x13x13 mm³ parallelepipeds

148 were built for mechanical samples; their small bases was rotated 45° in the YZ plane and their
 149 main axis was rotated 45° relative to the direction of the blade. 18 mm diameter and 22 mm
 150 high cylinders were built for electrical samples.

151 2.3. Material characterization techniques

152 The density of L-PBF CuCrZr was measured on polished samples (SiC P320), by Archimedes
 153 method using isopropanol thanks to the equation (1) :

$$\rho_{\text{relative density}} = \frac{M_{\text{L-PBF sample}}}{M_{\text{HIP}}} \quad (1)$$

154 where $M_{\text{L-PBF sample}}$ is the density of L-PBF CuCrZr, M_{HIP} is the density of Hot Isostatically
 155 Pressed (HIPed) CuCrZr samples obtained by HIPping the CuCrZr powder at 1040°C for 2
 156 hours under 1400 bar; their density was measured with helium pycnometer on an AccuPyc II
 157 1340 Micrometrics and used as a reference. The standard deviation on the relative density is
 158 ±0.25%. The chemical composition was verified by IGA and ICP-OES on three different parts
 159 for each CuCrZr (Table 1). The SA + AH heat treatments have been applied to L-PBF and
 160 wrought samples. They consist in a solution annealing followed by water quenching (WQ), and
 161 subsequent thermal ageing under air followed by air-cooling (Table 2). The temperature and
 162 exposure time were chosen according to previous research on this material for fusion nuclear
 163 reactor applications [19-20]. A DAH heat treatment, which consists in an age hardening under
 164 air followed by air-cooling [9] (Table 2), has been applied to as-built L-PBF samples. This heat
 165 treatment corresponds to the best compromise between mechanical and thermal properties
 166 according to [9].

167 Table 2: Heat treatments applied to the CuCrZr samples

Heat treatment	Temperature [°C] / Atmosphere	Exposure time [min]	Cooling type	Samples concerned
Solution Annealing + Age Hardening (SA+ AH)	980 / Ar + 490 / Air	60 + 360	Water quenching + Air cooling	L-PBF Wrought

Direct Age Hardening (DAH)	490 / Air	60	Air cooling	L-PBF
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168 For the SEM and TEM observations, samples were cut normal to the building direction (noted
169 \odot BD plan in Figure 2) or parallel to the building direction (noted \uparrow BD plan in Figure 2). The
170 plates were mechanically polished down to 100 μm thickness, punched out into 3 mm disks and
171 electro-polished. The electro-polishing was performed at room temperature with a solution of
172 25 vol.% ethylene glycol, 25 vol.% ortho-phosphoric acid and 50 vol.% deionized water at
173 20°C, under an applied potential of 12 V, and with a 200-300 mA current. For SEM analysis,
174 the electro-polishing was stopped quickly, to remove hundreds of nanometers of damaged
175 surface. For TEM analysis, the electro-polishing was carried on to obtain a thickness of around
176 20 μm . The disks were then polished using an argon ion beam polishing (PIPS 2 GATAN 691)
177 to create a hole and avoid oxidation issues observed after an electro-polishing.

178 SEM observations were performed on a field emission gun (FEG) SEM Zeiss Merlin equipped
179 with two Energy Dispersive Spectroscopy (EDS) detectors and an Electron Back-scattered
180 Diffraction (EBSD) QUANTAX detector from Bruker. EBSD analyses using Esprit 2.2
181 software for data processing were used to assess the average grain size and the median
182 misorientation angle. Grains boundaries are defined with a misorientation angle higher than 15°
183 and subgrains boundaries with a misorientation angle lower than 15°. The grain size is defined
184 as the equivalent diameter of a circle of the same surface as the observed grains. The average
185 grain size is weighted by the surface. A Kernel Average Misorientation map (KAM) analysis,
186 which measures the local misorientation of a pixel between 0.5° and 5° against the closest
187 pixels, was used to define the median misorientation angle. This angle (θ [rad]) is then used to
188 estimate the dislocation density (ρ_0) thanks to equation (2) [21].

$$\rho_0 = \frac{2\sqrt{3}}{3} \frac{\theta}{bs} \quad (2)$$

189 With b [m], the Burgers vector and s [m] the step size used during the EBSD analysis. The
190 Burgers vector is taken equal to 0.256 nm for a Cu matrix [12].

191 TEM analyses were performed on a TITAN Themis (FEI), operating at 200kV and equipped
192 with a Cs probe corrector, a Super-X system (4 Silicon Drift Detectors) for EDS analyses and
193 a Gatan Imaging Filter (GIF Quantum) for Electron Energy Loss Spectroscopy (EELS)
194 analysis. Images were acquired in scanning transmission electron microscopy (STEM) mode
195 using either a HAADF (high angle annular dark field) or a BF (bright field) detector.

196 **2.4. Mechanical and electrical analyses**

197 Vickers hardness was measured on a Matsuzawa MMT-X7B micro-hardness tester according
198 to EN ISO 6507-(1-4) [22] with a load of 1 kg during 15 seconds; 10 indents were made per
199 sample. Tensile tests perpendicular to the building direction were done on 3 specimens per
200 CuCrZr state under air, at 20°C on a MTS servo-hydraulic testing machine with a 100 kN load
201 cell at a $2.5 \times 10^{-4} \text{ s}^{-1}$ strain rate. Tensile bars were made according to NF EN ISO 6892-1 [23].
202 Electrical conductivity was measured, according to EN 2004-1 standard [24], at 20°C on 3
203 polished specimens per CuCrZr state (SiC P4000), by Eddy current on a Fischer FS40 machine.

204 **3. Experimental results**

205 **3.1. Relative density and chemical composition**

206 Figure 1.b shows the cubic L-PBF specimens. Their relative density as a function of the energy
207 density E_v [$\text{J} \cdot \text{mm}^{-3}$] input during the process is presented in Figure 1.a. E_v depends on the laser
208 power energy P [W], the laser scanning velocity v [$\text{mm} \cdot \text{s}^{-1}$], the hatch h [mm] and the layer
209 thickness l [mm], as given in equation (3) [25-26].

$$E_v = \frac{P}{v * h * l} \quad (3)$$

210 The relative density of the alloy increases with increasing E_v input. A minimum E_v of
211 approximately $300 \text{ J} \cdot \text{mm}^{-3}$ is needed to achieve a relative density equal to or higher than 99%.
212 At a laser power of 360 W, only a few sets of parameters leading to a high E_v with small scan

213 speeds (200 and 300 mm.s⁻¹), offer a relative density higher than 99%. Whereas, 480 W laser
214 power offers the widest range of Ev which can achieve a relative density higher than 99% even
215 with a laser speed of 700 mm.s⁻¹ that allows higher productivity. Consequently, a laser power
216 of 480 W, a scan speed of 700 mm.s⁻¹ and a hatch of 100 μm were used for building the samples
217 of this work.

218 The chemical composition of the samples is comparable to that of the powder (Table 1). The
219 oxygen content is stable, showing no evidence of oxidation during the process. In addition, no
220 evidence of impurities, cross contamination, or Zr loss, was detected.

221 **3.2. Microstructure of the L-PBF as-built CuCrZr**

222 Figure 3.a and Figure 3.d show SEM images of the L-PBF as-built CuCrZr taken in the ⊙ BD
223 and ↑ BD plans respectively. Figure 3.b and Figure 3.e are EBSD quality patterns images
224 superimposed with grain and subgrain boundaries defined by different misorientation angles.
225 The microstructure is anisotropic. In the ↑ BD plan, grains are elongated along the BD direction
226 (Figure 1.d-e). The average grain size is $217 \pm 80 \mu\text{m}$ ($363 \pm 160 \mu\text{m}$ long and $125 \pm 60 \mu\text{m}$
227 width). The grain cross-sections form a pavement in the ⊙ BD plan (Figure 3.b). This particular
228 shape is due to the combination of the spot size and the zigzag scan strategy [25]. The grains
229 have a nearly squared shape, 100 μm side, and in some cases, are elongated at 60° in regards to
230 the scan path direction. The average grain size in this plane is $115 \pm 60 \mu\text{m}$. A large number of
231 subgrains (misorientation angle <15°) are observed, they are distributed with high and low
232 density zones. These zones are also highlighted on the KAM map that image the local
233 misorientation (Figure 3 c).

234 Inside the subgrains, TEM observations revealed the presence of dislocation cells having an
235 average size of 300 nm (Figure 3f). They probably are solidification cells resulting from the
236 high solidification rate of the L-PBF process and are observed on other L-PBF alloys [27].

237 KAM analysis is used to estimate the dislocation density in the CuCrZr (equation (1)). The
238 measurement was performed at two different magnifications: at low magnification, which
239 underestimates the dislocation density but provides an average dislocation density in this non-
240 homogeneous CuCrZr, and at high magnification, with a step size of 0.1 μm that is smaller than
241 the solidification cells (300 nm) for a more relevant estimation. These values are used to
242 compare the different metallurgical states and the results are reported in Table 4. The as-built
243 CuCrZr presents a high dislocation density ($5 \pm 1 \times 10^{14} \text{ m}^{-2}$), comparable to the dislocation
244 density obtained on cold worked CuCrZr ($5 \times 10^{14} \text{ m}^{-2}$) [28]. The dislocations appear during
245 the L-PBF process due to high stresses induced by the thermal gradients generated during the
246 rapid solidification. The thermal history of the CuCrZr during the process is complex and
247 inhomogeneous, and so is the microstructure.

248 **3.3. Effect of the heat treatment on L-PBF CuCrZr and comparison with wrought** 249 **CuCrZr**

250 Figure 4 shows the SEM and EBSD microstructures of the wrought and the different L-PBF
251 heat-treated CuCrZr (heat treatments are reported in Table 2). The wrought SA+AH CuCrZr
252 whose microstructure (Figure 4.a and d) is different to the L-PBF alloy, shows large equiaxed
253 grains with numerous twins, leading to an average grain size (including twins) of $470 \pm 150 \mu\text{m}$
254 (Table 3). A dislocation density of 3×10^{13} was estimated using KAM analysis (Table 5). This
255 density is similar to the value found by [28] on wrought Cu-0.8Cr-0.1Zr (wt.%) in the same
256 metallurgical state.

257 For the L-PBF alloy, the SA + AH heat treatment caused an evolution of the microstructure
258 (Figure 4.b and e) compared to the as-built state (Figure 3). The pavement shape of the grain
259 cross-section in the \odot BD plan and the elongated grain cross-section in the \uparrow BD plan is partially
260 preserved however in some area, recrystallization has occurred and has resulted in larger

261 twinned grains. The average grain size is $276 \pm 150 \mu\text{m}$ in the \odot BD plan and $334 \pm 140 \mu\text{m}$ in
 262 the \uparrow BD plan (Table 3). This partial recrystallization (60% of the surface) is confirmed by the
 263 KAM analysis (Figure 4.g). No solidification cells are observed in both, recrystallized or non-
 264 recrystallized grains. The dislocation recovery should occur prior to the recrystallization during
 265 the 980°C SA heat treatment. Given the absence of solidification cells, a step size of 1.7 or 2.1
 266 μm was used for KAM analysis to estimate the dislocation density (Table 4). Dislocation
 267 density in the recrystallized zones is found to be close to the value of the wrought SA+AH
 268 CuCrZr ($3 \pm 1 \times 10^{13} \text{ m}^{-2}$), while in the non-recrystallized zone it is higher ($7 \pm 1 \times 10^{13} \text{ m}^{-2}$).

269 Table 3 : Average grain size of the different CuCrZr samples.

CuCrZr	L-PBF DAH		L-PBF SA+AH		Wrought SA+AH
	\odot BD	\uparrow BD	\odot BD	\uparrow BD	
Average grain size [μm]	112 ± 60	242 ± 100	276 ± 150	334 ± 140	471 ± 150
Number of grains counted	785	368	338	406	44

270 On the contrary, the DAH heat treatment involved no change of grain morphology and size
 271 compared to the as-built state (Figure 4.c and f), a similar average grain sizes of $112 \pm 60 \mu\text{m}$,
 272 in the \odot BD plan and $242 \pm 100 \mu\text{m}$ in the \uparrow BD plan were measured (Table 3). Moreover, the
 273 dislocation cells with similar size as the as-built state were still observed by TEM. It is however
 274 likely that the heat treatment at 490°C allows a dislocation recovery in the cell walls that can
 275 explain the slightly lower dislocation density measured by KAM analysis (Figure 4.h) than in
 276 the as-built state ($4 \times 10^{14} \text{ m}^{-2}$ versus $5 \times 10^{14} \text{ m}^{-2}$) although this difference is within the
 277 measurement error bar.

278 Table 4 : KAM median misorientation angle θ and average dislocation density ρ_0 as a function
 279 of the step size used s , estimated for L-PBF as built, L-PBF SA+AH and L-PBF DAH, and
 280 wrought SA+AH CuCrZr alloys.
 281

CuCrZr	Analysed surface	Cells size [nm]	s [μm]	θ [$^\circ$]	ρ_0 [m^{-2}]
L-PBF as-built	1 cm^2	300	2.0	1.9	$8 \pm 1 \times 10^{13}$
	4.5 mm^2		0.1	0.7	$5 \pm 1 \times 10^{14}$
	1 cm^2	No cell	1.7	0.9	$4 \pm 1 \times 10^{13}$

L-PBF SA+AH	0.6 cm ² (recrystallized zone)		1.7	0.7	$3 \pm 1 \times 10^{13}$
	0.4 cm ² (non-recrystallized zone)		1.7	1.5	$7 \pm 1 \times 10^{13}$
L-PBF DAH	1 cm ²	330	2.3	2.2	$7 \pm 1 \times 10^{13}$
	4.5 mm ²		0.2	0.7	$4 \pm 1 \times 10^{14}$
Wrought SA+AH	1 cm ²	No cell	2.1	0.7	$3 \pm 1 \times 10^{13}$

282 3.4. Micro- and nano-precipitation

283 In the as-built L-PBF CuCrZr, Cr, and Zr micro- or nano-precipitates are not detected (Figure
284 5.b and Figure 6.a), which confirms that Cr and Zr form a solid solution in the Cu matrix of this
285 material. After heat treatment and due to the low solubility of the Cr and Zr in the copper matrix,
286 Cr and Zr form micro or nano-precipitates.

287 Cr micro-precipitates were observed on SEM images (Figure 5). In the wrought SA+AH
288 CuCrZr, they are intragranular precipitates (Figure 5.a). In contrast, in the L-PBF SA+AH
289 CuCrZr, they are intergranular or located along sub-grain boundaries in the non-recrystallized
290 areas, but they are also intragranular in the recrystallized areas (Figure 5.d). Contrary to
291 SA+AH, the DAH heat treatment did not induce Cr micro-precipitation (Figure 5.c). Thus,
292 during the DAH heat treatment, a larger amount of Cr was involved in the nanoprecipitation as
293 confirmed in the following.

294 Zr nano-precipitates are observed in different locations and with different shapes after SA+AH
295 or DAH heat treatments: at grain boundaries, next to Cr nano-precipitates (the Zr precipitate
296 size is then between 5 and 30 nm as in Figure 6.d), inside the Cu matrix (Zr hexagonal
297 precipitate with 10-40 nm of diameter). EDS analyses of these Zr nano-precipitates show a
298 particularly high Cu peak suggesting these precipitates could be Cu₅Zr or Cu₄Zr according to
299 [12].

300 The Cr nano-precipitates were observed in all heat-treated CuCrZr samples; they are uniformly
301 dispersed in the Cu matrix (Figure 6.b and c), and display an ellipsoidal shape (Figure 6.e and
302 f). They have a face centered cubic (FCC) structure and are coherent with the matrix. In the

303 wrought SA+AH CuCrZr, the equivalent radius (r) is uniform at 1.8 ± 1.0 nm (Table 5). In the
 304 L-PBF DAH CuCrZr, r varies depending on the nano-precipitate location. For the precipitates,
 305 which have grown on dislocations or grain boundaries, it is around 3.2 ± 1.6 nm, whereas for
 306 one located in the Cu matrix it is around 2.1 ± 1.5 nm (Table 5). This could be explained by a
 307 specific precipitation occurring at the grain boundaries in DAH CuCrZr. Note the equivalent
 308 radius measurement gives a high standard deviation.

309 Table 5 : TEM analysis of the equivalent radius and volume fraction of Cr nano-precipitates
 310 on heat treated CuCrZr.

CuCrZr	Equivalent radius [nm]	Number of precipitates measured	Volume fraction of precipitates [%vol]
L-PBF DAH	2.1 ± 1.5	233	0.6
Wrought SA+AH	1.8 ± 1.0	54	0.3

311 To determine the volume fraction of the precipitates, the thickness of the CuCrZr thin foils
 312 where TEM analysis was performed was roughly estimated by EELS at 30 nm. Considering
 313 this value, the volume fraction of the Cr nano-precipitates in the CuCrZr matrix of the L-PBF
 314 DAH CuCrZr was estimated (3 images were analyzed) to be 0.6 % (Table 5). This is consistent
 315 with the theoretical volume fraction of Cr in solid solution in the L-PBF as built CuCrZr which
 316 is 0.62 vol% (estimation made with the chemical composition of Table 1, and thanks to the
 317 theoretical density of Cu, Cr and Zr [29]). Then the volume fraction of Cr nano-precipitates is
 318 twice higher in the L-PBF DAH CuCrZr than in the wrought SA+AH CuCrZr (Table 5). As the
 319 size of the precipitates in both L-PBF DAH and wrought SA+AH CuCrZr is equivalent, the
 320 number of precipitates is lower, and thus the distance between them is greater in the L-PBF
 321 DAH CuCrZr.

322 **3.5. Mechanical properties**

323 HV1 Vickers hardness performed on the different materials are presented in Table 6 and, as
 324 indicated by the standard deviation, the hardness testing has good repeatability. The hardness
 325 of the as-built L-PBF CuCrZr is 101 ± 4 HV1, which is close to the values found by [7,9] for

326 similar process parameters. This obtained value is high compared to that of the CuCrZr
 327 (SA+WQ) from literature (65-77 HV1 [30]), which is also a microstructural state free from
 328 nano-precipitates. Hardness was found to be similar for L-PBF SA+AH and wrought SA+AH
 329 CuCrZr tested here and compared to similar CuCrZr SA+AH from the literature [8-9,12,20].
 330 This is probably due to the recrystallization occurring during the SA heat treatment. By contrast,
 331 the L-PBF DAH CuCrZr hardness is much higher than the others, in agreement with literature
 332 [7,9].

333 Table 6: Tensile and hardness properties of wrought SA + AH, L-PBF as-built, L-PBF SA +
 334 AH and L-PBF DAH CuCrZr tested at 20°C.

CuCrZr	YS	UTS	Total Elongation	Vickers Hardness
	[MPa]	[MPa]	[%]	[HV1]
L-PBF As-built (⊙ BD)	270 ± 6	305 ± 5	26 ± 2	101 ± 4
L-PBF SA + AH (⊙ BD)	253 ± 8	380 ± 7	25 ± 2	112 ± 5
L-PBF DAH (⊙ BD)	527 ± 3	585 ± 1	14 ± 1	184 ± 4
Wrought SA + AH	221 ± 1	349 ± 3	33 ± 1	116 ± 2

335 Figure 7 shows tensile test curves for the different alloys recorded at 20°C (as the curves were
 336 qualitatively similar, only one for each condition is shown on the graph). The yield strength,
 337 ultimate strength and the elongation values are given in Table 6. The low elongation observed
 338 on the L-PBF SA+AH or DAH CuCrZr compared to wrought SA+AH CuCrZr (tested here, or
 339 from the literature [20]) can be explained by the residual porosity of the L-PBF CuCrZr
 340 samples, identified by the presence of few unmelted particles found on the fractography (Figure
 341 7.b). The ultimate tensile strength (UTS) and the yield strength (YS) of the L-PBF SA+AH
 342 CuCrZr are slightly greater than the wrought CuCrZr ones. The L-PBF DAH CuCrZr has
 343 different mechanical behavior: an elongation half as high as wrought SA+AH CuCrZr and a YS
 344 95% higher, even higher than the L-PBF DAH CuCrZr of [14]. A limited strain hardening is
 345 also observed on the L-PBF DAH CuCrZr. The presence of cells and extremely high dislocation
 346 density in L-PBF DAH CuCrZr is probably due to an equilibrium between creation and

347 annihilation of dislocations, which explains the shape of the curves. Moreover, in all tested
348 samples (Figure 7.c), dimples are visible on the fracture surface.

349 **3.6 Electrical properties**

350 The low electrical conductivity of L-PBF as-built CuCrZr is consistent with a supersaturated
351 solid solution state of the Cu matrix (Table 7) and the observations made in ref [7]. After
352 SA+AH, both the L-PBF and wrought CuCrZr samples show similar electrical conductivity,
353 even compared to the wrought SA+AH from literature [20]. Finally, L-PBF DAH CuCrZr
354 displays a lower conductivity compared to SA+AH samples, due to the still high amount of
355 dislocation density [31]. This tendency is in agreement with the values of other studies [7,14].

356 Table 7: Electrical conductivity measured by Eddy current

CuCrZr	Electrical Conductivity
	[10⁶ S.m⁻¹]
L-PBF As-built (⊙ BD)	14.3 ± 0.1
L-PBF SA + AH (⊙ BD)	51.1 ± 0.1
L-PBF DAH (⊙ BD)	41.6 ± 0.4
Wrought SA + AH	51.9 ± 0.3

357 **4. Discussion**

358 **4.1. Microstructural evolution of L-PBF CuCrZr**

359 During L-PBF process, the heat transfer through the already densified part tends to create
360 elongated grains in the building direction. Gorsse et al. [25] found similar grain morphology,
361 i.e. elongated grains in the ↑BD plan and pavement of the size of the laser hatch in the ⊙ BD
362 plan. Moreover, a cellular growth is observed due to high cooling rate typical of materials
363 fabricated by L-PBF [25,27]. This leads to a high dislocation density present in the as-built part.
364 They do not show any evidence of micro- or nano-precipitates (Figure 8). The solubility limit
365 of Cr is then 0.78 wt.%, more than the theoretical solubility limit of Cr in Cu-Cr alloy (0.72
366 wt.% [32]).

367 After SA+AH on L-PBF CuCrZr, recrystallization is observed on 60% of the surface. During
368 SA, at 980°C, partial recrystallization is possible, as shown by [33] on cold rolled wrought
369 CuCrZr. In the recrystallized zones, the microstructure is similar to the wrought CuCrZr, with
370 large twined grains showing no particular orientation. After WQ of the SA treatment, the Cr
371 and the Zr partially precipitate at a micrometric scale and are partially maintained in solid
372 solution (0.4 wt.% maximum [32]) (Figure 8). The AH treatment allows the Cr and Zr in solid
373 solution to precipitate at a nanometric scale (Figure 8).

374 After DAH, the specific microstructure of L-PBF as-built CuCrZr is globally preserved. A
375 slight dislocation recovery is observed, but the solidification cells remain. The age hardening
376 temperature (490°C) is not high enough to trigger recovery. All the Cr, which was in a
377 supersaturated solid solution state, precipitates at a nanometric scale, leading to a volume
378 fraction of nano-precipitates twice as high as after SA+AH (Figure 8).

379 **4.2. Hardening mechanisms**

380 In the following, the different hardening mechanisms acting on the mechanical behavior of our
381 four samples will be estimated, to discuss the effect of the processes and heat treatments. The
382 yield strength (*YS*) of such materials depends on several contributions according to equation
383 (4) [10,34-35].

$$YS = \sigma_0 + \Delta\sigma_{ss} + \Delta\sigma_{gs} + \Delta\sigma_{ds} + \Delta\sigma_{ps} \quad (4)$$

384 With σ_0 the friction lattice or Peierls-Nabarro stress, $\Delta\sigma_{ss}$ the solid solution strengthening, $\Delta\sigma_{gs}$
385 the grain size refinement contribution, $\Delta\sigma_{ds}$ the dislocation strengthening and $\Delta\sigma_{ps}$ the
386 precipitation strengthening. To investigate the increase of *YS* observed in the L-PBF CuCrZr,
387 and especially in the DAH CuCrZr, each contribution is individually examined for the four

388 metallurgical states in the following sections. Some parameters have been evaluated
 389 experimentally whereas the others have been taken from the literature (Table 8).

390 Table 8: Value of the parameters for pure Copper used in the calculations

	Parameters	Value	Unit	Reference
σ_0	Peierls-Nabarro stress	20	MPa	[16]
G	Shear modulus of the matrix	45.5	GPa	[34,36-37]
k	Hall Petch slope	180	MPa. $\mu\text{m}^{1/2}$	[16,34]
M	Taylor factor	3.06	-	[10,28,36]
b	Burgers vector	0.256	nm	[12,36]
α	-	0.23	-	[10]
ε	Misfit	0.015	-	[14,38]
ν	Poisson's ratio	0.34	-	[34,39]

391 4.2.1. Solid solution strengthening

392 The elements remaining in solid solution in the Cu matrix can play a strengthening effect caused
 393 by the induced crystal lattice distortion affecting dislocation movement (equation (5)) [10]:

$$\Delta\sigma_{ss} = MG\varepsilon^{3/2} \sqrt{\frac{x_a}{3}} \quad (5)$$

394 With x_a [wt. %] the mass concentration of the element in the solid solution. The Zr, O, Si and
 395 Fe contributions are neglected due to their low content and low solubility limits in the Cu matrix
 396 [40].

397 In the as-built L-PBF CuCrZr, all Cr atoms are in solid solution (x_a is then equal to 0.78 wt.%,
 398 Table 1), as no evidence of precipitation has been found during TEM observations. Thus, the
 399 contribution of solid solution strengthening to YS is 35 MPa. After SA+AH or DAH, nearly all
 400 Cr atoms have precipitated as the electrical conductivity proves. We decided to discard this
 401 contribution for these heat treatments. Indeed, even with 10 wt.% of the total content of Cr in
 402 solid solution, this contribution would represent less than 10 MPa.

403 4.2.2. Grain size

404 The contribution of the grain size to the YS is given by the Hall-Petch model (6) [41-42].

$$\Delta\sigma_{gs} = \frac{k}{\sqrt{D}} \quad (6)$$

405 With D [μm] the average grain size. As shown in Figure 3, the grains of L-PBF CuCrZr are
 406 columnar. Thus, an assumption has been made on the grain size. We decided to take the critical
 407 situation and thus consider the smallest grain size, i.e. in the \odot BD plan. In addition, twins
 408 appear in the SA+AH CuCrZr. As twins also impede the dislocation motion, they have been
 409 considered as grain boundaries, lowering the values given in Table 3. The calculated $\Delta\sigma_{gs}$ for
 410 the different CuCrZr are reported in Table 9. The twins in SA+AH CuCrZr do not affect
 411 significantly the grain contribution to YS. Whatever the metallurgical state, the grain size
 412 contribution to the YS is low and accounts for 3% to 8% of the total YS.

413 Table 9: Grain size contribution, dislocation density measured thanks to KAM analysis,
 414 dislocation strengthening contribution in the different CuCrZr, channel size between the nano-
 415 precipitates and strengthening contribution for the different CuCrZr.

CuCrZr	L-PBF As-built	L-PBF DAH	L-PBF SA+AH	Wrought SA + AH
Average equivalent grain diameter [μm]	115 \pm 60	112 \pm 55	80 \pm 40	186 \pm 108
Number of grains	902	785	1095	514
$\Delta\sigma_{gs}$ [MPa]	17	17	20	13
ρ_0 [m^{-2}]	5 \pm 1 $\times 10^{14}$	4 \pm 1 $\times 10^{14}$	4 \pm 1 $\times 10^{13}$	3 \pm 1 $\times 10^{13}$
$\Delta\sigma_{ds}$ [MPa]	184	153	52	41
L_p [nm]	\emptyset	36	Taken equal to wrought SA+AH values	45
$\Delta\sigma_{ps}$ [MPa]	\emptyset	402		304

416 4.2.3. Dislocation strengthening

417 The dislocation strengthening mechanism, due to the dislocation forest effect, can be estimated
 418 in an isotropic material thanks to equation (7) [28,43] (the heterogeneous distribution of
 419 dislocation density is neglected).

$$\Delta\sigma_{ds} = \alpha M G b \sqrt{\rho_0} \quad (7)$$

420 With $\rho_0[\text{m}^{-2}]$ the dislocation density, measured by KAM analysis (section 3.2 and Table 4). The
 421 dislocation strengthening magnitude depends on the process and the applied heat treatment
 422 (Table 9). On a wrought SA+AH CuCrZr, this contribution to the YS is low, since the heat
 423 treatment leads to a rather low dislocation density. By contrast, it is 4.5 times higher for the as-
 424 built L-PBF sample due to the high dislocation density induced by the high cooling rate. The
 425 SA part of the SA+AH strongly decreases the dislocation strengthening contribution to YS. The
 426 remaining non-recrystallized grains in this sample however contribute to an intermediate
 427 dislocation strengthening, which is 25% higher than the one of wrought SA+AH. With the
 428 DAH, the dislocation density slightly decreases due to a slight recovery of the dislocations
 429 located on the solidification cells walls. However, this contribution is 3.7 times higher than the
 430 one of wrought SA+AH.

431 4.2.4. Precipitation strengthening

432 In this part, we assumed that precipitation strengthening is driven by the Orowan-Ashby
 433 mechanism [12,28,44] which strongly depends on the channel size between the nano-
 434 precipitates, directly related to the duration and temperature of the age hardening step. The
 435 smaller this length, the harder it is for the dislocations to curve and to cross the precipitates.
 436 This impedes the dislocation motion and hardens the alloy. The contribution of the nano-
 437 precipitation to the YS is estimated using equation (8) [39,43,45].

$$\Delta\sigma_{ps} = \frac{0.8 * MGb}{2\pi\sqrt{1-\nu}} \cdot \frac{\ln\left(\frac{2r}{r_0}\right)}{L_p} \text{ with } L_p = r \left(\sqrt{\frac{2\pi}{3f}} - \frac{\pi}{2} \right) \quad (8)$$

438 The 0.8 factor is a statistic factor, reflecting the random repartition of the precipitates in the slip
 439 plan [46]. With r [nm] the mean radius of the nano-precipitates, r_0 [nm] the cut-off radius or
 440 radius of dislocation core, that can be taken equal to the Burgers vector [45], L_p [nm] the
 441 channel size between the nano-precipitates and f the volume fraction of precipitates. As the

442 quantity of Zr nano-precipitates in the Cu matrix is low, only the Cr nano-precipitation is taken
443 into account to estimate this contribution. r and f have been measured by TEM (Table 5).
444 Moreover, we assume that the L-PBF and wrought CuCrZr have the same Cr nano-precipitation
445 after the SA+AH heat treatments.

446 The calculated precipitation strengthening contribution (Table 9) is overestimated as the
447 experimental YS does not exceed 300 MPa (Table 6). This overestimation can come from the
448 imprecise determination of precipitates size (50% inaccuracy due to high standard deviation,
449 Table 5. Some high resolution TEM analyses made on the size of precipitate (Figure 6.e-f) seem
450 to confirm the underestimation of the radius. It is also possible that a shear hardening
451 mechanism is acting instead of the Orowan hardening mechanism. Nevertheless, the obtained
452 trends are consistent: this contribution is predominant in all heat-treated CuCrZr, and the
453 biggest in the L-PBF DAH CuCrZr. Such a heat treatment provides a high nano-precipitation
454 density in the Cu matrix reducing the average channel size, and thus increasing the precipitation
455 strengthening contribution.

456 4.2.5. Comparison between the experimental YS and the calculated YS contributions

457 The objective of the previous calculations was to quantify the contribution of the different nano-
458 scale strengthening mechanisms (nano-precipitation, dislocations, solid solution, grain size
459 refinement) for each CuCrZr sample (L-PBF as-built, L-PBF SA+AH, L-PBF DAH and the
460 reference wrought SA+AH). Some interesting results emerge from this analysis. Figure 9
461 summarizes the different contributions to the YS calculated for each heat-treated CuCrZr and
462 compared to the experimental YS (black spots). Qualitatively, we found the right trends for
463 every metallurgical states. In the L-PBF SA+AH and wrought SA+AH CuCrZr, the
464 predominant strengthening mechanism is the nano-precipitation strengthening, accounting for,
465 respectively, 80% and 85% of the total strengthening. The overestimation of 48% to 62% of the

466 calculated YS compared to the experimental one, respectively for the L-PBF SA+AH and
467 wrought SA+AH CuCrZr, can come from the high standard deviation on the mean radius of the
468 Chromium nano-precipitates. For the as-built L-PBF CuCrZr, there are two main acting
469 mechanisms: dislocation strengthening (78% of calculated YS) and solid solution strengthening
470 (15% of calculated YS). The difference between the measured and estimated YS is less than
471 15%. For the L-PBF DAH CuCrZr, the precipitation strengthening and the dislocation
472 strengthening account, respectively, for 70% and 27% of the total estimated YS. The difference
473 between the measured and estimated YS is less than 8%. Thus, the supersaturated Cu solid
474 solution obtained thanks to L-PBF process offers the possibility to precipitate more nano-Cr
475 after a DAH (0.6 % vol. as shown in Figure 8) than what is possible with a SA+AH (0.3 % vol.),
476 increasing the precipitation strengthening.

477 **5. Conclusions**

478 In this study, we have shown that:

- 479 (1) CuCrZr samples with a relative density higher than 99% have been successfully
480 processed by L-PBF.
- 481 (2) the L-PBF as-built CuCrZr alloy microstructure shows columnar grains, a high
482 dislocation density due to the presence of solidification cells of 294 ± 32 nm of diameter,
483 and it is in a supersaturated state without Cr micro- nor nano-precipitate, which is very
484 different from the well-known wrought CuCrZr alloy. In L-PBF as-built sample, the
485 volume fraction of Cr in solid solution is twice the one of the SA+WQ wrought alloy;
486 this is explained by the higher cooling rate of the L-PBF process.
- 487 (3) Applying a solution annealing at 980°C for 1h followed by an ageing at 490°C for 6h
488 on a L-PBF CuCrZr sample recrystallizes the microstructure at 60%. During the solution
489 annealing, a part of the Cr (0.4 wt%) forms micro-precipitates while the other part

490 remains in solid solution which will form nano-precipitates after the age hardening
491 treatment. The mechanical properties are comparable to wrought CuCrZr in the
492 direction perpendicular to the building one.

493 (4) A direct ageing at 490°C for 1 hour allows to precipitate all the Cr (0.78 wt%) at
494 nanometric scale but does not modify the microstructure of the as built L-PBF CuCrZr
495 (columnar grain, high dislocation density) to a huge extent. This particular heat
496 treatment offers high mechanical properties (Vickers hardness of 184 HV1, YS=527
497 MPa and UTS=585 MPa) while conserving a significant elongation (14%) and good
498 electrical properties (42 MS.m⁻¹) compared to SA+AH heat treatments. This is due to
499 the high dislocation density and the high Cr nano-precipitates density, which lead to a
500 lower distance between precipitates and a stronger structural hardening compared to the
501 one after SA+AH.

502 Further investigations on the SA+AH heat treatment on L-PBF CuCrZr may offer the possibility
503 to get totally rid of the anisotropic microstructure induced by the process. A further
504 investigation on the DAH heat treatment may offer the possibility to determine precisely the
505 hardening peak depending on the Cr concentration in the alloy. A TEM study of the Cr nano-
506 precipitates on CuCrZr tensile samples may confirm the structural hardening mechanism (shear
507 or bypass mechanism) playing a role here.

508 **Data availability**

509 The raw/processed data required to reproduce these findings cannot be shared at this time as
510 the data also forms part of an ongoing study.

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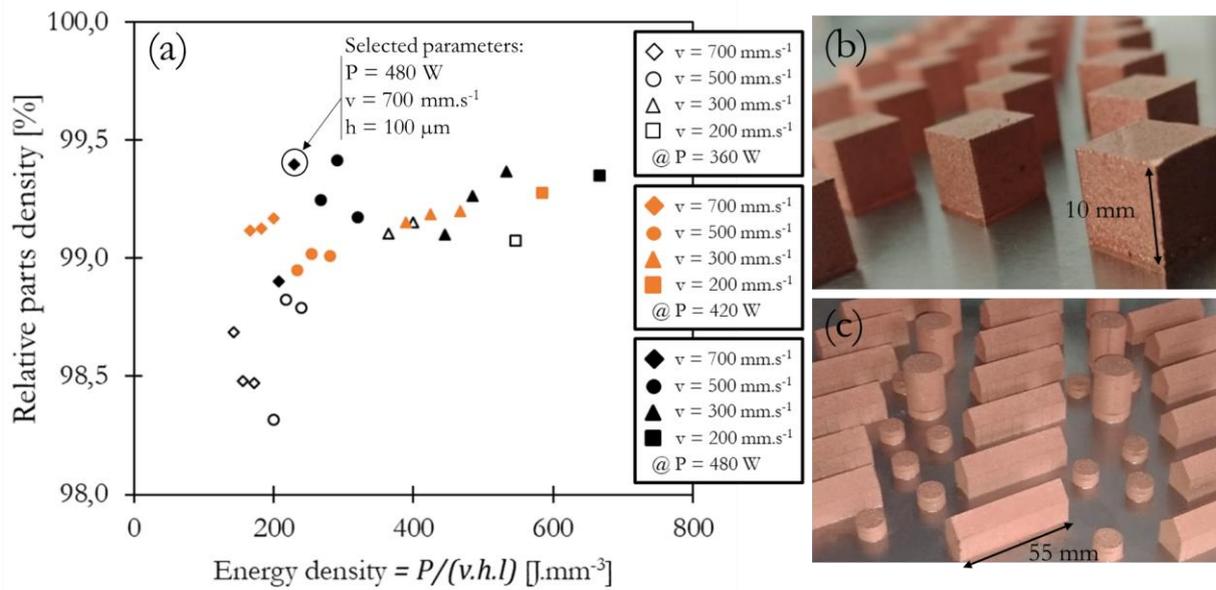
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517 References

- 518 [1] Z. Ma, K. Zhang, Z. Ren, D. Z. Zhang, G. Tao, and H. Xu, "Selective laser melting of Cu–
519 Cr–Zr copper alloy: Parameter optimization, microstructure and mechanical properties,"
520 *Journal of Alloys and Compounds*, vol. 828, no. 154350, Art. no. 154350, Jul. 2020, doi:
521 10.1016/j.jallcom.2020.154350.
- 522 [2] S. J. Zinkle, "Applicability of copper alloys for DEMO high heat flux components," *Phys.*
523 *Scr.*, vol. 2016, no. T167, Art. no. T167, 2016, doi: 10.1088/0031-8949/2015/T167/014004.
- 524 [3] V. Lindström *et al.*, "Laser Powder Bed Fusion of Metal Coated Copper Powders,"
525 *Materials*, vol. 13, no. 16, Art. no. 16, Aug. 2020, doi: 10.3390/ma13163493.
- 526 [4] S. D. Jadhav *et al.*, "Highly conductive and strong CuSn0.3 alloy processed via laser
527 powder bed fusion starting from a tin-coated copper powder," *Additive Manufacturing*, vol.
528 36, p. 101607, Dec. 2020, doi: 10.1016/j.addma.2020.101607.
- 529 [5] S. D. Jadhav *et al.*, "Laser powder bed fusion additive manufacturing of highly conductive
530 parts made of optically absorptive carburized CuCr1 powder," *Materials & Design*, vol.
531 198, p. 109369, Jan. 2021, doi: 10.1016/j.matdes.2020.109369.
- 532 [6] A. Popovich, V. Sufiiarov, I. Polozov, E. Borisov, D. Masaylo, and A. Orlov,
533 "Microstructure and mechanical properties of additive manufactured copper alloy,"
534 *Materials Letters*, vol. 179, pp. 38–41, Sep. 2016, doi: 10.1016/j.matlet.2016.05.064.
- 535 [7] K. Jahns, R. Bappert, P. Böhlke, and U. Krupp, "Additive manufacturing of CuCr1Zr by
536 development of a gas atomization and laser powder bed fusion routine," *The International*
537 *Journal of Advanced Manufacturing Technology*, vol. 107, no. 5–6, Art. no. 5–6, Mar.
538 2020, doi: 10.1007/s00170-020-04941-7.
- 539 [8] B. Buchmayr, G. Panzl, A. Walzl, and C. Wallis, "Laser Powder Bed Fusion – Materials
540 Issues and Optimized Processing Parameters for Tool steels, AlSiMg- and CuCrZr-Alloys,"
541 *Adv. Eng. Mater.*, vol. 19, no. 4, Art. no. 4, Apr. 2017, doi: 10.1002/adem.201600667.
- 542 [9] C. Wallis and B. Buchmayr, "Effect of heat treatments on microstructure and properties of
543 CuCrZr produced by laser-powder bed fusion," *Materials Science and Engineering: A*, vol.
544 744, pp. 215–223, Jan. 2019, doi: 10.1016/j.msea.2018.12.017.
- 545 [10] S. Zhang, H. Zhu, L. Zhang, W. Zhang, H. Yang, and X. Zeng, "Microstructure and
546 properties in QCr0.8 alloy produced by selective laser melting with different heat
547 treatment," *Journal of Alloys and Compounds*, vol. 800, pp. 286–293, Sep. 2019, doi:
548 10.1016/j.jallcom.2019.06.018.
- 549 [11] C. Zeng *et al.*, "Effect of temperature history on thermal properties of additively
550 manufactured C-18150 alloy samples," *Manufacturing Letters*, vol. 28, pp. 25–29, Apr.
551 2021, doi: 10.1016/j.mfglet.2021.02.002.
- 552 [12] U. Holzwarth and H. Stamm, "The precipitation behaviour of ITER-grade Cu–Cr–Zr
553 alloy after simulating the thermal cycle of hot isostatic pressing," *Journal of Nuclear*
554 *Materials*, vol. 279, no. 1, Art. no. 1, Mar. 2000, doi: 10.1016/S0022-3115(99)00285-8.
- 555 [13] A. Chbihi, X. Sauvage, and D. Blavette, "Atomic scale investigation of Cr precipitation
556 in copper," *Acta Materialia*, vol. 60, no. 11, Art. no. 11, Jun. 2012, doi:
557 10.1016/j.actamat.2012.01.038.

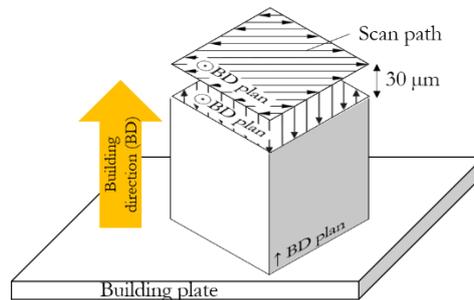
- 558 [14] P. Guan *et al.*, “Effect of selective laser melting process parameters and aging heat
559 treatment on properties of CuCrZr alloy,” *Materials Research Express*, vol. 6, no. 11, Art.
560 no. 11, Oct. 2019, doi: 10.1088/2053-1591/ab4e2f.
- 561 [15] C. Jinshui, Y. Bin, W. Junfeng, X. Xiangpeng, C. Huiming, and W. Hang, “Effect of
562 different Zr contents on properties and microstructure of Cu-Cr-Zr alloys,” *Mater. Res.*
563 *Express*, vol. 5, no. 2, Art. no. 2, Feb. 2018, doi: 10.1088/2053-1591/aaabc5.
- 564 [16] J. Chen, J. Wang, X. Xiao, H. Wang, H. Chen, and B. Yang, “Contribution of Zr to
565 strength and grain refinement in Cu Cr Zr alloy,” *Materials Science and Engineering: A*,
566 vol. 756, pp. 464–473, May 2019, doi: 10.1016/j.msea.2019.04.053.
- 567 [17] C. Watanabe, R. Monzen, and K. Tazaki, “Mechanical properties of Cu–Cr system
568 alloys with and without Zr and Ag,” *Journal of Materials Science*, vol. 43, no. 3, Art. no.
569 3, Feb. 2008, doi: 10.1007/s10853-007-2159-8.
- 570 [18] AFNOR, Standard EN12420:2014 “Cuivre et alliages de cuivre - Pièces forgées.” 2014.
- 571 [19] P.-E. Frayssines *et al.*, “CuCrZr alloy microstructure and mechanical properties after
572 hot isostatic pressing bonding cycles,” *Phys. Scr.*, vol. 2014, no. T159, Art. no. T159, 2014,
573 doi: 10.1088/0031-8949/2014/T159/014018.
- 574 [20] A. D. Ivanov, A. K. Nikolaev, G. M. Kalinin, and M. E. Rodin, “Effect of heat
575 treatments on the properties of CuCrZr alloys,” *Journal of Nuclear Materials*, vol. 307–
576 311, pp. 673–676, Dec. 2002, doi: 10.1016/S0022-3115(02)01110-8.
- 577 [21] A. P. Zhilyaev, I. Shakhova, A. Morozova, A. Belyakov, and R. Kaibyshev, “Grain
578 refinement kinetics and strengthening mechanisms in Cu–0.3Cr–0.5Zr alloy subjected to
579 intense plastic deformation,” *Materials Science and Engineering: A*, vol. 654, pp. 131–142,
580 Jan. 2016, doi: 10.1016/j.msea.2015.12.038.
- 581 [22] ISO Standard EN 6507-(1-4), “Matériaux Métalliques – Essai de dureté Vickers - Partie
582 1 : méthode d’essai – Partie 2 : vérification et étalonnage des machines - Partie 3 :
583 étalonnage des blocs de référence - Partie 4 : tableaux des valeurs de dureté.”
- 584 [23] ISO Standard EN 6892-1:2019 “Matériaux métalliques - Essai de traction- Partie 1:
585 Méthode d’essai à température ambiante.” 2019.
- 586 [24] ISO Standard EN 2004-1, “Série aérospatiale - Méthodes d’essais applicables aux
587 produits en aluminium et alliages d’aluminium - Partie 1 : détermination de la conductivité
588 électrique des alliages d’aluminium corroyés.” 2004.
- 589 [25] S. Gorsse, C. Hutchinson, M. Gouné, and R. Banerjee, “Additive manufacturing of
590 metals: a brief review of the characteristic microstructures and properties of steels, Ti-6Al-
591 4V and high-entropy alloys,” *Science and Technology of Advanced Materials*, vol. 18, no.
592 1, Art. no. 1, Dec. 2017, doi: 10.1080/14686996.2017.1361305.
- 593 [26] J. Metelkova, “On the influence of laser defocusing in Selective Laser Melting of 316L,”
594 *Additive Manufacturing*, p. 9, 2018.
- 595 [27] P. Krakhmalev *et al.*, “Microstructure, Solidification Texture, and Thermal Stability of
596 316 L Stainless Steel Manufactured by Laser Powder Bed Fusion,” *Metals*, vol. 8, no. 8,
597 Art. no. 8, Aug. 2018, doi: 10.3390/met8080643.
- 598 [28] S. Huang, W. Huang, W. Xie, H. Chen, H. Wang, and B. Yang, “Microstructure and
599 strengthening mechanisms of CuCrZr alloy by two-step thermomechanical treatment,”
600 *Journal of Materials Science: Materials in Electronics*, Sep. 2020, doi: 10.1007/s10854-
601 020-04333-3.
- 602 [29] D. R. Lide and Chemical Rubber Company, Eds., *CRC handbook of chemistry and*
603 *physics: a ready-reference book of chemical and physical data*, 90. ed., 2009–2010. Boca
604 Raton, FLa.: CRC Press, 2009.
- 605 [30] M. Merola *et al.*, “Influence of the manufacturing heat cycles on the CuCrZr properties,”
606 *Journal of Nuclear Materials*, vol. 307–311, pp. 677–680, Dec. 2002, doi: 10.1016/S0022-
607 3115(02)01186-8.

- 608 [31] H. Li, S. Xie, P. Wu, and X. Mi, "Study on improvement of conductivity of Cu-Cr-Zr
609 alloys," *Rare Metals*, vol. 26, no. 2, Art. no. 2, Apr. 2007, doi: 10.1016/S1001-
610 0521(07)60171-5.
- 611 [32] Z. Que, J. Lee, W. Cheng, S. Han, H. Jung, and K. Euh, "Microstructure Evolution of
612 the Cu-Cr Hypereutectic Alloys During Directional Solidification," in *Future Information
613 Communication Technology and Applications: ICFICE 2013*, H.-K. Jung, J. T. Kim, T.
614 Sahama, and C.-H. Yang, Eds. Dordrecht: Springer Netherlands, 2013, pp. 939–947. doi:
615 10.1007/978-94-007-6516-0_103.
- 616 [33] D. Liu, P. Wang, Y. Song, Q. Li, and J. Chen, "Effect of the ITER FW Manufacturing
617 Process on the Microstructure and Properties of a CuCrZr Alloy," *Plasma Sci. Technol.*,
618 vol. 17, no. 10, Art. no. 10, Oct. 2015, doi: 10.1088/1009-0630/17/10/13.
- 619 [34] Y. Liu, Z. Li, Y. Jiang, Y. Zhang, Z. Zhou, and Q. Lei, "The microstructure evolution
620 and properties of a Cu–Cr–Ag alloy during thermal-mechanical treatment," *Journal of
621 Materials Research*, vol. 32, no. 07, Art. no. 07, Apr. 2017, doi: 10.1557/jmr.2017.17.
- 622 [35] M. J. Starink and S. C. Wang, "A model for the yield strength of overaged Al–Zn–Mg–
623 Cu alloys," *Acta Materialia*, vol. 51, no. 17, Art. no. 17, Oct. 2003, doi: 10.1016/S1359-
624 6454(03)00363-X.
- 625 [36] Q. Lei, Z. Li, A. Zhu, W. Qiu, and S. Liang, "The transformation behavior of Cu–8.0Ni–
626 1.8Si–0.6Sn–0.15Mg alloy during isothermal heat treatment," *Materials Characterization*,
627 vol. 62, no. 9, Art. no. 9, Sep. 2011, doi: 10.1016/j.matchar.2011.06.008.
- 628 [37] J. Zhou *et al.*, "Microstructure and properties of powder metallurgy Cu-1%Cr-0.65%Zr
629 alloy prepared by hot pressing," *Vacuum*, vol. 131, pp. 156–163, Sep. 2016, doi:
630 10.1016/j.vacuum.2016.06.008.
- 631 [38] H. Feng, H. Jiang, D. Yan, and L. Rong, "Effect of continuous extrusion on the
632 microstructure and mechanical properties of a CuCrZr alloy," *Materials Science and
633 Engineering: A*, vol. 582, pp. 219–224, Oct. 2013, doi: 10.1016/j.msea.2013.06.031.
- 634 [39] A. J. Ardell, "Precipitation hardening," *METALLURGICAL TRANSACTIONS A*, p. 35,
635 1985.
- 636 [40] R. N. Caron, "Copper: Alloying," in *Reference Module in Materials Science and
637 Materials Engineering*, Elsevier, 2016, p. B9780128035818025000. doi: 10.1016/B978-0-
638 12-803581-8.02563-7.
- 639 [41] N. Hansen, "Hall–Petch relation and boundary strengthening," *Scripta Materialia*, vol.
640 51, no. 8, Art. no. 8, Oct. 2004, doi: 10.1016/j.scriptamat.2004.06.002.
- 641 [42] A. W. Thompson and W. A. Backofen, "The effect of grain size on fatigue," *Acta
642 Metallurgica*, vol. 19, p. 10, 1971.
- 643 [43] D. François, A. Pineau, and A. Zaoui, *Comportement mécanique des matériaux. vol. 1
644 vol. 1*. Paris: Hermès, 1991.
- 645 [44] T. Gladman, "Precipitation hardening in metals," *Materials Science and Technology*,
646 vol. 15, no. 1, Art. no. 1, Jan. 1999, doi: 10.1179/026708399773002782.
- 647 [45] R. M. Aikin and L. Christodoulou, "The role of equiaxed particles on the yield stress of
648 composites," *Scripta Metallurgica et Materialia*, vol. 25, no. 1, Art. no. 1, Jan. 1991, doi:
649 10.1016/0956-716X(91)90345-2.
- 650 [46] T. Torma, E. Kovacs-Csetenyi, T. Turmezey, T. Ungar, and I. Kovacs, "Hardening
651 mechanisms in Al-Sc alloys," *Journal of Materials Science*, vol. 24, no. 11, Art. no. 11,
652 Nov. 1989, doi: 10.1007/BF01168955.
- 653



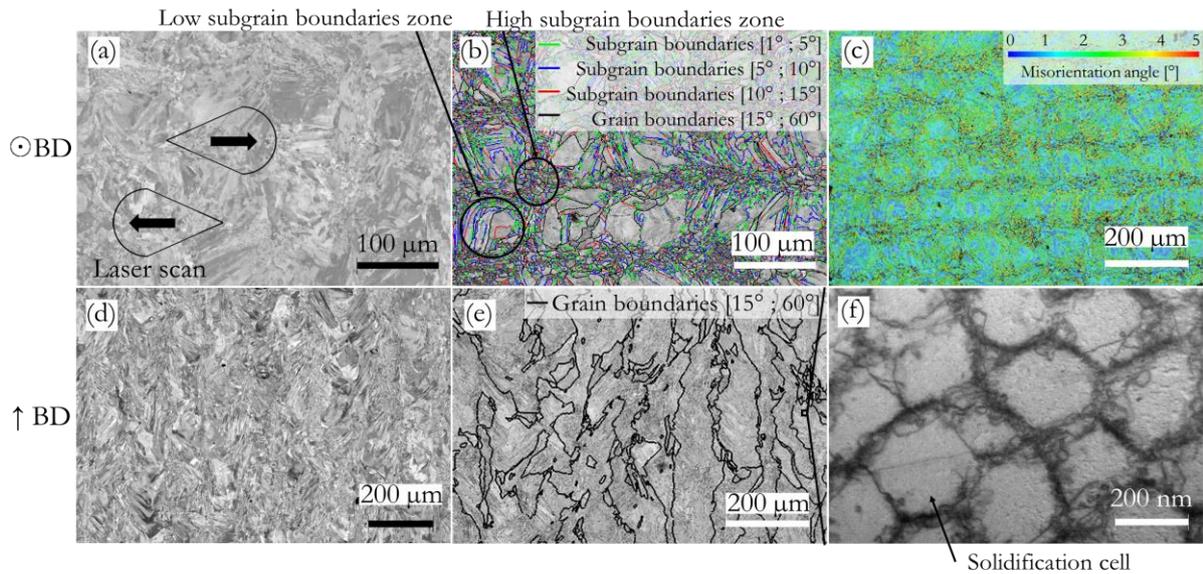
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655 Figure 1: (a) Relative parts density (compared to CuCrZr HIPped samples density of 8.908 g.cm⁻³) as a function of the energy density for various parameters sets. Varying scanning speed at a
 656 laser power of 360 W (white marks), 420 W (orange marks) and 480 W (black marks) using
 657 different hatch (100, 110 and 120 μm) and a layer thickness fixed at 30 μm. (b) L-PBF as-built
 658 cubes (10x10x10 mm³) and (c) mechanical (55x13x13 mm³ parallelepiped) and electrical
 659 samples (18 mm diameter and 22 mm high cylinder).
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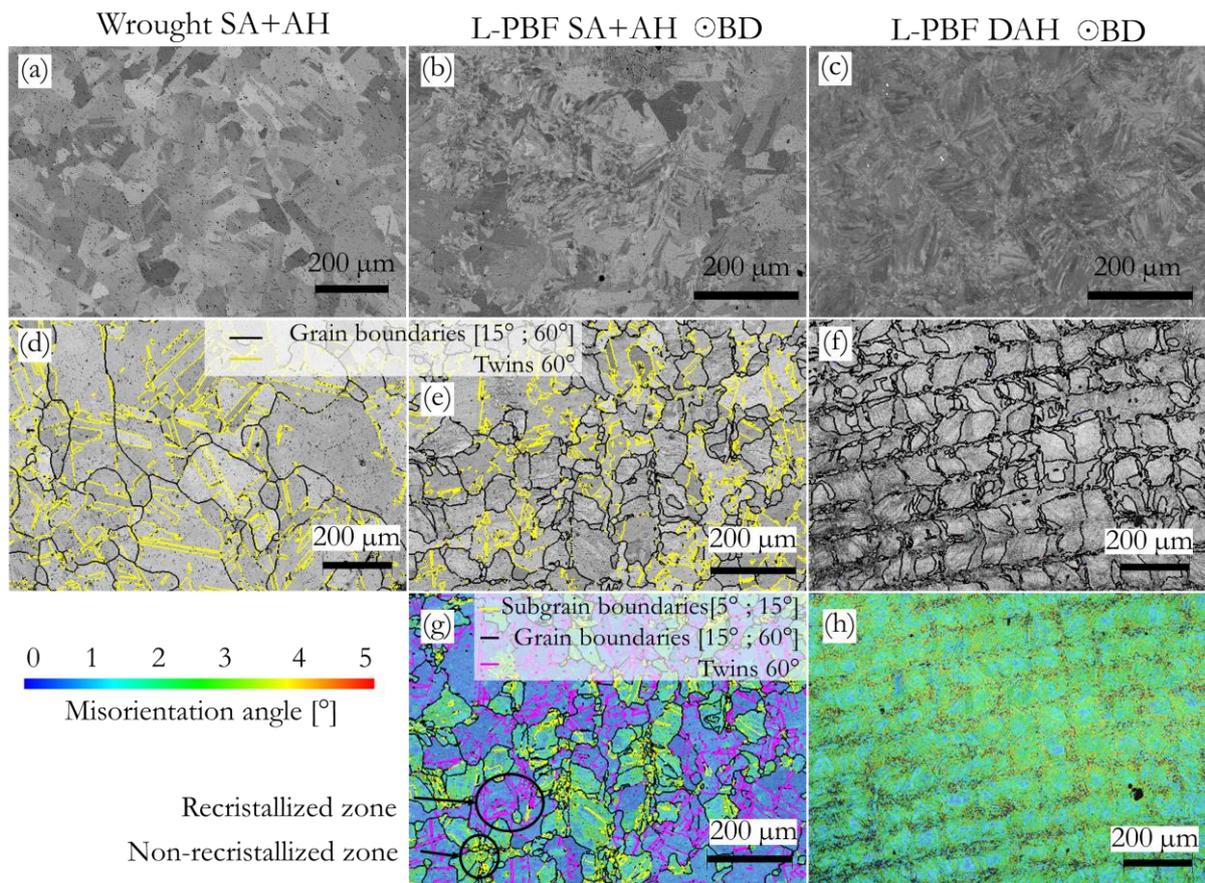


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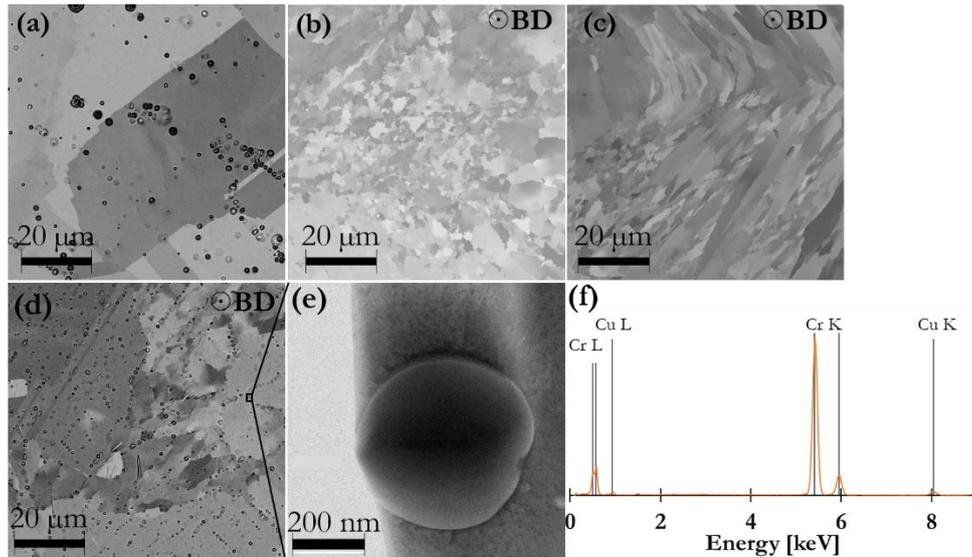
662 Figure 2 : Schema of the ⊙ BD plan and ↑ BD plan orientations in regard to L-PBF scan path
 663 and sample edges



664
 665 Figure 3: SEM images of as-built L-PBF CuCrZr sample in the (a) \odot BD and (d) \uparrow BD plans,
 666 (b) quality pattern image of (a) superimposed with grain and subgrain boundaries, and (e),
 667 quality pattern image of (d) superimposed with grain boundaries only. (c) KAM map of (a)
 668 and (f) TEM image of the solidification cells.

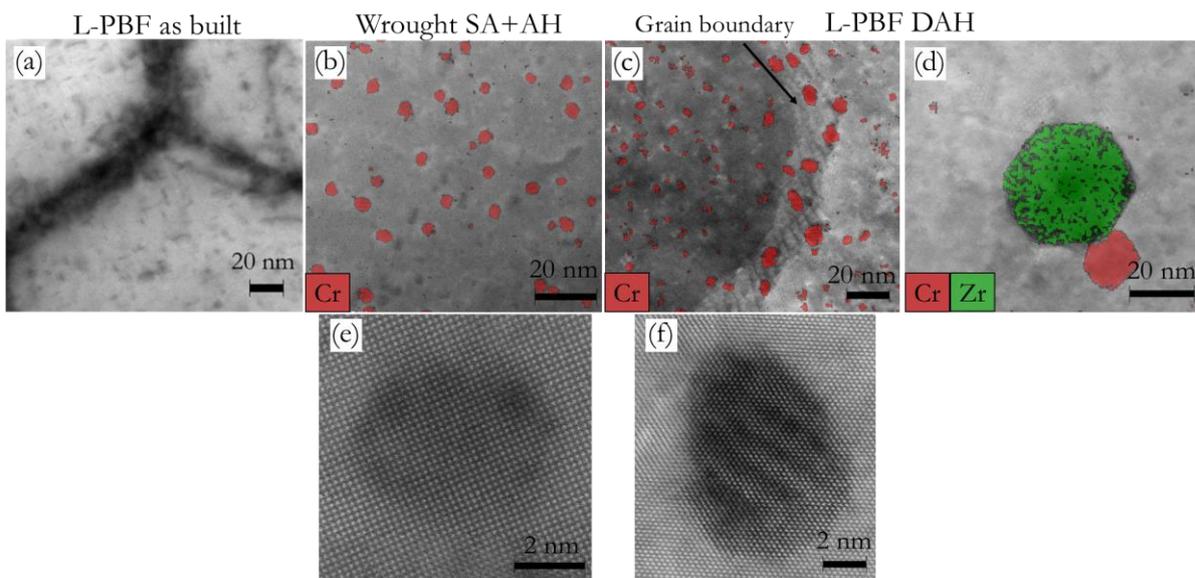


669
 670 Figure 4 : SEM-EBSD analysis of the (a, d) wrought, (b, e, g) L-PBF SA+AH and (c, f, h) L-
 671 PBF DAH CuCrZr samples. (a-c) SEM images in the \odot BD plan; (d-f) quality pattern images
 672 with grain boundaries and twins of (a-c) respectively. (g, h) KAM analysis of respectively L-
 673 PBF SA + AH and L-PBF DAH CuCrZr in the \odot BD plan.

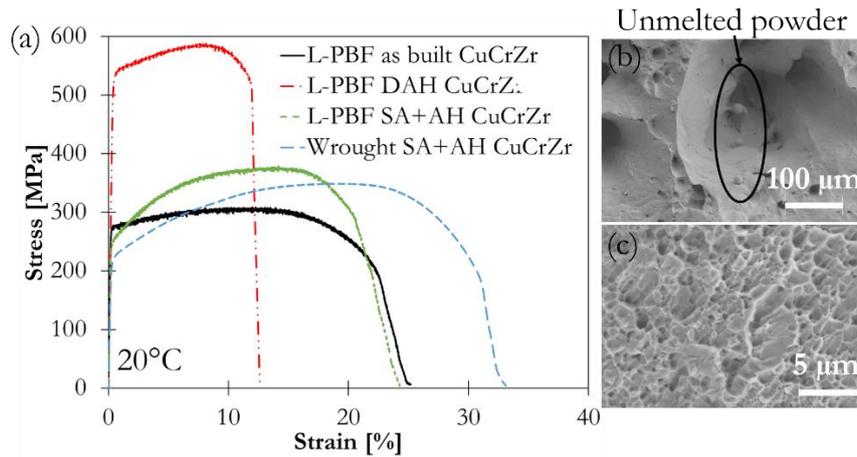


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 675 Figure 5: Study of the micro-precipitation: SEM images of (a) Wrought CuCrZr, (b) L-PBF
 676 as-built CuCrZr and (c) L-PBF DAH CuCrZr, both exempt of micro-precipitates, (d) L-PBF
 677 SA+AH CuCrZr. (e) TEM image focused on a Cr micro-precipitate, and (f) an EDX analysis
 678 of one of them.

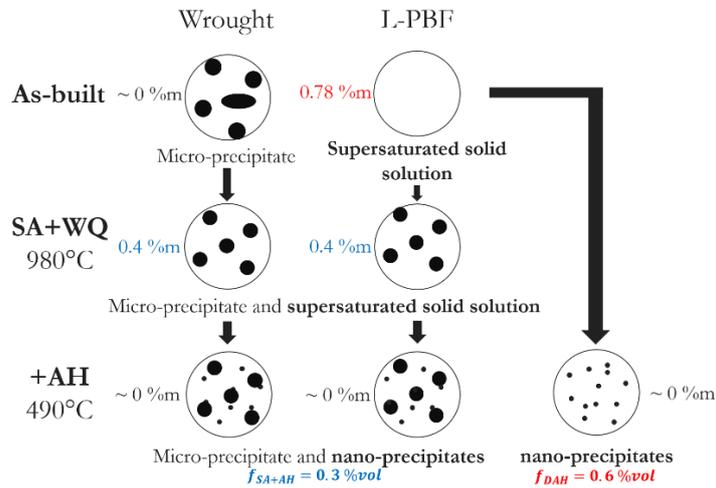
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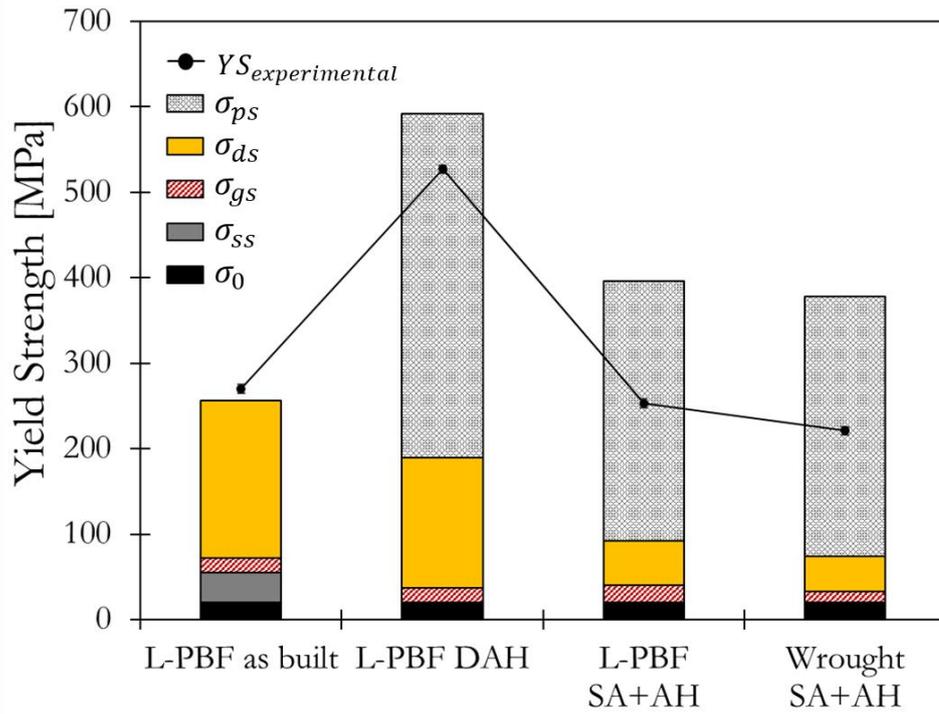
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 681 Figure 6: HAADF/STEM and Cr and Zr EDX analysis of the (a) L-PBF as built CuCrZr
 682 showing no nano-precipitates; (b, e) wrought SA+AH CuCrZr showing Cr nano-precipitation
 683 (no Zr detected; matrix is pure Cu on these images); (c, f) L-PBF DAH CuCrZr showing Cr
 684 nano-precipitation (no Zr detected; matrix is pure Cu on these images); (d) L-PBF DAH
 685 CuCrZr showing a Zr nano-precipitate next to a Cr nano-precipitate



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 687 Figure 7: (a) Engineering stress-strain response of wrought SA + AH, L-PBF as-built, SA +
 688 AH and DAH CuCrZr samples at a test temperature of 20°C (as the curves were qualitatively
 689 similar, only 1 of the 3 curves obtained for each condition is shown); SEM images of tensile
 690 bars fractography of (b) L-PBF as-built CuCrZr and (c) L-PBF SA+AH CuCrZr.



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 692 Figure 8 : Microstructural evolution of L-PBF and wrought CuCrZr as a function of the heat
 693 treatments. The Cr content in solid solution is noted next to the pictures. The final volume
 694 fractions of Cr nano-precipitates are given at the bottom.



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Figure 9: Calculated hardening mechanisms contributions to the yield strengths of CuCrZr alloys processed by four different routes, compared to experimental values (black spots)