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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<sup>-1</sup>). 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  $\mu\text{m}$  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 mm<sup>3</sup>, 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<sup>-1</sup> 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<sup>-1</sup> 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 mm<sup>3</sup> 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,  $M_{\text{HIP}}$  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  $\mu\text{m}$  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  $\mu\text{m}$ . 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 ( $\theta$  [rad]) is then used to  
188 estimate the dislocation density ( $\rho_0$ ) 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<sup>-1</sup>), 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<sup>-1</sup> that allows higher productivity. Consequently, a laser power  
216 of 480 W, a scan speed of 700 mm.s<sup>-1</sup> 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 ± 80 μm (363 ± 160 μm long and 125± 60 μm  
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 ± 60 μm. 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  $\mu\text{m}$  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  $3 \times 10^{13}$  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  $980^\circ\text{C}$  SA heat treatment. Given the absence of solidification cells, a step size of 1.7 or 2.1  
 266  $\mu\text{m}$  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 [ $\mu\text{m}$ ]	$112 \pm 60$	$242 \pm 100$	$276 \pm 150$	$334 \pm 140$	$471 \pm 150$
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  $490^\circ\text{C}$  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  $\theta$  and average dislocation density  $\rho_0$  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 [ $\mu\text{m}$ ]	$\theta$ [ $^\circ$ ]	$\rho_0$ [ $\text{m}^{-2}$ ]
L-PBF as-built	1 $\text{cm}^2$	300	2.0	1.9	$8 \pm 1 \times 10^{13}$
	4.5 $\text{mm}^2$		0.1	0.7	$5 \pm 1 \times 10^{14}$
	1 $\text{cm}^2$	No cell	1.7	0.9	$4 \pm 1 \times 10^{13}$

L-PBF SA+AH	0.6 cm <sup>2</sup> (recrystallized zone)		1.7	0.7	$3 \pm 1 \times 10^{13}$
	0.4 cm <sup>2</sup> (non-recrystallized zone)		1.7	1.5	$7 \pm 1 \times 10^{13}$
L-PBF DAH	1 cm <sup>2</sup>	330	2.3	2.2	$7 \pm 1 \times 10^{13}$
	4.5 mm <sup>2</sup>		0.2	0.7	$4 \pm 1 \times 10^{14}$
Wrought SA+AH	1 cm <sup>2</sup>	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 Cu<sub>5</sub>Zr or Cu<sub>4</sub>Zr 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  $1.8 \pm 1.0$  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  $3.2 \pm 1.6$  nm, whereas for  
 306 one located in the Cu matrix it is around  $2.1 \pm 1.5$  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.

<b>CuCrZr</b>	<b>Equivalent radius [nm]</b>	<b>Number of precipitates measured</b>	<b>Volume fraction of precipitates [%vol]</b>
L-PBF DAH	$2.1 \pm 1.5$	233	0.6
Wrought SA+AH	$1.8 \pm 1.0$	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  $101 \pm 4$  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

<b>CuCrZr</b>	<b>Electrical Conductivity</b>
	<b>[10<sup>6</sup> S.m<sup>-1</sup>]</b>
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  $\sigma_0$  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

	<b>Parameters</b>	<b>Value</b>	<b>Unit</b>	<b>Reference</b>
$\sigma_0$	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]
$\alpha$	-	0.23	-	[10]
$\varepsilon$	Misfit	0.015	-	[14,38]
$\nu$	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 [ $\mu\text{m}$ ] 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.

<b>CuCrZr</b>	<b>L-PBF As-built</b>	<b>L-PBF DAH</b>	<b>L-PBF SA+AH</b>	<b>Wrought SA + AH</b>
Average equivalent grain diameter [ $\mu\text{m}$ ]	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
$\rho_0$ [ $\text{m}^{-2}$ ]	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  $294 \pm 32$  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 ( $42 \text{ MS.m}^{-1}$ ) 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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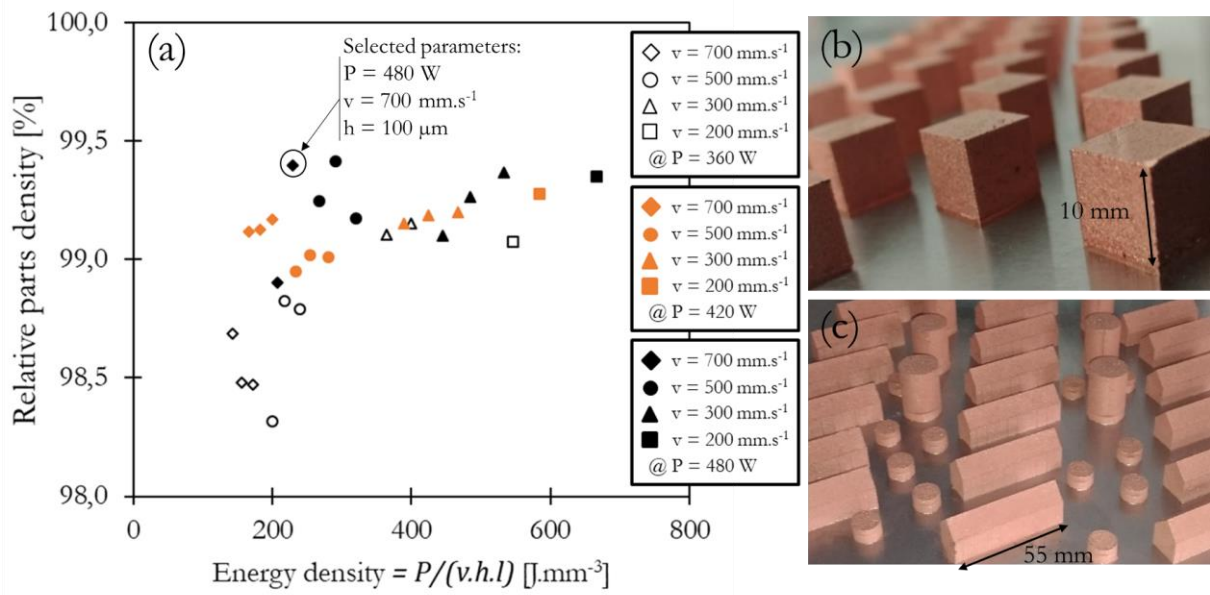
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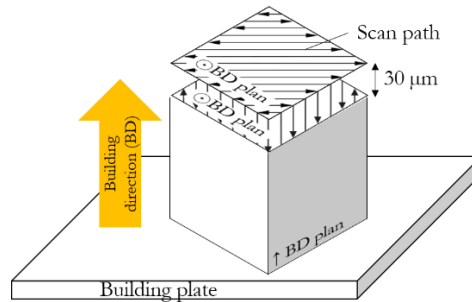
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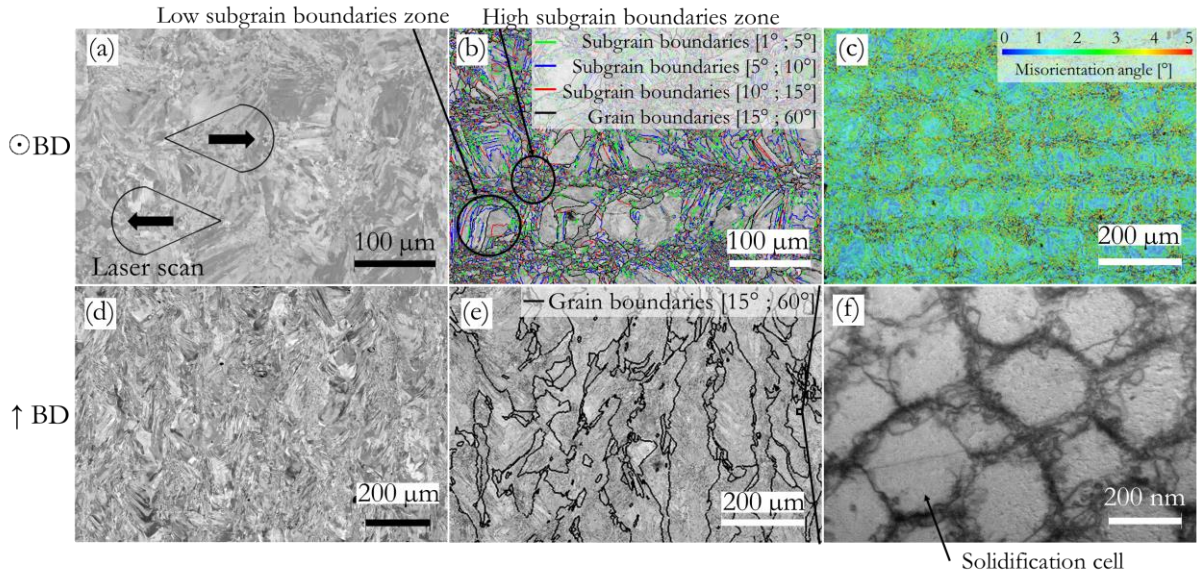
655 Figure 1: (a) Relative parts density (compared to CuCrZr HIPped samples density of 8.908 g.cm<sup>-3</sup>) as a function of the energy density for various parameters sets. Varying scanning speed at a  
 656 laser power of 360 W (white marks), 420 W (orange marks) and 480 W (black marks) using  
 657 different hatch (100, 110 and 120 μm) and a layer thickness fixed at 30 μm. (b) L-PBF as-built  
 658 cubes (10x10x10 mm<sup>3</sup>) and (c) mechanical (55x13x13 mm<sup>3</sup> parallelepiped) and electrical  
 659 samples (18 mm diameter and 22 mm high cylinder).  
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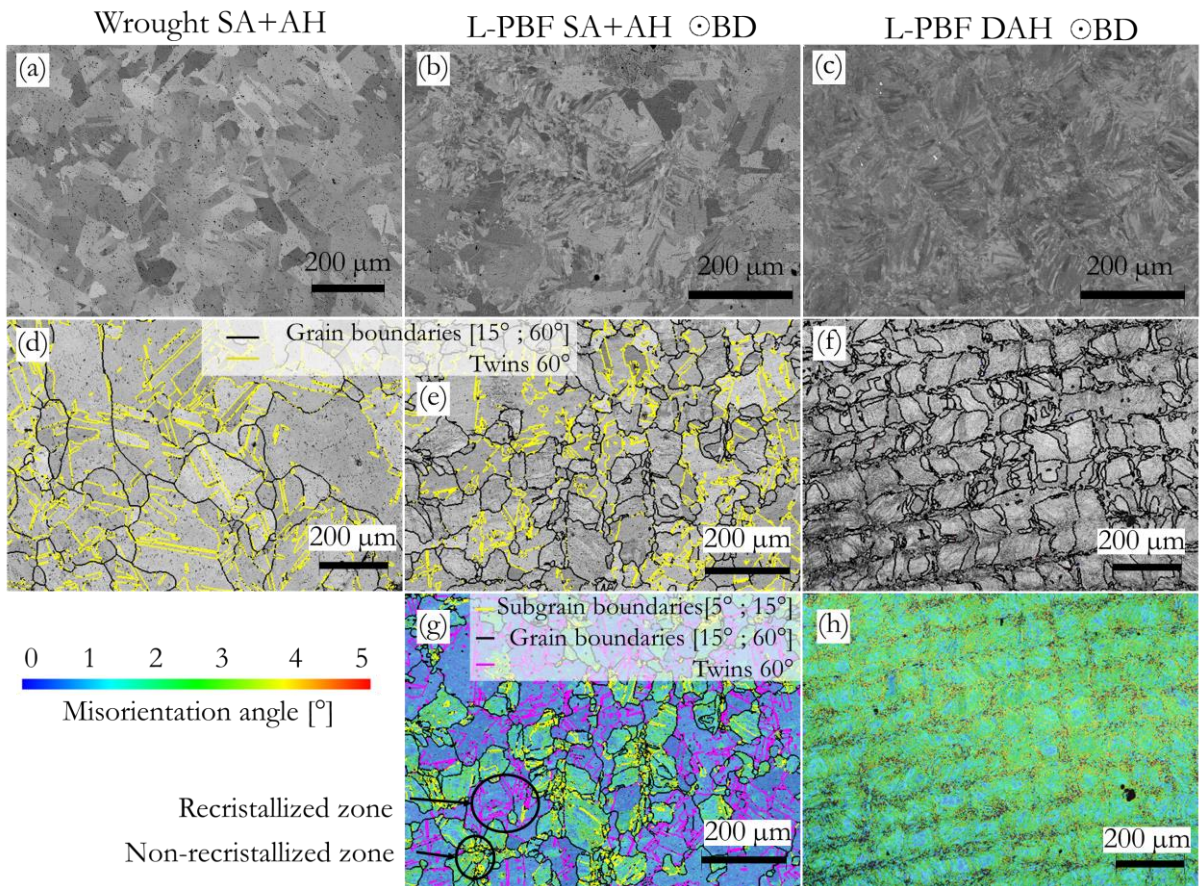
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662 Figure 2 : Schema of the ⊙ BD plan and ↑ BD plan orientations in regard to L-PBF scan path  
 663 and sample edges



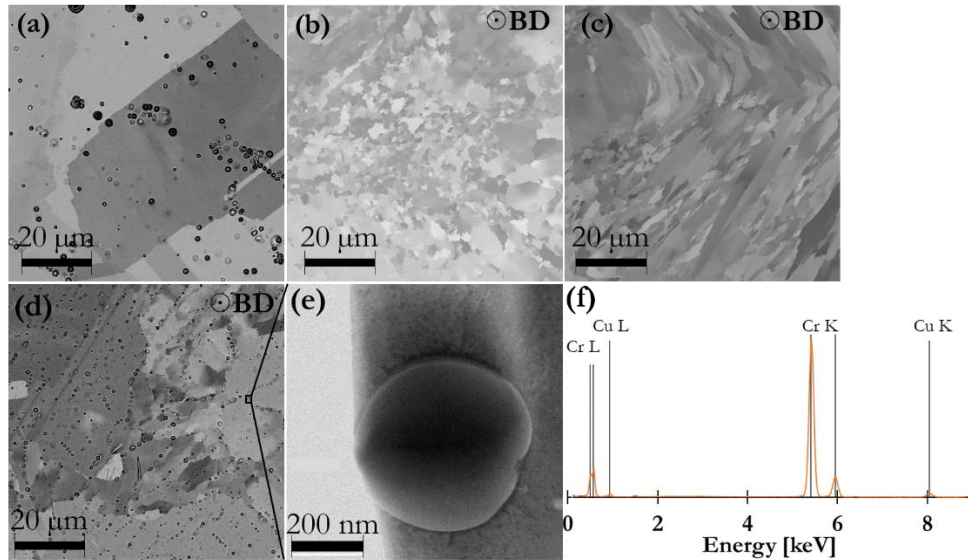


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 665 Figure 3: SEM images of as-built L-PBF CuCrZr sample in the (a)  $\odot$  BD and (d)  $\uparrow$  BD plans,  
 666 (b) quality pattern image of (a) superimposed with grain and subgrain boundaries, and (e),  
 667 quality pattern image of (d) superimposed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



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 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.

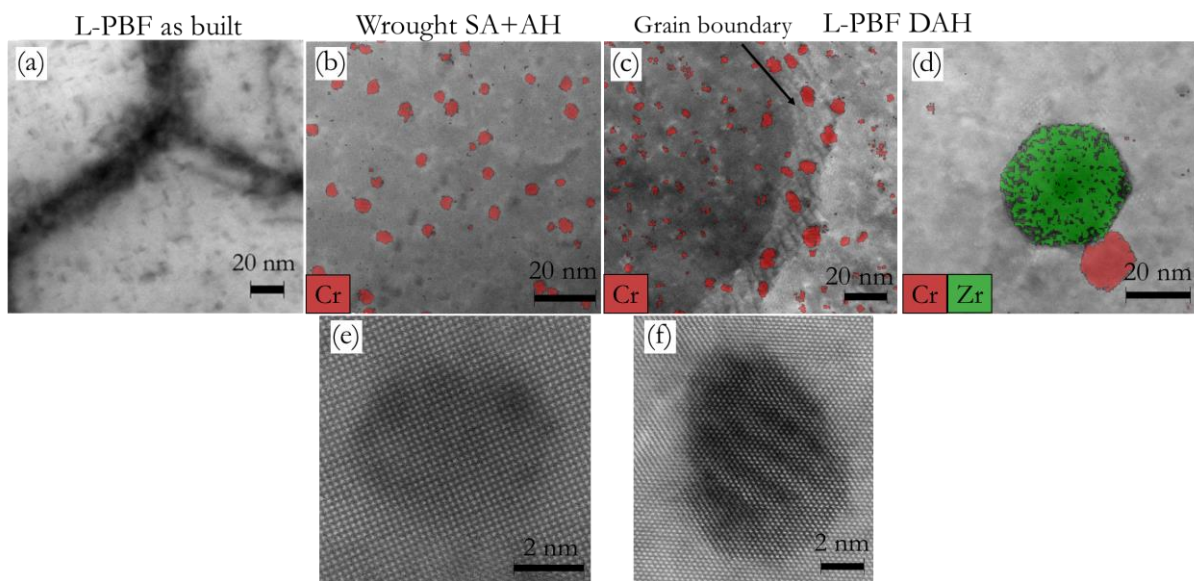




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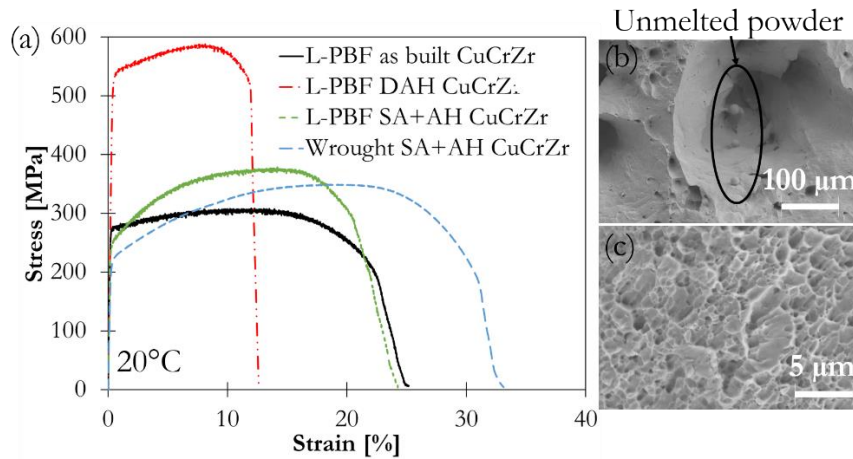
Figure 5: Study of the micro-precipitation: SEM images of (a) Wrought CuCrZr, (b) L-PBF as-built CuCrZr and (c) L-PBF DAH CuCrZr, both exempt of micro-precipitates, (d) L-PBF SA+AH CuCrZr. (e) TEM image focused on a Cr micro-precipitate, and (f) an EDX analysis of one of them.

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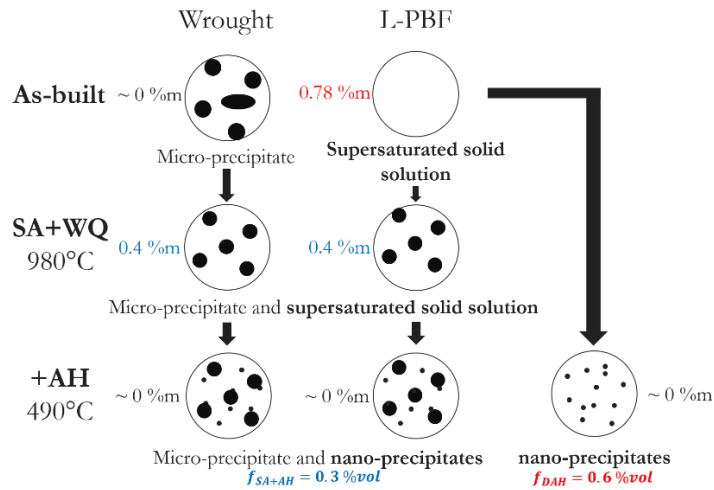


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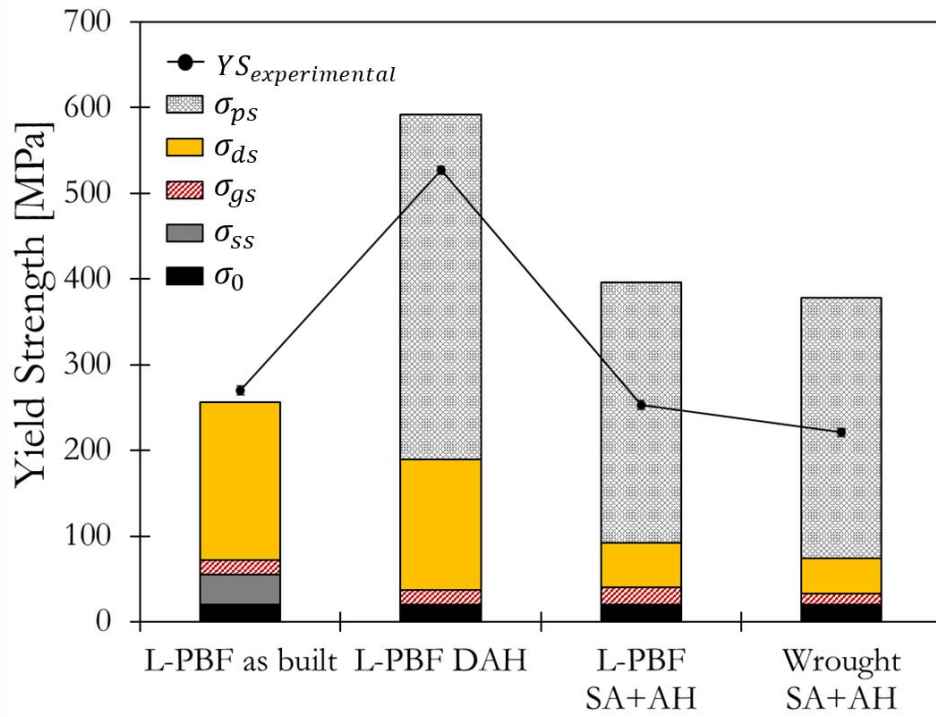
681 Figure 6: HAADF/STEM and Cr and Zr EDX analysis of the (a) L-PBF as built CuCrZr  
682 showing no nano-precipitates; (b, e) wrought SA+AH CuCrZr showing Cr nano-precipitation  
683 (no Zr detected; matrix is pure Cu on these images); (c, f) L-PBF DAH CuCrZr showing Cr  
684 nano-precipitation (no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