Effect of silver addition in copper-silver alloys fabricated by laser powder bed fusion in situ alloying

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Abstract

In this study copper-silver (CuAg) alloy structures with varying Ag content were fabricated using Selective Laser Melting (SLM), Laser Powder Bed Fusion (L-PBF) Additive Manufacturing (AM). Powder morphology, distribution and elemental analysis were conducted using Scanning Electron Microscopy (SEM) and dynamic imaging for CuAg10, CuAg20 and CuAg30 atomised powder. The resultant pore defect morphology and distribution for each as built and annealed CuAg alloy structure was investigated and reported using X-ray Computed Tomography (XCT) and 3D visualisation. The atomic crystal structure for each as built and annealed CuAg alloy is reported through X-Ray Diffraction (XRD) analysis. Yield strength, Young’s Modulus, failure strain and Ultimate Tensile Strength (UTS) of as built and annealed AM CuAg structures are reported and sample fracture surfaces are analysed using SEM and Energy Dispersive X-Ray (EDX) techniques. Increased Ag content from CuAg10% to CuAg30% is shown to decrease the number of pore defects by 87% and 83% for as built and annealed samples with average pore size decreasing by 40% and 9.5%. However, the annealing process was found to increase the porosity by up to 164%. Furthermore, the annealing process resulted in atomic lattice contractions resulting in increased yield strength, Young’s Modulus and Ultimate Tensile Strength (UTS) for CuAg30%.

Keywords: Additive Manufacturing; Selective Laser Melting; CuAg; In situ; Computed Tomography; X-Ray Diffraction; Atomic Lattice Structure;
1. Introduction

Silver (Ag) and copper (Cu) are highly reflective materials with desirable antimicrobial, thermal and electrical conductive properties [1–5]. As such these materials are of interest for a wide range of applications such as renewable energy, biomedical, electronics and thermal management [3,4,6–8]. Ag is usually utilised as an alloying element [9–11], however, research has shown that increasing Ag addition by as little as 2 and 3% can increase thermal conductivity and diffusivity as well as hardness and compressive strength of aluminium-copper-silver (AlCuAg) alloys [12]. A 10% increase of Ag in titanium-silver (TiAg) alloy lowered the compressive stress by 80% and hardness by 30% [7]. Ag addition between 0.5% - 2% in molybdenum-copper-silver (MoCuAg) alloys increased electrical and thermal conductivity with negligible effect on the Coefficient of Thermal Expansion (CTE) [8].

Although the studies mentioned highlight the potential benefits of CuAg alloys, the powder metallurgy associated with manufacturing techniques utilised for alloy fabrication are limited with little research on advanced manufacturing technologies such as Additive Manufacturing (AM). Cu and its alloys are gaining popularity due to lower material cost and as such are undergoing research utilising AM techniques such as Selective Laser Melting (SLM) [13–17]. During the SLM process 3D components are fabricated by laser melting a 2D layer on preceding layer. SLM is capable of creating complex 3D geometries unfeasible with conventional manufacturing techniques [18–20] and therefore the creation of complex metallic alloys and metal matrix composite materials and structures are being increasingly reported [19,21]. However, the SLM process has over 130 variables including the feedstock and process [22] and these include material absorptivity and reflectivity, laser diffusion and scattering, heat transfer and material phase transformation [23]. Furthermore, SLM material feedstock properties such as apparent density, particle distribution and powder flowability can have a significant effect on powder layer delivery and therefore the creation of porosity defects. In addition the laser and material interaction and selected process parameters and scanning strategy can result in lack of fusion, keyhole and blowhole defects [24]. Previous studies on the SLM of pure silver have shown material failure at lack of fusion porosity sites with the unmolten powder particles visible at fracture sites [25].

Therefore, the SLM processing of reflective and thermally conductive materials such as Ag and Cu can be difficult [2,26,27] with some studies reporting maximum pure Cu densities of 85.8% utilising SLM [2]. Subsequently Ag and Cu are usually utilised as alloying elements to exploit their desired properties [28,29]. The SLM process is known to cause cracking and pore defects in fabricated components [22,24,30,31], which subsequently lead to material failure [32,33]. Therefore, AM pore defects have seen significant investigation [24,31,34] regarding the creation mechanisms and porosity types which are generally well understood. Consequently, pore defects are usually categorised to be keyhole, blowhole or lack of fusion defects [24]. These porosity
defects as a result of manufacturing are shown to have a negative effect on the properties of the AM fabricated components [31,35,36] and therefore understanding the correlation between SLM process, material and pore defect morphology and distribution is critical. While the SLM of Ag and Cu as alloying and base elements is undergoing increasing research, the morphology and distribution of porosity throughout CuAg in situ SLM fabricated structures are yet to be understood. Understanding this aspect is critical for the development of novel alloys as pore defects have a significant effect on the thermomechanical properties [35,37] of the components. Therefore, understanding SLM pore defect distribution for CuAg in situ structures will aid in their optimum fabrication for a variety of industries and applications. Accordingly, this study reports the SLM fabrication of CuAg10, CuAg20 and CuAg30 in situ alloys and their resultant mechanical performances both as built and annealed. SLM powder composition, morphology and distribution and reported using dynamic imaging, Scanning Electron Microscopy (SEM) and Energy Dispersive X-Ray (EDX) analysis. Fabricated pore defect morphology and distribution are described through X-ray Computed Tomography (XCT) 3D visualisation and CuAg in situ crystal structure is analysed through X-Ray Diffraction (XRD) techniques. Yield strength, Young’s Modulus, failure strain and Ultimate Tensile Strength (UTS) of as built and annealed CuAg structures are reported and sample fracture surfaces are analysed using SEM and Energy Dispersive X-Ray (EDX). This research offers an insight into the mechanical properties and pore defect morphology and distribution in SLM highly reflective and thermally conductive CuAg in situ alloy structures with varying Ag content.

2. Material and methods

The SLM L-PBF investigations presented in this study were carried out on an EOS M290 industrial grade AM system using CuAg10%, CuAg20% and CuAg30% powders comprising of atomised pure Cu and Ag powders. The L-PBF system featured a 400W laser with 100µm spot size and all builds were completed in an argon atmosphere with oxygen content in the process chamber below 0.1%. The process was carried out on substrates heated to 35°C. Following fabrication all samples were removed from the build platform using none contact Electrical Discharge Machining (EDM) techniques. Half of the as built samples were post heat treated with a CuAg annealing process and subsequent mechanical testing was conducted using a Zwick Roell 1474 material test system with 100 kN maximum load capacity. A Bruker Skyscan 2211 X-ray nanotomograph was used to analyse sample pore defect distribution and morphology while fracture surfaces were analysed using Scanning Electron Microscopy (SEM). Atomic lattice structure analysis was conducted using Panalytical Empyrean, copper anode X-Ray Diffraction system operating at 40 KV and 40 mA.
2.1. Powder Characterisation

Powder morphology and particle distribution can affect the packing density and flowability of AM powders [38] and therefore dictate the thermomechanical behaviour during the AM process [38]. Atomised CuAg powder combinations utilised in this study were created using pure Cu and Ag powders proven to be suitable for SLM processing in previous studies [25]. Pure Ag powder displayed a larger distribution of powder particles below 20 µm with visible satellite particles while pure Cu powder particles displayed a larger distribution above 20 µm with fine particles also visible. However, both pure Cu and Ag displayed an evenly distributed particle size and relatively spherical powder morphology which is desired for the PBF process to enhance both the packing density and the flowability of the powder [38]. Pure Ag was shown to have a PVD of D_{10} of 20.3 µm, D_{50} of 30.2 µm and D_{90} of 41.4 µm while pure Cu featured a PVD of D_{10} of 44.0 µm, D_{50} of 52.1 µm and D_{90} of 58.2 µm. As a D_{90} of 10 µm can result in unusable powder for PBF processing [39], the pure Cu and Ag are suitable for PBF AM. Energy Dispersive X-Ray Spectroscopy (EDX) analysis was completed using a Zeiss EVO50 SEM to confirm the elemental content of pure Cu and pure Ag powders before mixing. Pure Cu and Ag powders were shown to be 99.08% (Cu) and 99.73% (Ag) respectively with balance oxygen. To confirm homogenous distribution the element content, morphology and Particle Size Distribution (PSD) of the CuAg powders were characterised using SEM and digital particle analysis techniques. A Retsch Technology Camsizer x2 was used to analyse particle distribution. The resulting SEM data for CuAg powders are shown in Fig 1. CuAg powder particles can be seen to be spherical in shape, however, the morphology and Particle Size Distribution (PSD) varies with Ag content due to the differences in Cu and Ag morphology. Cu particles are generally larger with a mix of smaller Cu and Ag powder particles within the powder samples.

![Scanning Electron Microscopy (SEM) images for CuAg powders showing (a) CuAg10, (b) CuAg20 and (c) CuAg30.](image)

**Fig 1.** Scanning Electron Microscopy (SEM) images for CuAg powders showing (a) CuAg10, (b) CuAg20 and (c) CuAg30.

To confirm the element content of the powders, Energy Dispersive X-Ray (EDX) analysis was conducted using a Zeiss EVO50 SEM. Fig 2 shows the EDX spectra data with table 1 showing...
the elemental composition for each of the CuAg powder mixes highlighting that the respective increase in Ag content as expected with the respective 10, 20 and 30% addition.

![Energy Dispersive X-Ray (EDX) element spectra for (a) CuAg10, (b) CuAg20 and (c) CuAg30.](image)

**Fig 2.** Energy Dispersive X-Ray (EDX) element spectra for (a) CuAg10, (b) CuAg20 and (c) CuAg30.

**Table 1.** Elemental weight composition of the different CuAg mixtures as informed by the EDX spectrum.

<table>
<thead>
<tr>
<th>Material</th>
<th>Element</th>
<th>Weight (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuAg10</td>
<td>Cu</td>
<td>92.51</td>
</tr>
<tr>
<td></td>
<td>Ag</td>
<td>07.49</td>
</tr>
<tr>
<td>CuAg20</td>
<td>Cu</td>
<td>72.50</td>
</tr>
<tr>
<td></td>
<td>Ag</td>
<td>27.50</td>
</tr>
<tr>
<td>CuAg30</td>
<td>Cu</td>
<td>64.20</td>
</tr>
<tr>
<td></td>
<td>Ag</td>
<td>35.80</td>
</tr>
</tbody>
</table>

Although the content of Ag increases as anticipated with expected elemental compositions, the actual weight % for each CuAg powder mix varies. This could be due to non-homogenous distribution within the powder mix or variations in the EDX results due to powders nonuniform morphology. To establish excessively high or low particle distribution that can affect the powders processability for SLM AM the CuAg powders $D_{10}$, $D_{50}$, and $D_{90}$ volume fractions were identified. Particle Volume Distribution (PVD) and corresponding $D_{10}$, $D_{50}$, and $D_{90}$ for each CuAg alloy
are shown in Fig 3. $D_{10}$ volume decreases as Ag content increases due to pure Ag lower PSD. $D_{50}$ and $D_{90}$ volume remain relatively unchanged for all CuAg powder mixes. A $D_{90}$ of 10 µm can result in unusable powder for PBF processing [39] and therefore the PVD values shown in Fig 3 suggest that the CuAg powders measured in this study are suitable for PBF AM.

![Figure 3. Particle Volume Distribution (PVD) for CuAg10, CuAg20 and CuAg30 powders.](image)

### 2.2. Annealing Process

SLM CuAg alloys have seen limited investigations, in any case compositions with a relatively high Ag content alloys of 10%, 20% and 30% have not been investigated to date. However, cast CuAg alloys with high compositions have been investigated. Shannon et al. [40] studied ingot cast CuAg alloys at compositions including CuAg30, CuAg20 and CuAg5 and reported the recrystallisation and optimum annealing process. For cast and work hardened CuAg alloys the investigations determined the recrystallisation temperature for CuAg30 to be 500°C for a 30 minute anneal time. During annealing the internal residual stresses introduced by the work hardening were shown to be relieved without change in strength or hardness [40]. Although not work hardened, the SLM process is known to create internal stresses within fabricated components due to the rapid heating and cooling cycles associated with the laser melting process [41,42]. Accordingly, to investigate post heat treatment and recrystallisation for SLM CuAg in situ alloys, 50% of the as built samples were annealed at 500°C for a 30 minute period and left to cool. Atomic lattice structure variations were then investigated using X-Ray Diffraction (XRD) and the results reported alongside the resultant effects on mechanical performance and pore defect distribution.
3. Results and discussion

3.1. Additively manufactured test coupons

SLM process parameters developed in previous studies were used for initial CuAg sample fabrication and are displayed in Table 2 while as built CuAg10, CuAg20 and CuAg30 samples are shown in Fig 4. Although all CuAg samples were fabricated with the same parameters and had visibly similar surface finish there was a clear colour variation throughout due to the increased Ag content, particularly with the higher Ag 30% content.

![Sample images](image)

Fig 4. As built CuAg in situ alloy samples on build substrates showing (a) CuAg10, (b) CuAg20 and (c) CuAg30

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Laser Power (W)</th>
<th>Scan Speed (mm/s)</th>
<th>Hatch Distance (mm)</th>
<th>Layer Thickness (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Values</td>
<td>370</td>
<td>400</td>
<td>0.14</td>
<td>30</td>
</tr>
</tbody>
</table>

3.2. Density and pore defect analysis

Understanding SLM porosity morphology and distribution is crucial for understanding the effects of SLM processing and material failure. While industrial grinding and polishing techniques combined with SEM imaging can supply an indication of fabricated component density and defect content, they offer limited information on distribution throughout the sample due to only supplying a as a result of the 2D data. Accordingly, X-Ray Computed Tomography (XCT) analysis was conducted to ascertain a 3D visualisation of porosity morphology and distribution and to investigate any resultant pore defect variations associated with increased Ag addition.

XCT is a nondestructive analysis technique, which can be used for AM pore defect analysis [35,43]. Incorrect powder feedstock properties such as PVD and poor flowability can lead to nonuniform powder layer delivery and porosity defects. However pore defects can also result
from laser and material interaction and process and scanning strategy parameters [24]. XCT analysis for this study was conducted utilising a Bruker Skyscan 2211 X-ray nanotomograph. While XCT sample analysis is a valuable tool for nondestructive pore defect analysis, the results achieved are dependent on the scanning and threshold parameters set by the operator. Therefore, XCT techniques are better utilised for comparative rather than absolute analysis. Comparative analysis ensures XCT scanning and threshold parameters are kept constant and therefore any variations in density and porosity defects can be attributed to AM feedstock material, process parameters used for manufacturing or post processing techniques such as annealing. For this reason, all samples were scanned with the same XCT scanning, threshold and reconstruction parameters to ensure any notable changes in porosity can be attributed to either the difference of Ag in the AM material feedstock or the annealing process.

XCT porosity data for SLM CuAg in situ alloys at Ag 10%, 20% and 30% are shown in Fig 5. The number of pores and average pore size were found to decrease as Ag content increases for both CuAg as built and annealed samples. Overall, the quantity of pores decreased by 87% and 83% while average pore size decreased by 40% and 9.5% for as built and annealed samples respectively.

![Number of closed pore defects and Average pore size](image)

**Fig 5.** XCT pore defect data for SLM CuAg alloys as built and annealed showing (a) number of closed pore defects and (b) average closed pore size

The annealed samples display a larger proportion of pores and larger average pore size clearly showing the annealing process increases pores content, particularly at lower (10%) Ag content, which showed a 164% increase between as built CuAg10 as built sample to annealed CuAg10 sample. Furthermore, the annealing process can be seen to increase pore defect content with
corresponding samples displaying either similar or higher number of pores and average pore sizes in 11 out of the 12 cases.

X-ray absorption rates varied for both as built and annealed CuAg samples as shown in Fig. 6a-c and Fig. 7a-c respectively. High X-ray absorption signifies a relatively dense material as identified by 1 (blue), on the contrary 0 (black) represents areas of lowest X-Ray absorption and therefore potential voids (absence of material). To analyse the pore defect morphology and distribution throughout the samples the internal closed pore porosity voids were isolated for as built and annealed samples as shown in Fig. 6c and 7c respectively. Higher Ag content was found to correspond with less pore defects for both as built (Fig. 6) and annealed (Fig. 7) samples, however as built samples displayed significantly lower pore defects (Fig. 6) in comparison to annealed samples (Fig. 7). The XCT data and 3D visualisations seen in Figs. 6 and 7 show clear variation in the number of pores and average pore size as Ag content increases. The addition of Ag reduces pore content and average pore size significantly while annealing increased pore content and pore size for all CuAg compositions. CuAg30 with the largest Ag content was found to have the lowest pore defect content for both as built (Fig. 6) and annealed (Fig. 7) samples.
Fig 6. X-ray computed tomography scans of as build CuAg samples under different compositions as identified showing (a) the full scan of the specimen, (b) highlighted porosity within the structure and (c) internal closed pores isolated for clarity.

Fig 7. XCT 3D visualisation of density and porosity content and distribution for annealed samples for (a) CuAg10 (b) CuAg20 and (c) CuAg30.

Pore defects have been shown to negatively affect a materials mechanical performance [25,34,44] and therefore the larger content of these defects seen in the annealed and lower Ag content samples would expect to exhibit lower mechanical strength. Reduced porosity due to increased Ag content could be due to lower powder PVD resulting in improved packing density and layer delivery or atomic bonding in the CuAg alloy system. Accordingly, atomic lattice structure was investigated utilising X-Ray Diffraction (XRD) techniques.

3.3. Influence on crystal structure

Pure Cu and Ag with face centered cubic (fcc) atomic lattice structures [3,45] but varying atomic size differences result in relatively large lattice mismatches in the CuAg alloy system [3,46]. However, at $\alpha \sim 12\%$ the CuAg system still conforms to the Hume–Rothery criteria for fcc metals, with atomic size differences within 15% [45,46]. Therefore, the CuAg system is of significant interest and as such has seen investigations relating to alloying behavior, atomic vacancy effects, miscibility, phase stability and recrystallisation [40,46–48] utilising atomistic and molecular dynamic simulations, electrodepositing, casting and XRD [3,40,45,47,49]. Despite this SLM CuAg alloy crystal lattice structures at relatively high Ag content (Ag10%, Ag20% and Ag30%)
have not seen investigation. Accordingly, SLM CuAg alloy lattice structures and atomic d-spacing were investigated using a Panalytical Empyrean, copper anode X-Ray Diffraction system operating at 40 KV and 40 mA.

The XRD cluster analysis as shown in Fig. 8 was carried out to identify any variations between CuAg structures at an atomic level with SLM pure Cu used as a reference sample. Using the eigenvector mathematical procedure, a smaller data set is created, and data variables are collated into corresponding groups or principal components. Although using a reduced data set, cluster analysis allows for XRD data visualisation highlighting data variances and similarities [50] and displaying them in within related coloured spheres. Fig 8 clearly demonstrates separation and variation in atomic structure for SLM pure Cu and as built and annealed CuAg alloy samples.

Although all CuAg samples (both as built and annealed) were shown to have the same cubic crystal structure, the addition of Ag and the annealing process have obvious effects at the atomic level. The annealing process can be seen to create a similar atomic structure for annealed samples due to recrystallisation with all annealed samples clustered in proximity. As built samples also display similar atomic structure to each other however cluster analysis shows there is more variance.

**Fig 8.** X-Ray Diffraction (XRD) cluster analysis for SLM pure Cu and as built and annealed CuAg in situ alloys.

The cluster analysis displays clear variations in atomic lattice structure between annealed samples and as built (none heat-treated) samples and therefore XRD data for pure Cu and all CuAg samples was investigated further to investigate atomic lattice variations. SLM pure Cu
was used as reference sample and the XRD spectrum data was obtained for pure Cu as shown in Fig 9. Pure Cu peaks appeared at 2 Theta = 43.2º, 50.3º and 74.2º respectively, which is consistent with fcc Cu JCPDS (Joint Committee on Powder Diffraction Standard) cards.

![Fig 9. XRD spectra data for SLM pure Cu](image)

XRD spectrum data for CuAg in situ alloys as built and annealed can be seen in Figs 10, 11 and 12. New Ag peaks are present, which increased in count and height as Ag composition content increased from 10% to 20% and 30%. This confirmed the homogenous distribution of Ag throughout all CuAg in situ samples which all also displayed cubic atomic structures. Furthermore, all samples saw 2º Theta values decrease (Fig 13a) with increased Ag content suggesting an increase in d-spacing (Fig 13b) which is explained by the presence of the relatively larger silver atoms within the CuAg atomic lattice structures.

![Fig 10. XRD spectra data for (a) CuAg10 as built and (b) CuAg10 annealed](image)
Fig 11. XRD spectra data for (a) CuAg20 as built and (b) CuAg20 annealed

Fig 12. XRD spectra data for (a) CuAg30 as built and (b) CuAg30 annealed.

However, following the annealing process d-spacing saw significant reductions in relation to as built samples (Fig 13b) due to the recrystallisation and contraction of atomic lattice structures. This atomic lattice contraction therefore explains the increase in pore defects seen in XCT 3D visualisation (Fig 6 and 7). As atomic lattice contractions occur, number of pores and the average size increase where voids are present throughout the CuAg samples. D-spacing reduced by 0.29%, 1.29% and 2.26% respectively for CuAg10, CuAg20 and CuAg30 following the annealing process. As built d-spacing displayed a 1.93% increase with increased Ag content from CuAg10 to CuAg30 while annealed samples saw a maximum 0.2% change in d-spacing for all three samples. Furthermore, annealed samples exhibited d-spacing values below that of as built SLM pure Cu.
3.4. Mechanical Performance

The addition of Ag to Cu has seen significant research [4,51] and has been shown to have strengthening effects due to fine dendrites and an increase in CuAg phase boundaries, which have a strong binding effect. Furthermore, Cu matrix and CuAg interfaces were shown to hinder dislocation movements [52]. Investigations regarding the interaction between Cu and Ag at an atomic level for SLM CuAg in situ alloys has not been investigated. Accordingly, Fig 14 presents the stress-strain ($\sigma - \varepsilon$) curve for AM CuAg10, CuAg20 and CuAg30 in situ alloys with the corresponding performance parameters such as the Yield strength ($\sigma_y$), Youngs Modulus (E), failure strain ($\varepsilon_f$) and Ultimate Tensile Strength (UTS) values shown in Fig 15.
Fig. 15. Influence of Ag content and annealing on the mechanical performance of SLM CuAg alloys showing (a) yield strength, (b) Young’s Modulus, (c) failure strain and (d) ultimate tensile strength.

The $\sigma - \varepsilon$ data clearly displays an increase in $E$ (Fig 15b), $\sigma_y$ (Fig 15a) and UTS (Fig 15d) with increased Ag addition for both as built and annealed samples with the highest $E$, $\sigma_y$ and UTS displayed with Ag 30% for all samples. As built samples showed an increase in $\sigma_y$ of 23% and 48% as Ag content increased from 10% to 20% and 30% while annealed samples saw $\sigma_y$ increase by 36% and 87% respectively (Fig 16a). Similarly, UTS as built samples saw increases of 22% and 37% while UTS annealed samples increased by 31% and 68% (Fig 16 b). With $\sigma_y$ and UTS increases of 87% and 68% for Ag addition at 30% it is clear the annealing process has a more profound effect on material strength with higher Ag addition above 20%. While as built CuAg10 samples display higher $E$, $\sigma_y$ and UTS than the equivalent CuAg10 annealed samples. The CuAg20 samples whether as built or annealed have comparable $\sigma_y$ and UTS values. The results confirm that the Ag addition does create an increase in mechanical properties within SLM CuAg in situ alloys. Furthermore, Ag addition increased E which saw increases of 23% and 15% for as built samples and 15% and 36% for annealed samples.
Fig. 16. Influence of Ag content and annealing process on the mechanical performance of SLM CuAg alloys showing (a) yield strength and (b) ultimate tensile strength.

Effects of Ag addition on $\varepsilon_f$ was less obvious with CuAg20 displaying the largest $\varepsilon_f$ values for both as built and annealed samples. However, $\varepsilon_f$ was seen to reduce for all samples (Fig 15c and 17a) following annealing due to recrystallisation and atomic lattice contraction resulting in stronger binding effect on CuAg interfaces reducing dislocation movements which also increasing $E$ (Fig 17b).

Fig. 17. Influence of Ag content and annealing process on the mechanical performance of SLM CuAg alloys showing (a) failure strain and, (b) Young’s modulus.
3.5. Fractography

SEM data for SLM CuAg fracture surfaces are shown in Fig 18, 19 and 20. Although none of the CuAg fracture surfaces exhibited unmolten powder particles expected at lack of fusion pore sites some porosity voids are clearly visible as confirmed by the XCT data.

![Fractography](image)

**Fig 18.** Scanning Electron Microscopy (SEM) data for CuAg alloy fracture surfaces showing (a) as built CuAg10 and (b) CuAg10 Annealed

![Fractography](image)

**Fig 19.** Scanning Electron Microscopy (SEM) images for CuAg alloy fracture surfaces showing (a) as built CuAg20 and (b) CuAg20 Annealed
Fig 20. Scanning Electron Microscopy (SEM) images for CuAg alloy fracture surfaces showing (a) as built CuAg30 (b) CuAg30 annealed

To ascertain pore defect content at each CuAg fracture surface Olympus Stream Essentials software was utilised for comparative porosity analysis. Results (Fig 21) concluded pore content at the fracture site decreases with Ag addition for both as built and annealed samples while porosity content values were higher for all annealed samples in comparison to as built structures confirming the XCT data results (Fig 5a and 5b).

![Porosity Voids](image)

**Fig. 21.** Influence of Ag addition on fracture surface porosity content of SLM CuAg in situ alloys

To confirm homogenous element distribution throughout the CuAg structures, EDX analysis was conducted on each fracture surface and compared with EDX elemental content of the CuAg powder. Spectrum analysis (Fig 22) confirms increase in Ag content at the sample fracture surface. While CuAg10 Ag fracture content differed from CuAg10 Ag powder content both CuAg20 and CuAg30 Ag content for powder and fracture surfaces was shown to be comparable. Although EDX analysis highlights some variations the Ag content throughout all fabricated
CuAg structures was relatively close to the initial Ag powder composition confirming a homogeneous distribution throughout powder and fabricated structures.

![Fig 22](image_url)

**Fig 22.** Energy Dispersive X-Ray (EDX) element analysis for CuAg fracture surfaces (a) CuAg10, (b) CuAg20 and (c) CuAg30.

<table>
<thead>
<tr>
<th>EDX Element Analysis for CuAg Fracture Surfaces</th>
</tr>
</thead>
<tbody>
<tr>
<td>Material</td>
</tr>
<tr>
<td>----------</td>
</tr>
<tr>
<td>(a) CuAg10</td>
</tr>
<tr>
<td>(b) CuAg20</td>
</tr>
<tr>
<td>(c) CuAg30</td>
</tr>
</tbody>
</table>

**Fig 23.** Energy Dispersive X-Ray (EDX) element analysis for CuAg fracture surfaces (a) CuAg10, (b) CuAg20 and (c) CuAg30.

4. Conclusions

The study presents CuAg in situ structures with varying Ag content fabricated using the Selective Laser Melting (SLM) process. The resultant pore defect distribution, atomic lattice structures and mechanical performance are reported for both as built and annealed conditions. The XCT analysis showed that as Ag content increased both the number of pores and average pore size decrease for both as built and annealed samples. Increasing Ag content from 10% to 30% saw the number of pores decrease by 87% and 83% for as built and annealed samples with
average pore size decreasing by 40% and 9.5% respectively. However, the annealing process increased pore content significantly with CuAg10 alloy experiencing a 164% increase between as built and annealed conditions. The subsequent XRD analysis showed that the AM CuAg samples confirmed the presence of a cubic atomic structure where the increase in Ag content increased the atomic d-spacing. This is explained by the inclusion of the relatively large silver atoms within the CuAg atomic lattice structures. However, following the annealing process atomic d-spacing reduced due to atomic lattice contractions. D-spacing reduced by 0.29 %, 1.29 % and 2.26 % respectively for CuAg10, CuAg20 and CuAg30 following the annealing process. As built d-spacing displayed a 1.93% increase with increased Ag content from CuAg10 to CuAg30 while annealed samples saw a maximum 0.2% change in d-spacing for all three samples. It was also found that the atomic lattice contraction combined with recrystallisation had a significant effect on mechanical performance due to stronger binding effects at the CuAg interfaces reducing dislocation movements. While CuAg10 samples displayed higher yield and ultimate strength than the equivalent annealed samples, CuAg20 showed comparable yield and ultimate strength values for both as built and annealed cases. Nevertheless, as built samples saw an increase in yield strength of 23% and 48% as Ag content increased from 10% to 20% and 20% to 30%. Annealed samples saw yield strength increase by 36% and 87% respectively. Similarly, UTS of as built samples saw increases of 22% and 37% while annealed samples increased by 31% and 68%. With increases of 87% (yield strength) and 68% (UTS) for Ag addition at 30%, it is clear the annealing process has a profound effect on material strength for Ag addition of above 20%. When it comes to Youngs modulus Ag increase from CuAg10 to CuAg30 resulted in a 23% and 15% increase for as built samples and 15% and 36% for annealed samples.

Evaluating the fracture surfaces revealed that the Ag content was like the powder feedstock confirming a homogeneous distribution throughout the SLM build and sample fabrication. Although, the SEM analysis of the fracture surfaces showed no visible lack of fusion porosities and unmolten powder some porosity voids were visible. Overall, the SEM data showed that the fracture surface pore content decreased with increase in Ag content.

Acknowledgements
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Data availability
The data that supports the findings of this study are available from the corresponding author upon reasonable request.

References


[31] F.H. Kim, S.P. Moylan, E.J. Garboczy, J.A. Slotwinski, Investigation of pore structure in cobalt chrome additively manufactured parts using X-ray computed tomography and three-dimensional image analysis,


