3D-Printed Pure Copper: Density and Thermal Treatments Effects

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Abstract. The increasing research and engineering of pure copper in the field of experimental nuclear physics is motivated by its outstanding physical properties making such material the key constituent of many types of detectors and particle accelerators. The Italian Research Institute on Nuclear Physics (INFN – Istituto Nazionale di Fisica Nucleare) is in charge of research in this field and, taking advantage of its expertise in the field of additive manufacturing (AM), has equipped the HAMMER (https://hammer.lngs.infn.it/) Lab with a 3D printer, characterized by a powder bed together with a laser beam, in order to evaluate the possibility of producing pure copper objects compatible with the requirements of experimental apparatuses using Selective Laser Melting (SLM) technique and specific post-processing thermal treatments. Notwithstanding the growing request of pure copper components realized via AM processes techniques, their processability via SLM technology is still challenging due to the high reflectivity of copper at the emission wavelength of the conventional SLM laser sources (1064 nm) along with the thermal issues resulted from copper's high conductivity. This work aims to verify the quality of parts produced in pure Cu in terms of density and mechanical properties as well as to evaluate the effect of heat treatments during post-processing, in order to achieve the highest consolidation for the material and, thus, improved functional properties.

Keywords: Additive Manufacturing, Pure Copper, Density, Thermal Treatments

1 Introduction

In the last few decades, research focusing on Additive Manufacturing (AM) technologies - or 3D printing, since these two terms are now used interchangeably [1,2] - experienced a significant increase. [3-5]. The noteworthy interest for AM methods, deriving from both academia and industry, has been driven by several advantages (*i.e.*, material efficiency, possibility to fabricate complex components and integrate multifunctional elements, reduced tooling requirements and manufactured times) [6]. Thanks to the extraordinary capability to generate highly intricate shapes and customized parts - without dedicated tooling - directly from 3D Computer Aided Design (CAD) models, AM approaches may transform conventional manufacturing techniques into more powerful and cost/time-effective production processes, thus providing novel design schemes to realize components of any arbitrary shape and, in addition, locally tune material properties [7].

The rising engineering of additively manufactured pure copper is motivated by the benefits characterizing AM technologies combined with copper's unusual electrical and thermal properties, required for many applications (*i.e.*, aeronautics, naval, electronics, microelectronics, radio frequency) [8]. For instance, the possibility to realize heat exchange with internal cooling channels and the consequent increase of the surface-to-volume ratio given by AM methods, may improve the performances of copper-based devices. Despite the continuous demand of copper components realized via AM processes, their industrial production is strongly limited by several processing challenges to face, especially in the case of laser-based methods. Two main issues limit the processability of pure copper via Selective Laser Melting (SLM): i) the very high reflectivity of Cu when conventional SLM laser sources (IR 1064 nm) are employed [9-10] and ii) the remarkable thermal conductivity of copper; both of these factors, by reducing the amount of energy available for the melting, allow to realize highly porous copper, thus characterized by failing electrical and thermal properties. As a result of the abovementioned technological limits, the entire existing literature on metal AM technologies reports only an exiguous amount of works on the successful production of highly conductive and dense pure copper obtained via SLM [11-13]. In order to boost copper powder bed densification, different innovative approaches have been followed [10-11,14-15]. For instance, it is reported that by properly adjusting and combining the process parameters of a SLM system (*i.e.*, scanning speed, hatch spacing, laser power and beam diameter) implemented with a 200 W CO2 laser source, copper powders were selectively melted; however, the relative density of the printed copper parts did not exceed 88.1% [16]. Moreover, to further reduce porous structures of the SLM-realized copper parts, consequently improving their relative density, conventional SLM systems have been updated in terms of power and emission wavelength of laser sources, strongly influencing the selective melting of copper powders and typically characterized by moderate power levels (200 - 500 W) and emission wavelength of ~1 μm. Among all the research attempts made in this sense, it is worth mentioning the adoption of a 400 W laser presenting a shorter emission wavelength [17-18] as well as the use of a fiber laser with a higher laser power up to 1 kW [10-11]. As an example of a successful study, very recently Jadhav and Coworkers [13] have evaluated the impact of various laser scan parameters (*i.e.*, laser power, hatch spacing, and scan speed) on the texture evolution of the SLM-manufactured copper parts. The SLM process optimization led the authors to fabricate Cu samples presenting high density, great purity, crystallographic isotropy and thus very high electrical conductivity (88% of the International Annealed Copper Standard). Although the remarkable findings achieved by upgrading commercially available SLM machines through the increment of laser power or the reduction of laser emission wavelength, the possibility to realize 3D manufactured parts with required geometry and properties via SLM processes based on the adoption of conventional and widespread 200 W lasers, could be very interesting for both industries and academia; this is primarily due to the fact the majority of the installed SLM machines are equipped with these fiber lasers.

In this scenario, this study aspires to explore the suitability of a commercial SLM machine, presenting a typical 200 W laser source and a laser spot diameter of 30 μm, for the fabrication of highly dense copper parts characterized by desired and predicted geometry and properties. The chemical composition and microstructure of the SLM-manufactured Cu materials are investigated by X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM), respectively. Additionally, since in specific high-challenging applications related to fundamental physics as well as to other sectors (*i.e.*, aerospace, automotive, naval, electronic, biomedical) it is crucial to predict the behavior of the components, a mechanical characterization of the SLM samples is performed with the final goal to tune these properties. Finally, the impact of different post-processing thermal treatments on the microstructural, chemical and mechanical properties of the here-produced copper parts is evaluated.

2 Materials and Methods

In this experimental session, 99 wt% pure copper powder was used, characterized by a particle size ranging from 5 to 25 μm, and consolidated processability through additive manufacturing; STL file preparation was realized by adopting the Materialise Magics software.

A SLM machine, produced by SISMA S.p.a. (MYSINT100 RM model), was employed to fabricate different Cu-based samples with a size of 25 x 25 x 2 mm under a nitrogen atmosphere to avoid possible oxygen contamination during the printing process. The SLM machine is equipped with a 200 W fiber laser with a wavelength of 1 μm and a laser spot diameter of 30 μm. The density of the here-fabricated samples was quantified by adopting the Archimedes method and by considering a theoretical density of copper as 8.93 g/cm^3. The optimum SLM processing window was identified through numerous printing experiments and is characterized by the following parameters: the laser power is 175 W, the scanning speed is 2000 mm/s, the hatch space is 40 μm, and the layer thickness is 20 μm.

The as-manufactured samples, after being detached from the substrate, were subjected to different thermal treatments in order to develop a specifically tailored post-treatment aiming to improve the density and, therefore, the properties of the copper-built parts. Specifically, the specimens were heated in an electric resistance furnace under argon at 800 °C for 10 and40 h; on the other hand, one specimen per each batch was excluded from these treatments in order to compare their as-built characteristics with those of their heat-treated counterpart, thus working as reference samples.

SEM imaging was conducted on the copper SLM-processed parts by collecting back-scattered electrons on a TESCAN MIRA3 operating at an accelerating voltage of 15 keV in order to explore the morphology, the porosity along with the presence of possible defects in the as-produced samples.

The crystalline phase analysis was performed by Xray diffraction (XRD, Philips Analytical PW1830) equipped with a Ni-filtered Cu Kα (1.54056 Å) radiation over 5-90° of diffraction angle (2θ) with a step size of 0.02°. The data were collected with an acceleration voltage and applied current of 40 kV and 30 mA, respectively. The crystalline phases in the resulting diffractograms were identified through the COD database (Crystallography Open Database – an open-access collection of crystal structures) [Grazulis et al., 2009].

The mechanical performances were evaluated through a mechanical testing machine (Instron 5584, Norwood, MA, USA) equipped with a load cell of 150 kN and at a crosshead rate of 1 mm/min according to the ASTM E8 standard. These tests were carried out on cylindrical samples with a diameter of about 6 mm and a gauge length of about 30 mm. The deformation was measured during the test with a contact type extensometer and each sample was tested until rupture. Porosity evaluation was carried out on digital images of cross sections (ASTM E-2109-01) at 200× magnification using a Nikon Eclipse L150 optical microscope (Nikon Instruments B.V., Amsterdam, The Netherlands) with the LUCIA Measurement image analysis software. For this purpose, the images were first digitally binarized through a grey-scale threshold, then the porosity was evaluated by the software has the ratio between the dark and clear areas.

3 Results and Discussion

It has been demonstrated that the fabrication of fully dense Cu parts by exploiting commonly available SLM machines, equipped with 200 W lasers, is a challenge. As a matter of fact, all the efforts carried out in the perspective of reducing the porosity of the printed pure copper components, by taking advantage of standard SLM systems, have led to densities not exceeding 90% [10-19]. In particular, the possibility to fabricate pure copper via a SLM system with 200 W Yb fibre laser was explored [20]. The authors were able to achieve pure copper parts characterized by an average density of 83.01%; however, an evaluation of the mechanical behavior of the printed samples was not performed in such study. Later, it was proven the significant influence of copper powder grain size and shape on the resulting porosity of the SLM-manufactured pure copper parts [21-23]. Indeed, fine-grained powders have unequivocally demonstrated their ability to promote the manufacturing of pure copper parts showing a notably increased density (98.1%) if compared to previous studies (*i.e.*, 88.1%, 83.01%) [12,16,20]. Such improvement in densification of the copper parts was obtained by using a standard 200 W SLM machine, without technical modifications (green-blue lasers, high power fiber lasers), but only by adopting a Cu powder with a small grain size (10 - 35 μm) along with a small layer thickness, thus promoting the melting process. The achieved relatively high density of the pure copper components fabricated by Sinico and co-workers has determined, consequently, an increase also in terms of mechanical properties, getting to a tensile strength of more than 200 MPa [12].

In this context, this work aims to consolidate the knowledge and experience of additive manufacturing of pure copper parts - by employing a standard SLM machine with a conventional 200 W laser - and to verify the effect of annealing heat treatment in a controlled atmosphere, with the objective of improving the physical and mechanical properties through this step., changing only the time parameter in this phase.
Common pure Cu samples with dimensions of 25 x 25 x 2 mm were fabricated, as described in the previous section and, afterwards, a morphological and chemical-structural characterization was conducted.

SEM imaging was performed on the as-grown specimens by considering both the central part and the border of sections under investigation. It has been found that the external region presents higher porosity compared to the core probably ascribed to the temperature gradient between the two zones with higher temperatures reached in the most internal regions. The resulting density of the as-built materials is approximately 86.93±2.41%. Afterwards, these samples were subjected to different post-processing heat treatments leading to an evident improvement in terms of material density. In particular, samples heated for 10 h at 800 °C present a density of 89.66±1.83%, while a 40 h annealing treatment led to a value as high as 91.89±2.07% (see Fig. 1).

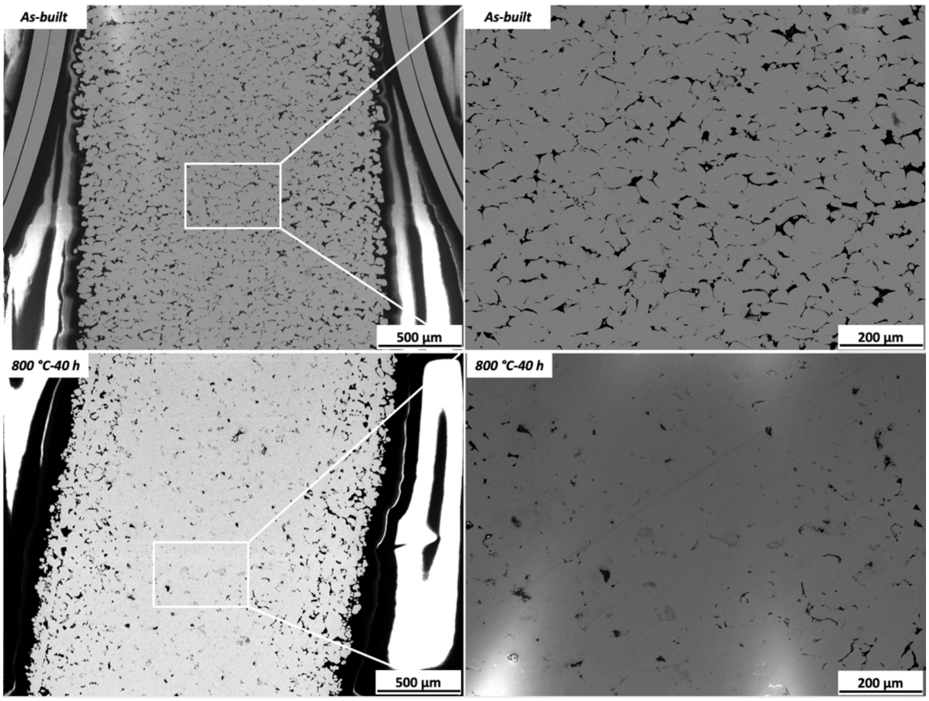

Fig. 1. SEM micrographs representative of several 3D-built Cu-based samples showing their morphology before (As-built) and after the thermal treatment (800 °C for 40 h).

To investigate the structural parameters of the here-manufactured Cu-based samples, before and after annealing, X-Ray Diffraction (see Fig. 2) analysis was carried out. The XRD diffraction patterns of untreated and treated samples at 800 °C for 40 h reveal the 2θ values of 43.4°, 50.5°, and 74.2° corresponding to the (111), (200) and (220) planes of FCC crystal structures of bulk copper and no impurities or changes due to thermal treatment can be detected [19].

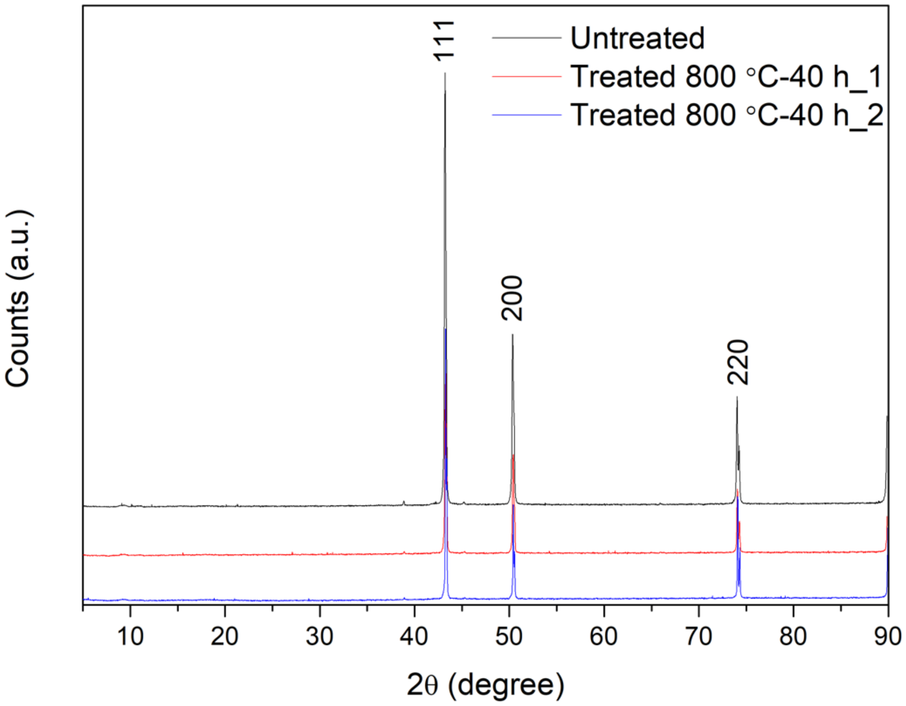

Fig. 2. XRD diffraction patterns of the Cu specimens before and after the annealing treatment performed at 800 °C for 40 h.

The mechanical properties of the copper specimens, before and after the heat treatments for 40h at 800°C, were investigated in order to explore the effect of the post-processing approach on the mechanical behaviour of 3D-built copper parts. Table 1 summarizes the averaged tensile properties evaluated for the SLM-realized samples as well as for the heat-treated counterpart.

Table 1. Results of the mechanical tests performed on the 3D-built copper samples before (TQ) and after the annealing treatment for 40 h @800 °C (TT). Data are presented as the average plus or minus the standard deviation (SD) derived from at least three independent experiments.

Specimen ID	**Young's Modulus (GPa)**	**Ultimate Tensile Strength (MPa)**	**Uniform Elongation (%)**
Cu 175W 2000 mm/s TQ	74.23 ± 1.97	166.95 ± 9.21	6.42 ± 2.58
Cu 175W 2000 mm/s TT	78.36 ± 0.98	179.70 ± 0.17	30.87 ± 0.92

Observing the data in Table 1, it is clear that the annealing treatment, performed at 800 °C for 40 h, induced a fourfold increase of the elongation at break along with a rise in the Young's modulus and in the Tensile strength. Furthermore, Fig. 3 shows an example of the different trend observed after the heat treatment: because of the heat treatment the elastic region is reduced, the yield stress decreases and a larger plastic area can be observed. (see Fig. 3). From a metallurgical point of view, it is believed that recrystallization generates new grains at the edges of existing grains as early as about 200-250 °C, and then with increasing temperature up to 800°C - a level at which they are maintained for 40 hours - these grains enlarge at the expense of the nearby original grains until they form a completely renewed crystalline structure devoid of residual stresses. Between the aforementioned edges, porosity zones are believed to be privileged areas of accretion; therefore, the overall effect is that of an increase in density.

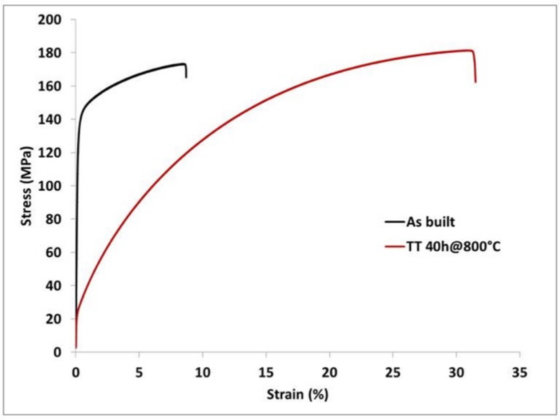

Fig. 3. Stress/Strain curves from tensile test on specimens As-built and after thermal treatment.

4 Conclusions

Herein, the processability of pure copper powders via a commercial SLM machine, presenting a typical 200 W fiber laser with a wavelength of 1 µm and a laser spot diameter of 30 µm, was evaluated. The obtained results have revealed that, despite the high reflectivity of copper, highly dense pure Cu parts can be produced by properly tuning both SLM process parameters and post-processing thermal treatments. The optimal SLM processing window as well as the best post-processing annealing process were identified through numerous printing experiments producing high density (>91%) pure Cu parts, thus demonstrating the validity of the here-proposed technologic approach.

Moreover, the mechanical properties of the SLM-realized pure Cu parts were investigated. Such analysis has disclosed that post-synthesis thermal process performed at 800°C for 40 h leads to a strong increase in the elongation at break along with in the ultimate tensile stress and the general ductility of the material (plastic phase extended on the stress/strain curves). Nevertheless, further studies will be necessary in order to achieve the highest densification of copper parts and process repeatability, in particular working on the SLM machine printing parameters because the copper powder resulted extremely sensitive to some of them, such as the laser scanning speed.

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