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Additively manufactured CuCrZr alloy: improvement of mechanical properties by heat treatment

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Abstract

CuCrZr alloy plays a fundamental role for the production of critical components because it is characterized by good thermal and electrical conductivity and by high mechanical strength after precipitation hardening treatment. In the framework of a wider research on the mechanical behaviour of additively manufactured CuCrZr alloy, this study focuses on the effects of heat treatment parameters on the alloy strength. The additive manufacturing process, characterized by very high cooling rates, determines the formation, in the as-built condition, of a supersaturated solid solution. The results obtained reveal that aging temperature and time are critical parameters for improving the mechanical behaviour of CuCrZr alloy which behaves differently than the alloy produced through the use of traditional techniques.

Keywords: Additive manufacturing; Cu alloys; CuCrZr alloy; Selective laser melting; Thermal treatment.

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1. Introduction

Age-hardenable CuCrZr alloys have many industrial applications. Due to a favorable combination of high strength, high electrical and thermal conductivity, CuCrZr alloy can be used in the production of high heat flux components of ITER, in the manufacturing of contact wire in railways and of resistance welding electrodes (Ostachowski et al.(2019), Barabash et al. (2011)).

Many works available in literature highlighted thermal and thermomechanical treatments able to increase mechanical properties of the these types of alloys. Considering that CuCrZr alloy is also considered an interesting candidate for high temperature applications such as combustion chamber liner of rocket engines, many studies have been performed to analyse mechanical performances at high temperatures, creep and fatigue resistance (Mishnev et al.(2015), Zhang et al. (2016), Xia et al. (2012), Vinogradov et al. (2002), Peng et al. (2014)). It has been also studied because it is considered a suitable material for the construction of passive satellites (Brotzu et al (2019), Brotzu et al. (2020)).

In the last few years many studies have been carried out on CuCrZr alloy production by means of additive manufacturing. Many difficulties arise in the additive manufacturing process of CuCrZr alloy due to its high thermal conductivity and high optical reflectivity at 1070 nm (Popovich et al. (2016)). Several recent studies showed the ability to create dense CuCrZr parts in particular by using laser power over about 300 W. Many papers available in literature reported the relationship among process parameters, heat treatment and mechanical properties of CuCrZr alloy (Salvan et al. (2021), Kuai et al. (2022), Wallis et al. (2019), Hu et al. (2022), Sun et al.(2020), Guan et al. (2019), Tang et al. (2022)). Some authors highlighted that cooling rates of about 10^6 K/s allow to obtain microstructures that can be directly aged (Salvan et al. (2021)) with a consequent considerable increase of the hardness and thus of the mechanical strength. By comparing the hardness and yield strength data it is possible to see that they are not always in accordance. Some authors explained the strength increase of these alloys by attributing the formation of Cr–Zr–Cu nano precipitates, formed in the specimen, to the effect of intrinsic heat treatment during the SLM process (Hu et al. (2022)). Other authors attributed the increase in strength to the precipitation of Cr-enriched phases and to the high dislocation density, while the increased electrical conductivity was attributed to the decomposition of the supersaturated solid solution (Tang et al. (2022), Zhou et al. (2022)). Aim of this paper is to evaluate the effect of heat treatment on the mechanical behaviour of CuCrZr alloy. The effect of the solution annealing treatment and of the aging time and temperature are investigated.

2. Experimental

Specimens were manufactured by means Laser Powder Bed Fusion (L-PBF) technology, in particular using the Selective Laser Melting (SLM) technique. The used machine (SISMA MySint100 PM/RM) is equipped with a InfraRed (IR) laser source with a focus of 30 µm and a nominal power up to 175 W. The building volume is 100 mm x 100 mm and the layer thickness is adjustable between 20 and 100 µm.

The volumetric energy density (VED) applied to the CuCrZr powder bed is ~260 J/mm^3 and it was obtained with a Laser Power (P) of 175 W, a Layer Thickness (L) of 20 µm, a Laser Scanning Speed (S) of 850 mm/s and an Hatch Distance(H) of 40 µm. The printing process was performed under a Nitrogen (N_2) atmosphere and a gas speed of 2.5 m/s.

As it is well-known, copper has high thermal conductivity and poor adsorption coefficient at the wavelengths of the IR laser. This reduces the energy density available for the melting process, generating defects such as cavities and lack of fusion. These characteristics did not make possible to achieve material density close to 100%.

The CuCrZr is an ASTM C18400 alloy with chemical composition: 0.5 – 1.5 wt% Cr, 0.03 – 0.3 wt% Zr. For the production of the specimens, a Hovadur® CCZ powder (15-45 µm) produced by Schmelzmetall has been used. The powder nominal composition is reported in Table 1.

The geometry of the specimens have been designed considering the ASTM E-9 standard and the requirement of the Hopkinson bar machine used for the dynamic tests. A part of the specimens were also heat-treated (HT) with an ageing process carried out at 580 °C and at 450 °C under Nitrogen (N_2) atmosphere, followed by cooling in air. Figure 1 shows the produced specimens.

Table 1. Hovadur® CCZ Schmelzmetall powder chemical composition (wt%).

Cu	Cr	Zr	Fe	Si	Others
98.1 - 99.4	0.5 – 1.2	0.03 – 0.3	0.08	0.1	0.2

(a) (b) (c)

Fig. 1. Specimens produced for quasi-static and dynamic tests before (a and b) and after (c) aging treatment.

Samples were ground using SiC papers ranging from 80 to 2400 grit, polished with 0.1 μm alumina suspension, and then etched with ferric chloride to observe the microstructure by using SEM and optical microscope. Aging curves have been obtained by using a microindenter. XRD measurements were made with a diffractometer equipped with a Philips X'PERT vertical Bragg–Brentano powder goniometer. A step–scan mode was used in the 2θ range from 30° to 100° with a step width of 0.02° and a counting time of 1 s per step. The radiation used was the monochromatic Cu Kα radiation.

3. Results and discussion

As a first step of this investigation the powders used for producing the specimens were analysed by SEM/EDS. Figure 2 shows the morphology of the powders. They have a size varying between 15 and 45 μm and a spherical shape. The micrographs in Figure 2 show the presence of satellites justified by the fact that powders are partially recycled during the production process. EDS analyses reported in Table 2 show that the powder composition is the nominal one.

The additive manufactured specimens have been analysed to investigate the alloy microstructure. As it can be observed in Figure 3 the microstructure is constituted by irregular grains having a variable size and, in particular, it is possible to observe grains elongated in the direction of heat removal. Moreover the high thermal conductivity and the high reflectivity of this alloy determine the formation of lack of fusion (indicated by arrows) and of cavities that sometimes contain frozen metallic droplets or unmolten particles.

This inhomogeneous microstructure depends on the very high cooling rates and on the process parameters that affect the material local thermal cycle. EDS analyses of the additively manufactured alloy (Table 3) reveal that Zr is below the detectability limit and that Cr concentration is about 60% of that of the powders. The high localized temperatures reached during the production process determine the evaporation of part of the alloying elements. This is an important finding because the use of different values of VED could produce different alloying element concentrations in the manufactured part and thus different mechanical properties. By comparing the microstructure of additive manufactured alloys with the one of alloys produced by using traditional techniques it is evident that in the latter case (Fig. 4) the grains are quite regular and characterized by the presence of twins. Moreover Fig. 4b highlights the presence of Zr and Cr rich precipitates (small grey phases). They form during solidification because both Cr and Zr have a very low solubility in copper. These precipitates are not visible in the microstructure of additively manufactured specimens because, as suggested by other authors (Salvan et al.(2021)), the high cooling rates involved in the additive manufacturing process of copper alloys, produce the formation of a supersaturated solid solution, whose presence influences not only the mechanical properties of the alloy, but also the type of thermal treatment necessary to increase the alloy mechanical strength.

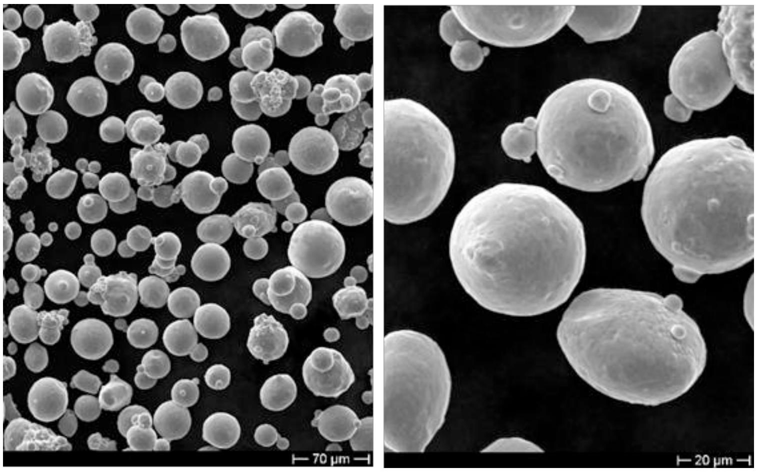

Fig 2. SEM micrographs showing the CuCrZr powder morphology.

Table 2. EDS analyses of CuCrZr powders.

Element	Weight (%)	Atom (%)
Cr	0.97	1.18
Cu	98.93	98.75
Zr	0.10	0.07

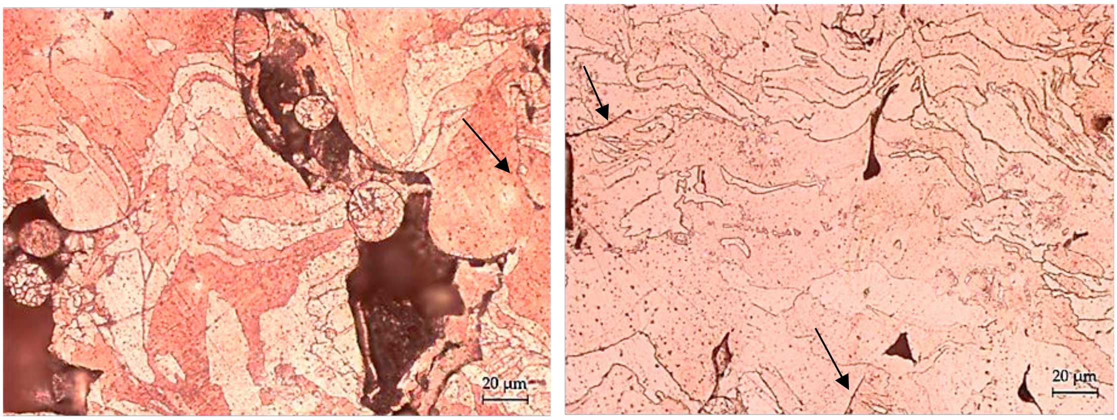

Fig. 3. Optical micrographs the alloy microstructure after etching with ferric chloride and a detail of cavities (micrograph on the left).

Table 3. EDS analyses of the additively manufactured specimens.

Element	Weight (%)	Atom (%)
Cr	0.58	0.71
Cu	99.42	99.29
Zr	nd	nd

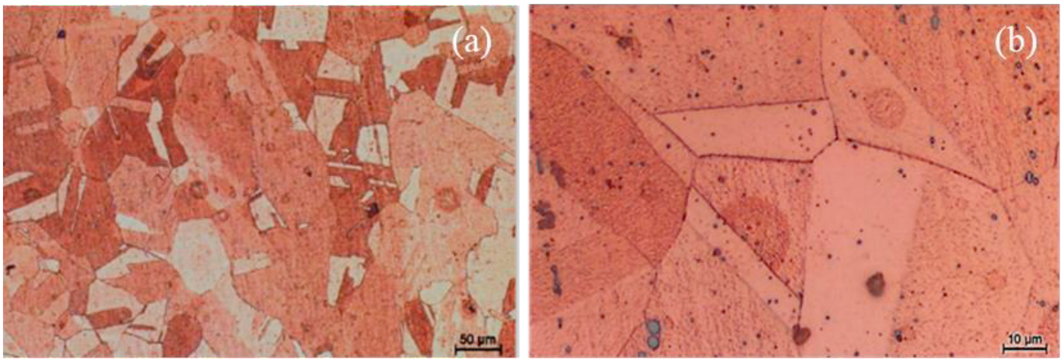

Fig. 4. Optical micrograph showing the microstructure (a,b) of a CuCrZr alloy produced by using traditional techniques after forging and aging and Cr-rich precipitates (b).

In order to study the aging treatment a thermal treatment at 580 °C has been performed on the as-built specimens and on the specimens previously subjected to solution annealing at 980 °C for 1 h. The aging curves reported in Fig. 5 show that both types of specimens reach the hardness peak after a very short time interval and that after solution annealing the alloy hardness is much lower. XRD patterns of the CuCrZr specimens in the as-built conditions and after annealing (Fig. 6) show that in the as-built conditions (Fig.6a) only copper peaks are visible, while, after solution annealing, a small peak characterizing a Zr-rich phase appears (Fig.6b). This suggests that the heat treatment at 980 °C determines the formation of Zr-rich phases that are not coherent with the metallic matrix and that in the aging stage limit the formation of coherent particles that would be able to increase the alloy hardness and strength.

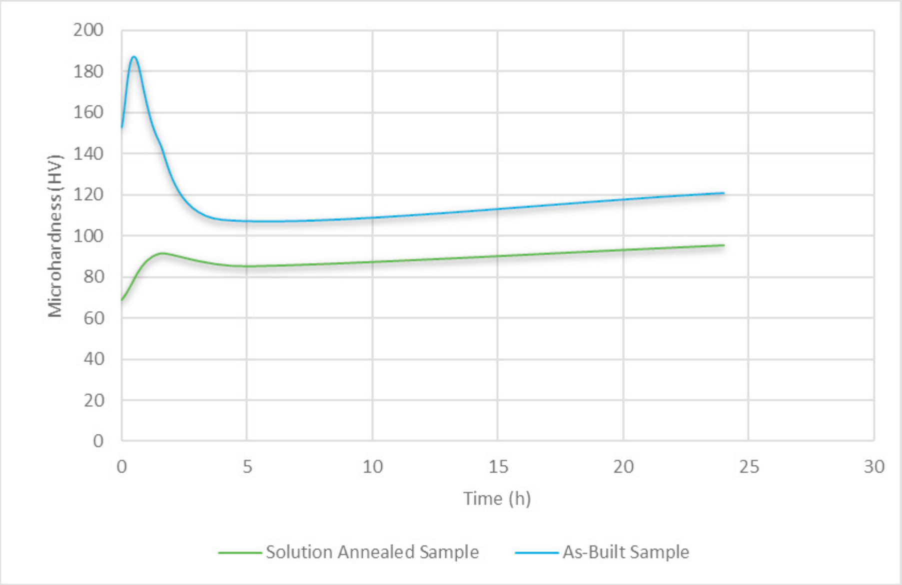

Fig. 5. Aging curves obtained by treating at 580 °C solution annealed (green line) and as-built (blue line) samples.

Considering that the temperature affects the aging treatment, we evaluated the effect of aging temperature on mechanical properties. Figure 7 highlights that the aging treatment temperature has a strong effect on the mechanical performances of the alloy. By aging as-built specimens at 580 °C the hardness peak is reached after only 30 minutes, but due to overaging, hardness quicky decreases. Aging performed at 450 °C allows to attain higher hardness values, even after the peak. This could be explained considering that a lower temperature treatment requires more time to reach the hardness peak because the diffusivity value is lower, but probably in these conditions is possible to form nanometric particles that are more effective in hindering dislocation movement with consequent strength increase.

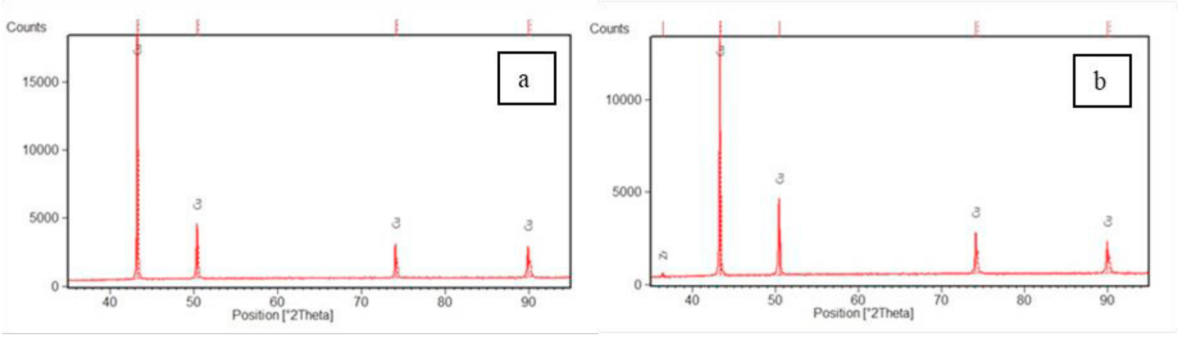

Fig. 6. XRD pattern of an as-built sample (a) and of a solution annealed sample (b).

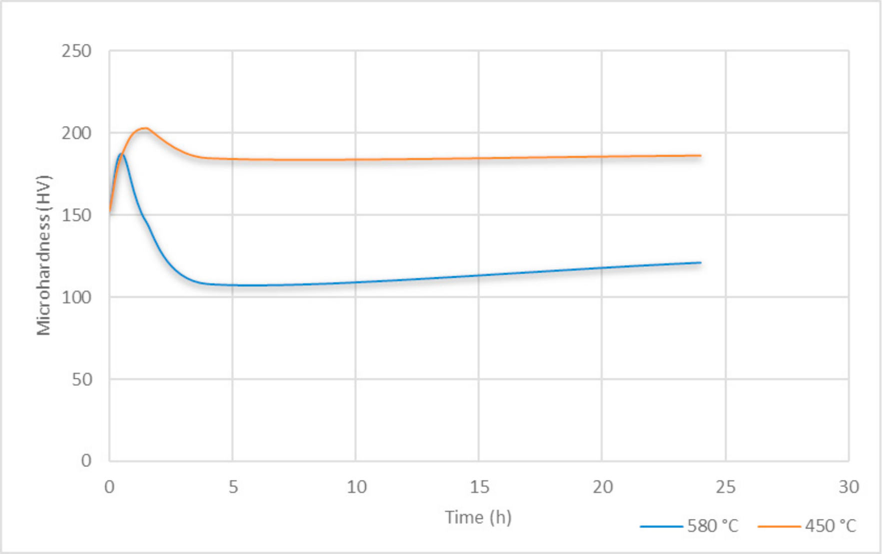

Fig. 7. Aging curves obtained by aging as-built specimens at 450 °C (red line) and at 580 °C (blue line).

4. Conclusions

The research reported in this paper highlights that CuCrZr alloys produced by means of additive manufacturing are very different from the traditional ones. Metallurgical defects like lack of fusion and cavities are difficult to avoid because of the high thermal conductivity and reflectivity of copper. The alloy microstructure is strongly affected by the extremely high cooling rates involved in the additive manufacturing process. These high cooling rates determine also the formation of a supersaturated solid solution in the as-built samples that can be subjected to a direct aging process. The experimental results highlighted also that aging temperature and time considerably affect the mechanical behaviour of CuCrZr alloy. In order to tailor the alloy for a specific application it is essential to carefully select both additive manufacturing parameters and aging temperature and time.

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