



Additive manufacturing of graphene-reinforced copper matrix composites produced via cold spray[☆]

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ARTICLE INFO

Keywords:

Cold spray additive manufacturing

Cu–Gr composites

2DMMC

Thermal management applications

ABSTRACT

Graphene (Gr)-reinforced composites offer significant potential for enhanced thermal, mechanical, and functional performances, yet their fabrication via energy beam-based additive manufacturing (AM) is challenging due to the thermal sensitivity of Gr, the risk of agglomeration, and limitations of high-temperature processes. As a solution, Cu-1 wt% Gr deposits were successfully produced using cold spray additive manufacturing (CSAM), providing a solid-state route to fabricate dense 2D metal matrix composites (2DMMCs). The effects of Gr incorporation and gas temperature were systematically investigated on microstructural evolution, dynamic recrystallization, and functional properties. 2DMMCs properties were compared with pure Cu to isolate the effects of Gr reinforcement. The effect of microstructural homogenization induced by post-deposition heat-treatment was analysed on thermal, electrical and mechanical performances. Findings indicate that the presence of Gr alters how strain and thermal energy are distributed within the deposits, promoting heterogeneous microstructures and increasing microhardness. Higher gas temperature led to higher density and thermal conductivity. However, mechanical and electrical properties were moderately reduced due to Gr-induced stress concentrations and interparticle bonding limitations. Subsequent post-deposition annealing partially reduced bulk defects and led to enhanced thermal and electrical performance.

Our findings demonstrate that CSAM enables the efficient production of Cu–Gr 2DMMCs. The structure–property relationships established in this work identify interfacial bonding and Gr distribution as the key factors governing composite performance, providing a foundation for future optimization of solid-state AM strategies for large scale 2DMMCs.

Abbreviations: Cu, Copper; TC, Thermal conductivity; Gr, Graphene; 2DMMC, Two-dimensional metal matrix composite; AM, Additive manufacturing; L-PBF, Laser powder bed fusion; DED, Directed energy deposition; CSAM, Cold spray additive manufacturing; CS, Cold spray; SPD, Severe plastic deformation; MD, Molecular dynamics; SEM, Scanning electron microscopy; EBSD, Electron backscatter diffraction; BSE, Back scattered electron; EDX, Energy dispersive X-ray spectroscopy; IPF, Inverse pole figure; PSD, Particle size distribution; EDM, Electrical discharge machining; AS, As-sprayed; XRD, X-ray diffraction; KSS, Kinetic Spray Solution; FWHM, Full width at half maximum; DE, Deposition efficiency; HV, Vickers microhardness; TPS, Transient plane source; EC, Electrical conductivity; DRX, Dynamic recrystallization; CDRX, Continuous dynamic recrystallization; DDRX, Discontinuous dynamic recrystallization; GND, Geometrically necessary dislocation; CTE, Coefficients of thermal expansion; DSRX, Discontinuous static recrystallization; UTS, Ultimate tensile strength; TEM, Transmission electron microscopy; ADF-STEM, angle annular dark field scanning TEM; EELS, Electron energy loss spectroscopy; FIB, Focused ion beam; GIF, Quantum Gatan Imaging Filter.

[☆] This article is part of a special issue entitled: 'Additive Manufacturing' published in Materials & Design.

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<https://doi.org/10.1016/j.matdes.2026.116929>

Received 29 April 2026; Received in revised form 28 July 2026; Accepted 31 August 2026

Available online 31 August 2026

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1. Introduction

Copper (Cu) is a crucial material used extensively in thermal management, power electronics, lightweight conductive components, and multifunctional systems. This is due to its high electrical and thermal conductivities (TC), workability, and corrosion resistance [1–4]. The incorporation of Graphene (Gr) as a two-dimensional reinforcement inside a metallic matrix has attracted interest thanks to its exceptional mechanical strength and TC [5–7]. Two-dimensional metal matrix composites (2DMMCs) have been reported to exhibit enhanced mechanical, thermal and electrical properties, enabling the creation of high-performance multi-functional materials [8,9].

Traditionally, 2DMMCs have been fabricated using conventional powder metallurgy and casting routes [10]. However, additive manufacturing (AM) is now being explored to meet the increasingly complex geometrical and functional requirements [6,11]. Despite the high potential of Cu as a metal matrix, its processing via energy beam-based AM techniques is challenging due to Cu's high TC and reflectivity [12,13]. Various AM techniques including laser powder bed fusion (L-PBF), and directed energy deposition (DED) have been evaluated for processing Cu, each with specific limitations ranging from incomplete fusion, porosity, or difficulties in controlling the microstructure and residual stresses [14–17]. Recent studies, however, indicate that high-power lasers, and green lasers induced-PBF can produce dense Cu components, with carefully optimized process parameters [18,19]. Researchers have also attempted to address this issue by alloying Cu with elements such as Cr and Zr (e.g., GRCo-42 and GRCo-84 alloys); however, this approach introduces other drawbacks, such as reduced TC [20,21]. While these advances demonstrate the feasibility of AM processing for Cu, such processes still pose significant challenges for fabricating Cu–Gr composites. Addition of Gr will further complicate the AM process since it is thermally sensitive and can undergo structural disordering, degradation and chemical reactions at high temperatures typical of fusion-based AM, which limits reinforcement retention and composite performance [6,22].

Solid-state AM processes, particularly cold spray additive manufacturing (CSAM), can provide a promising alternative. In cold spray (CS), metallic particles are accelerated to supersonic velocities and undergo severe plastic deformation (SPD) upon impact, thereby promoting bonding [23,24]. CS is therefore well suited for manufacturing of Cu–Gr composites with minimal oxidation, high deposition rates and deposition efficiency, and tuneable microstructures through process variables such as gas temperature, particle velocity, and powder characteristics [25,26]. As the CS deposition relies on kinetic rather than thermal energy, problems associated with high temperature processing for consolidation of 2DMMCs can be minimized, if not eliminated. This relatively low processing temperature in CS reduces Gr defects and limits interfacial reactions, and preserves the structural integrity of Gr [27].

Previous studies on CS deposition of Cu–Gr composites are very limited and have primarily focused on feasibility and Gr distribution [28–30]. Choi et al. [29] showed that Gr grown on Cu particles via chemical vapor deposition can be used for CS to produce deposits with improved wear resistance and reduced friction. Yin et al. [28] reported uniform Gr dispersion in Cu–Gr deposits, improving tribological performance, while Dardona et al. [31] used micro-CS to print conductive Cu–Gr traces with good adhesion. In our preliminary study [30] we demonstrated that the optimized gas pressure and other spray parameters enhance deposit density, hardness, and Gr retention. Despite the available insights, the specific influence of Gr on particle bonding, microstructural features of the deposit, and the resulting mechanical and physical properties remain insufficiently understood. The presence of Gr complicates the deposition process, through sliding, or fragmentation of the Gr reinforcement, since inter-particle cohesion depends on a delicate interplay between strain-induced metallurgical bonding of Cu particles, and their mechanical interlocking. Molecular dynamics (MD)

simulations investigating the impact of a single particle partially covered by Gr nanoplatelets, indicate that the latter have a role in impeding plastic flow and restricting solid-state metallurgical bonding by limiting the metallic contact area at the interface [32]. Gr is known to affect particle–particle interfaces and, in studies related to rolling, it has been reported to influence dynamic recrystallization, texture evolution, and residual strain accumulation, which collectively govern the final microstructure and properties of the material [33,34]. Although previous studies have demonstrated the feasibility of depositing Cu–Gr composites by CS, they have mainly focused on specific aspects such as deposition feasibility, Gr distribution, or tribological performance. A systematic understanding of how particle interactions govern microstructural evolution and how these features influence the overall performance of CS Cu–Gr composites is still lacking.

The present work provides a systematic investigation of the influence of Gr on particle bonding mechanisms, microstructural evolution (including dynamic recrystallization and dislocation density) and the resulting mechanical, thermal, and electrical properties of CS-deposited Cu–Gr 2DMMCs, toward the definition of structure–property relationships for this composite family. We systematically examined how particle interactions affect microstructural evolution and how the resulting structures correlate with the final mechanical, thermal and electrical properties of the composites, toward the definition of robust structure–properties relationships. The conclusions report the main findings of the research and the open points to be investigated, drawing possible actions to overcome the present limitations of the application of CSAM for Gr reinforced-Cu matrix composites and guiding the optimization of solid-state AM strategies for next-generation 2DMMC materials.

2. Materials and methods

2.1. Powder feedstock preparation and characterization

Spherical Cu powder (99.95 % purity, Safina, CZ) was used as the metal matrix material. Multi-layer Gr was produced in-house via mechanical dry ball milling of industrial-grade graphite flakes (Sigma Aldrich, DE). To determine the optimal Gr content for incorporation into the Cu matrix, various Gr weight percentages were initially blended with Cu powder and subjected to ball milling as reported in previous works [35,36]. At higher Gr contents (3 wt%, 10 wt%, and 20 wt%), the effective TC of the composite powder decreased by approximately 33 % compared to that of pure Cu [35]. This reduction was attributed to the limited contact between Cu particles caused by Gr, which restricts heat conduction through the composite powder [35]. Based on this, Cu 1 wt% Gr composite (hereafter referred to as Cu–Gr) was selected and prepared using low-energy dry ball milling in a planetary ball mill. Milling was performed for 6 h at 150 rpm with a powder-to-ball weight ratio of 1:10, using 300 mL stainless steel 304 jars and 5 mm diameter grinding balls. Furthermore, ball milling was conducted under argon atmosphere to prevent oxidation.

The powder morphology and internal microstructure were characterized using scanning electron microscopy (SEM) and electron backscatter diffraction (EBSD). SEM and back scattered electron (BSE) analyses were conducted using a Zeiss Sigma 500 microscope equipped with an Aztec Energy Advanced energy-dispersive X-ray spectroscopy (EDX) system for elemental analysis and an EBSD detector (C-Nano, Oxford Instruments) for crystallographic investigation. Powder particles were mounted and polished down to 1 μm grit size using diamond suspension, followed by final polishing with colloidal silica for EBSD analyses. Particle size distribution (PSD) was measured using the Malvern Morphology 4 automated imaging system, analysing 20,000 particles (Malvern Analytical, Malvern, UK). The representative bar charts for the PSDs of the pure Cu and the Cu–Gr composite powders are shown in Figs. S1a and S1b, respectively. The Cu–Gr powder displays a broader size distribution and a higher D_{10} , D_{50} , and D_{90} values (21.98 μm , 44.65 μm , 71.38 μm) compared to pure Cu (18.72 μm , 30.33 μm , 51.92 μm),

indicating increased heterogeneity resulting from ball milling.

2.2. Cold spray deposition and post-processing

High-pressure CS deposition was performed using an Impact 5/11 system equipped with a SiC OUT1 nozzle (Impact Innovations GmbH, DE). The process was carried out using a water-cooled converging–diverging De Laval nozzle with an expansion ratio of 5.6 and a total length of 160 mm. Nitrogen was employed as both the propellant and the powder carrier gas. The process parameters were chosen based on our prior study of Cu–Gr deposition behaviour and properties [30]. In this study, pure Cu deposited at 800 °C was used as the reference deposit, based on previously optimized deposition conditions [37–40], while the effect of deposition temperature was systematically investigated for Cu–Gr deposits due to the sensitivity of Gr to impact conditions and thermal exposure during CS deposition. Two gas temperatures of 500 °C (MidT) and 800 °C (HighT) were investigated, with other parameters held constant. Considering pure Cu powder as a reference and Cu–Gr with two process gas temperatures, a total of three conditions were investigated and summarized in Table 1. For all samples, a gun traverse speed of 50 mm/s, stand-off distance of 40 mm, feed rate of 4 rpm and step size of 1.2 mm were used.

Prior to spraying, the KSS (Kinetic Spray Solution) software was used to predict the particle velocity and temperature under the selected spray parameters. These predictions were used to estimate particle impact conditions during the deposition process. Fig. S2a shows the window of deposition calculated using KSS. Since pure Cu and Cu–Gr powders exhibit different PSDs, the plot shows marginally different impact velocities and temperatures for the two powder systems. All three conditions fall well within the deposition window, confirming successful deposition in all cases. Fig. S2b shows the η -value (ratio of particle impact velocity to critical velocity) as a function of gas temperature and particle diameter, calculated by KSS simulations. The η -value directly reflects the extent of plastic deformation upon impact and, consequently, the quality of inter-particle bonding. An η -value below 1 indicates that deposition is unlikely to occur, whereas higher η -values generally correspond to stronger inter-particle cohesion. However, excessively high η -values can be detrimental, as the elastic strain energy generated upon impact may exceed the bonding energy when η is greater than approximately 2, leading to erosion rather than deposition [41].

Al alloy substrates (110 × 50 mm²) were coated to at least 10 mm thick deposits for tensile test coupon and TC sample extraction as shown in Fig. S3. To achieve this thickness, all deposits were fabricated using six spray layers under identical processing conditions.

The deposits were separated from the substrates and sectioned using a Cut AM 500 electrical discharge machining (EDM) (GF machining solutions, CH). Each deposit was cut into disks with approximate dimensions of 50 × 50 × 1 mm³ for TC testing, in dog-bone geometries for mechanical tests and in cubes of 10 × 10 × 10 mm³ for density measurements, microstructural and electrical characterization.

Samples from each series were subjected to an annealing treatment to relieve residual stress and promote microstructural homogenization. Annealing was performed in a cylindrical Nabertherm furnace at 500 °C for 1 h under vacuum condition (5 × 10^{−2} bar). The annealing condition

was selected based on previous studies on CS deposited Cu, which have shown that this temperature is sufficient to promote recovery and recrystallization [38,40,42]. In particular, the work of Li et al. [40] demonstrated that annealing at approximately 400 °C to 500 °C effectively reduces the high dislocation density introduced during CS. The samples were placed in graphite crucibles, and the cooling rate was controlled at approximately 10 °C/min. Initially, the influence of Gr on the microstructural evolution was assessed by comparing a Cu–Gr deposit with a pure Cu deposit processed under identical spraying parameters (HighT). Subsequently, the effect of gas temperature on the composite's microstructural, mechanical and physical properties was examined by comparing Cu–Gr 800 and Cu–Gr 500 series. Moreover, a high-speed wipe test was performed on Al substrates to qualitatively assess single-particle deformation and Gr behaviour during CS for both process parameters.

2.3. CS deposits characterization

2.3.1. Microstructural analysis

The cross-sections of all as-sprayed (AS) and annealed deposits for microstructural analysis were prepared using the same grinding and polishing procedure as described for the powder feedstock for SEM and EBSD analyses. Bulk density was measured using ASTM B962 standard (Archimedes principle) [43] for three 10 × 10 × 10 mm³ cubes per deposit. Samples were weighed in air and distilled water using a Sartorius balance, and the average was calculated for reliability. Raman spectroscopy of both powder feedstock and deposits was carried out using a WITec Alpha 300R system (532 nm laser, 600 g/mm grating), with each spectrum averaged over 50 scans. X-ray diffraction (XRD) measurements were performed using a Rigaku SmartLab XE diffractometer equipped with a Cu anode source ($\lambda = 1.5406 \text{ \AA}$), a solid-state 1D detector, and data acquisition and analysis were carried out with High Score Expert software. The surface roughness was measured using an Alicona InfiniteFocus G6 optical 3D profiler. The arithmetic mean height (S_a) was determined by scanning five randomly selected areas on each sample and averaging the results after applying an L-filter with $\lambda_c = 0.8 \text{ mm}$. Cross-sectional profiles were extracted from 3D profilometry measurements and the area under each profile curve was calculated using numerical integration. Since both pure Cu and Cu–Gr 800 deposits were produced under identical spray parameters, standoff distance, and traverse conditions, the ratio of cross-sectional areas provides a reliable and reproducible relative measure of deposition efficiency (DE). The absolute DE of pure Cu was independently estimated as ~ 93 % using KSS simulation software, consistent with reported values for CS Cu in the literature [38,39].

The cross-sectional sample was prepared by a DualBeam FIB-SEM system (Carl Zeiss Auriga), equipped with platinum (Pt) deposition cartridge and nanomanipulator (Kleindiek Nanotechnik). To minimize the ion beam damage, the sample was protected by a ~ 100 nm platinum first by electron beam deposition (2 kV). After that, a several micrometer thick platinum layer was deposited using the gallium ion beam. After rough milling by 30 kV ion beam, the ~ 2 μm thick plate was lifting out and attached on the edge of a Cu finger, following thinning processes were using a 15 kV ion beam for minimized the ion beam damage and the final lamella was less than 100 nm thick.

Transmission electron microscopy (TEM) and angle annular dark field scanning TEM (ADF-STEM) were performed using uncorrected FEI Titan with Schottky field emission S-FEG source operated at 300 kV. Electron energy-loss spectroscopy (EELS) mapping was carried out with Quantum Gatan Imaging Filter (GIF) detector with energy dispersion of 0.5 eV per channel.

2.3.2. Mechanical tests

Mechanical properties were assessed by tensile and microhardness tests. A tensile testing module from Kammrath & Weiss GmbH (DE) was used with two different sample geometries for in-situ SEM and ex-situ

Table 1
CS deposition process parameters and sample coding.

Sample ID	Gas Temperature (°C)	Gas Pressure (bar)	PSD D ₅₀ (μm)	Powder Morphology
Pure Cu	800	45	30.33	Spherical
Cu–Gr 800	800	45	44.65	Mix (spherical and flaky)
Cu–Gr 500	500	45	44.65	Mix (spherical and flaky)

tests at a constant strain rate of 0.5 $\mu\text{m/s}$ as illustrated in Fig. S3a. It should be noted that strain values were derived from actuator displacement normalized to the initial gauge length. For each case, three ex-situ and one in-situ tensile specimens were extracted parallel to traverse direction by EDM from the same distance relative to the substrate to ensure consistency across all tests, then cleaned ultrasonically in ethanol for 10 min. In-situ specimens were additionally polished to 1 μm surface finish to enable SEM imaging during deformation. The in-situ SEM setup (Fig. S3b) allowed for real-time observation of local deformation and fracture behaviour under mechanical loading inside the SEM chamber. The tensile specimens were machined with the loading direction parallel to the traverse direction of the CS deposits. For the SEM and EBSD characterizations, samples were extracted from the middle region of the deposits and analysed on the plane perpendicular to the tensile loading direction to investigate the microstructural features associated with crack initiation and propagation. Since CS deposits can exhibit anisotropic microstructural features due to the particle impact direction and deposition process, all samples were characterized using the same sampling location and orientation to ensure a consistent comparison between different conditions. Vickers microhardness (HV) measurements were performed using an FM-810 microhardness tester (Future-Tech Corp., JPN) with a 100 g test load and a dwell time of 15 s. Ten indentations were carried out across each sample's cross-section in accordance with ASTM E384, and the average hardness values were reported.

2.3.3. Thermal and electrical conductivity tests

TC was measured using the transient plane source (TPS) method (MP-1, Thermtest Inc, CA). The EDM-ed disks were used to measure the in-plane TC of Cu-Gr composites [44]. A pair of disks was placed with the active TPS sensor in between. The TC was calculated from the sensor's temperature response using the Gustafsson equation, with a

measurement error below 4 % [45].

Electrical conductivity (EC) was measured with a Sigmatest 2.069 eddy-current meter (Foerster, DE) across 60–960 kHz. Conductivity (MS/m) was recorded after calibration, with multiple surface measurements taken for each sample to ensure repeatability.

Thermal conductivity was measured in-plane, whereas electrical conductivity was measured through-plane using a non-contact eddy-current method; as these directions are not directly comparable due to the material's structural anisotropy.

3. Results and discussion

3.1. Powder characterization

Fig. 1a and 1c show representative morphologies of as-received high-purity Cu powder and ball-milled Cu-Gr powder, respectively. The atomized Cu powder exhibits predominantly spherical particles, whereas the ball-milled Cu-Gr powder shows a mixed morphology comprising spherical, semi-spherical, and flake-like particles. Fig. 1b and 1d present the Inverse Pole Figure (IPF) maps of powders' cross-sections. According to EBSD results, grain sizes range from a few micrometres up to $\sim 10 \mu\text{m}$ for both powders, indicating similar size distributions. No internal voids were observed within the particles. Fig. 1e displays the BSE image with an EDX elemental map overlay of a Cu-Gr powder particle. EDX maps evidence the presence of Gr on Cu particle surfaces. More comprehensive details on the particle morphology, the effects of the ball-milling process, and the Raman spectroscopy analysis, including the assessment of structural defects and Gr layer number, have been reported in our previous work [36].

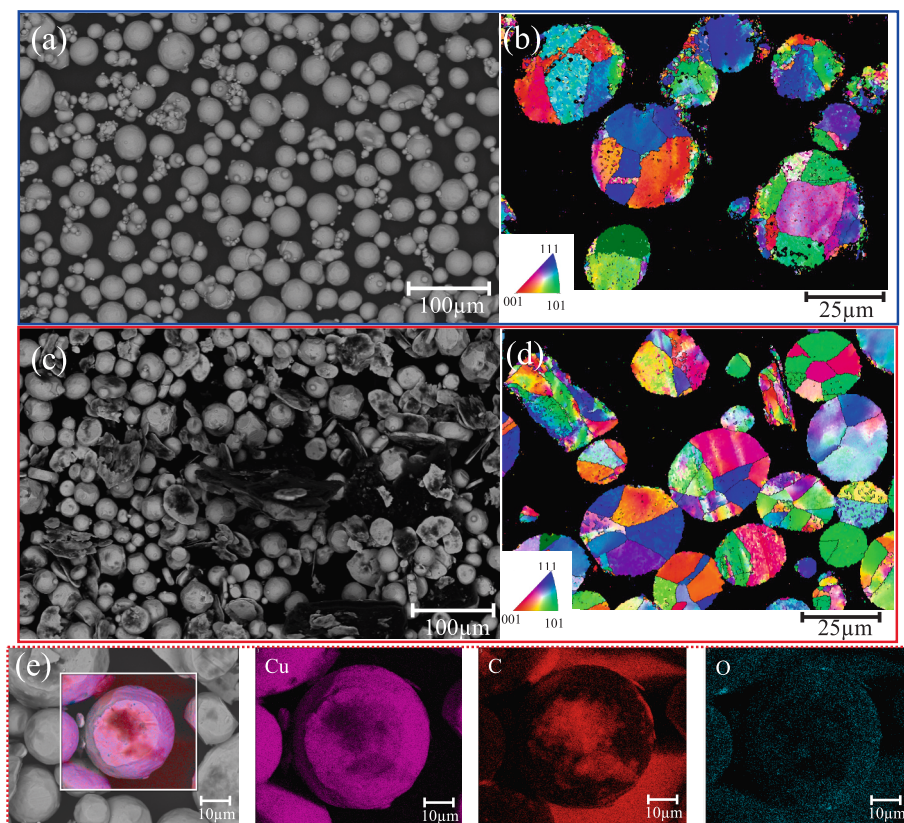


Fig. 1. SEM-BSE micrograph and EBSD orientation IPF X maps of (a-b) pure Cu, (c-d) Cu-Gr powders and (e) EDS image of a magnified Cu-Gr particle with the corresponding EDX elemental maps showing the distribution of Cu, C (representing Gr) and O.

3.2. Assessing Gr presence and deposits quality

This section focuses exclusively on pure Cu and Cu-Gr 800 samples, with the primary objective of evaluating the effect of Gr on the behaviour of the Cu deposits. Fig. 2a-2c illustrate the 3D tomography and cross-sectional profiles of pure Cu and Cu-Gr 800 deposits. Cross-sectional profiles were analysed to determine the deposited cross-sectional area, which was used as a quantitative indicator of relative DE. Since both samples were sprayed under identical process parameters and traverse conditions, the ratio of cross-sectional areas provides a reliable relative measure of DE. The cross-sectional area was 408.45 mm² for pure Cu and 349.24 mm² for Cu-Gr 800, indicating a ~ 14.5 % reduction in DE for the Cu-Gr 800 deposit, attributed to the presence of Gr at particle interfaces reducing the effective metallic contact area and inter-particle bonding during impact. These observations likely result from combined effects of Gr presence and the heterogeneous particle morphology of the ball milled powder feedstock.

These effects were confirmed through experimental analysis of thick deposits and the wipe test, which revealed more regular features for the pure Cu deposit. Fig. 2d and 2e present the top view of the wipe test of pure Cu and Cu-Gr 800, respectively, confirming that the presence of Gr, the varied PSD and inhomogeneous particle morphology in the Cu-Gr 800 feedstock can result in more craters (indicating rebound particles), which contribute to the lower DE.

Surface roughness measurements further supported these findings. The average Sa value for pure Cu was $9.7 \pm 3.2 \mu\text{m}$ and $14.5 \pm 2.6 \mu\text{m}$ for Cu-Gr 800 deposit. This increase in surface roughness indicates a more heterogeneous surface topography, likely associated with the reduced deformability and less uniform packing behaviour of the Cu-Gr feedstock of mixed morphology particles and the presence of Gr at interparticle interfaces, which may hinder particle bonding, reduce

flattening upon impact and thus decrease their packing density. Furthermore, they can cause more particle rebounds and hence create more craters. Cross-sectional SEM images are presented in panels (d1) and (e1) of Fig. 2, showing individual particle cross-sections for pure Cu and Cu-Gr 800, respectively. Pure Cu particle (panel d1) exhibits a flattened lens-shaped splat morphology, characteristic of successful plastic deformation during CS impact and indicative of effective inter-particle bonding. In contrast, Cu-Gr 800 particles (panel e1) display a more irregular morphology, which is primarily attributed to the irregular and flattened morphology of the ball-milled Cu-Gr powder feedstock.

EDX elemental mapping (Fig. 3) and Raman spectroscopy analyses confirmed the presence of Gr in the deposited areas. Fig. 3a shows carbon-rich region (representing Gr) attached to the top part of the flaky particles, after deposition, while Fig. 3b shows carbon-rich region located between particle-particle interfaces, which may indicate redistribution or partial slip of Gr during impact. This interpretation is consistent with the MD simulations, which showed that Gr nanoplatelets covering the Cu particles can undergo local sliding along the impact interface under the high compressive and shear stresses generated during CS deposition [32].

Raman spectroscopy results indicate D ($\sim 1350 \text{ cm}^{-1}$), G ($\sim 1580 \text{ cm}^{-1}$), and 2D ($\sim 2700 \text{ cm}^{-1}$) peaks, confirming the presence of Gr. Table 2 presents average I_D/I_G and I_{2D}/I_G relative values for the Cu-Gr samples sprayed at different temperatures as well as for the initial powder feedstock. The original full Raman spectra for both samples are presented in Fig. S4. In general, the I_D/I_G ratio is associated with the defect density in Gr, while the I_{2D}/I_G ratio provides information on the number of Gr layers [46]. The I_D/I_G ratio of the Cu-Gr powder feedstock (Table 2) indicates that ball milling introduces a degree of structural defects in the Gr platelets prior to deposition, which has been

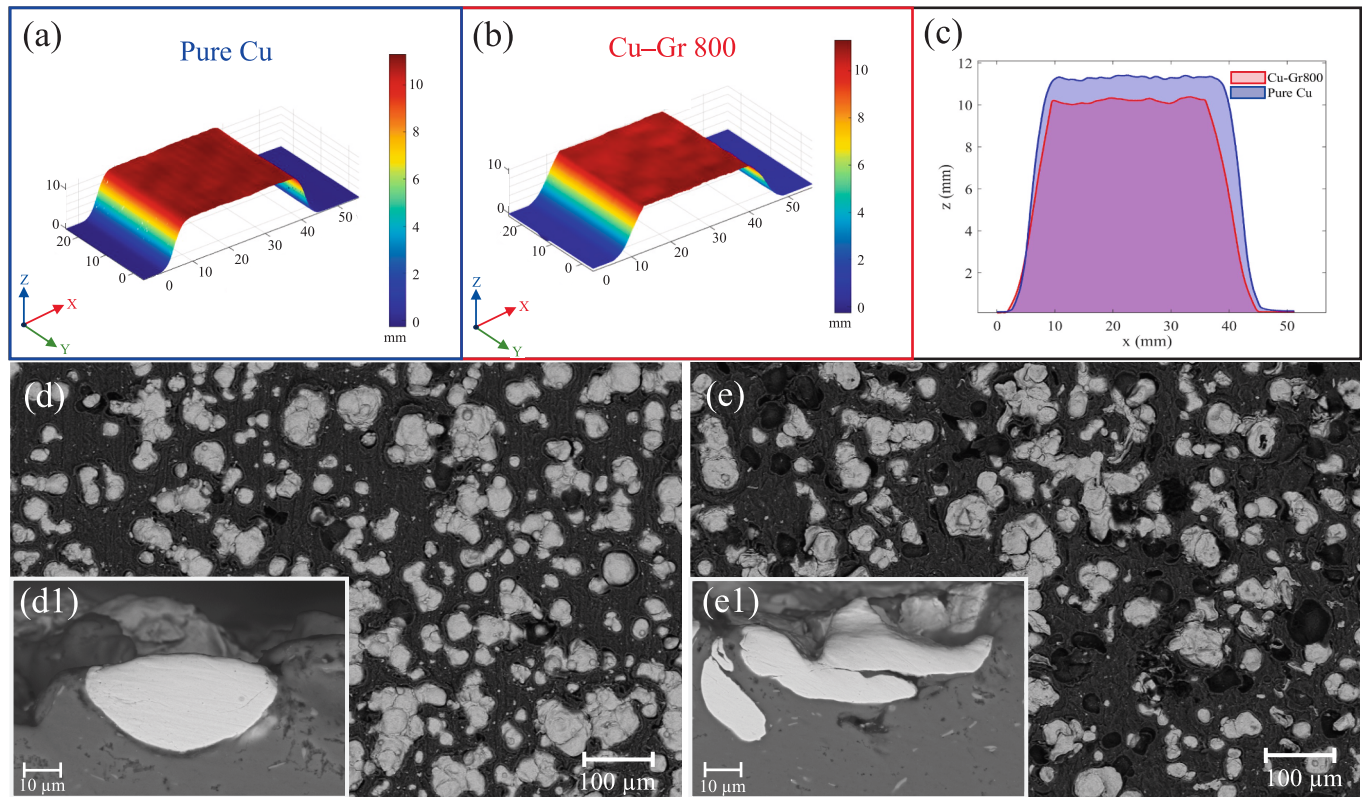


Fig. 2. (a-b) Three-dimensional surface topography maps of pure Cu and Cu-Gr 800 deposits, respectively. (c) Cross-sectional height profiles extracted from deposits with the same number of layers. (d-e) BSE top-view micrographs of wipe tests for pure Cu and Cu-Gr 800, respectively, illustrating deposited particles and impact-induced craters formed during particle-substrate interaction. Insets (d1 and e1) show cross-sectional SEM images of individual particles: (d1) pure Cu and (e1) Cu-Gr 800.

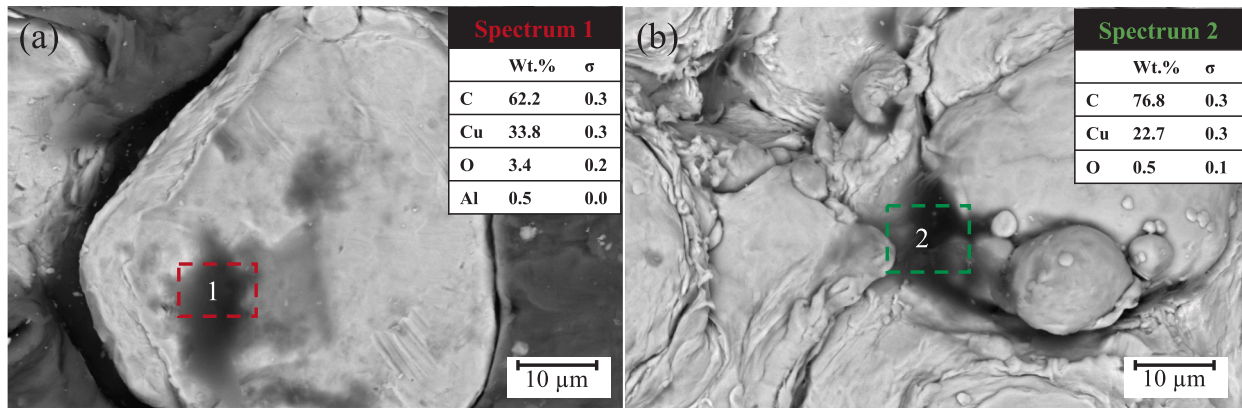


Fig. 3. (a-b) SEM micrographs and the corresponding EDX spectra acquired from selected regions of CS wipe test deposits; in Cu-Gr samples C-rich areas represent Gr.

Table 2

Raman spectroscopy intensity ratios (average I_D/I_G and average I_{2D}/I_G) for the initial Cu-Gr ball-milled powder feedstock and the CS Cu-Gr deposits.

Sample ID	Average I_D/I_G	Average I_{2D}/I_G
Cu-Gr powder	0.66 ± 0.28	0.24 ± 0.05
Cu-Gr 800	1.34 ± 0.03	0.35 ± 0.02
Cu-Gr 500	0.88 ± 0.01	0.31 ± 0.06

investigated and reported in detail in previous works [30,36]. The powder I_D/I_G value serves as the baseline for evaluating the additional defect density introduced during CS impact. Raman analysis detected distinct Gr peaks in both Cu-Gr 500 and Cu-Gr 800 samples, with measurements taken at three random locations spanning from the bottom to the top of the deposits' cross-sections. The comparable average I_{2D}/I_G values observed for both Cu-Gr samples indicate that the higher processing temperature did not significantly affect the number of Gr layers or their stacking state. However, average I_D/I_G ratio for Cu-Gr 800 was noticeably higher than that of Cu-Gr 500, suggesting an increased defect formation in the Gr structure attributed to the elevated gas temperature during deposition, which led to higher particle impact velocity and consequently higher strain rates during impact, thus promoting Gr damage. Because the Cu-Gr interaction is governed mainly by weak van der Waals bonding, the local interfacial shear generated during particle flattening can exceed the adhesion strength of Gr to Cu. This can cause partial slip, delamination, or even complete detachment of Gr flakes located in the most severely deformed regions, as observed also in MD simulation results for CS process [32]. At the same time, Gr that remains trapped at particle-particle interfaces may become folded,

wrinkled, or fragmented, contributing to the increased defect density in Raman spectra after spraying.

To evaluate the phase composition and potential structural changes resulting from mechanical ball milling and CS, XRD analysis was performed on Cu-Gr powder and Cu-Gr 800 deposits, alongside with pure Cu powder and pure Cu deposit as reference. Fig. 4 shows the XRD patterns which revealed only Cu peaks across all samples, indicating that no carbide or oxide phases were formed during ball milling and CS processing. The as-received Cu powder exhibited sharp diffraction peaks, while peak broadening was observed in the milled Cu-Gr powder and in both Cu and Cu-Gr deposits. The diffraction peak at approximately 43.2° corresponds to the Cu (111) reflection and was selected for quantification of full width at half maximum (FWHM) to evaluate peak broadening across all samples. The as-received Cu powder exhibited the lowest FWHM value, whereas an increase in FWHM was observed after ball milling of the Cu-Gr powder. This increase indicates the introduction of lattice strain and reduction in crystallite size induced by the mechanical milling process.

For the deposited samples, a further increase in FWHM was observed compared with the as-received Cu powder. In addition, the Cu-Gr deposit showed a higher FWHM value than the pure Cu deposit, suggesting that the incorporation of Gr contributes to additional lattice distortion and microstructural refinement during deposition.

The broadening in the milled powders is attributed to ball milling, where repeated cold welding and fracturing lead to crystallite refinement, dislocation accumulation, and lattice strain [47]. In contrast, the broadening observed in the deposited samples is associated with the CS process, where high-velocity particle impacts induce severe deformation of Cu matrix, further increasing dislocation density and grain distortion. These results collectively confirm that both ball milling and CS

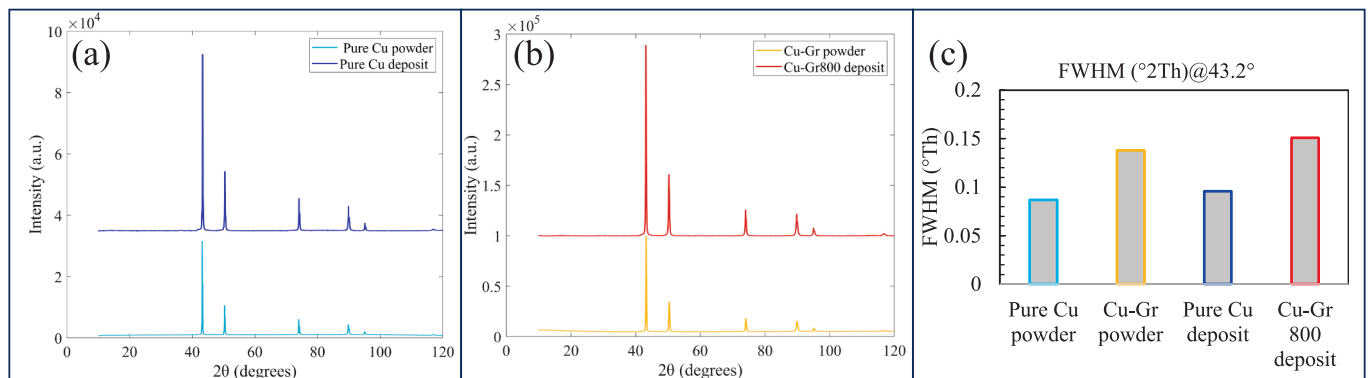


Fig. 4. XRD patterns of (a) pure Cu powder and deposit, (b) ball milled Cu-Gr powder and deposit, and (c) FWHM values at the Cu (111) reflection ($2\theta \approx 43.2^\circ$) for all four samples.

deposition influence the degree of peak broadening, reflecting changes in crystallite size and lattice strain.

The cross-sectional BSE images shown in Fig. 5 reveal that pure Cu and both Cu–Gr deposits exhibit highly compact microstructures. In the Cu–Gr samples, the presence of dark lines may indicate either embedded Gr layers or porosity; however, distinguishing between the two solely based on image analysis is challenging. Therefore, we relied on the Archimedes method for quantitative validation, which indicated slightly lower densities for the Cu–Gr deposits compared to pure Cu. Specifically, the Archimedes measurements yielded densities of 8.903 ± 0.002 g/cm³ for pure Cu and 8.80 ± 0.018 g/cm³ for the Cu–Gr 800 composite. This suggests that the addition of 1 wt% Gr did not introduce significant porosity into the CSAM samples deposited at higher temperature. In contrast, the Cu–Gr 500 deposit exhibited a lower density of 8.688 ± 0.001 g/cm³. This reduction can be attributed to the reduced plastic deformation, which limits particle flattening and interparticle bonding. The Cu–Gr composite powder produced by ball milling exhibits a broader PSD and a more heterogeneous morphology consisting of a mixture of spherical and flake-like particles compared to the spherical pure Cu powder. This morphological heterogeneity influences the CS deposition process. Flake-like particles exhibit greater resistance to deformation upon impact compared to spherical particles, contributing to local porosity and the slightly lower deposit density of Cu–Gr compared to pure Cu [18]. The broader PSD further introduces heterogeneity in local plastic deformation, smaller particles achieve higher η values and deform more effectively, while larger particles deform less, contributing to the more heterogeneous microstructure of Cu–Gr deposits.

To better understand the role of Gr in the CS Cu–Gr composite, TEM was performed on the Cu–Gr 800 deposit. Fig. 6 presents the TEM characterization of an inter-splat boundary containing a Gr-rich interfacial region. The lamella was extracted from the boundary between two adjacent Cu splats.

HRTEM analysis (Fig. 6a and 6b) resolves the Cu–Gr interface, where the upper region exhibits ordered fringes of multilayer 2H-graphite, corresponding to the (0 0 2), (0 1 0) and ($\bar{1}$ 0 0) lattice planes. Meanwhile, the lower region displays Cu (1 1 1) and ($\bar{2}$ 0 0) lattice fringes, confirming the crystallographic identity of both phases. Direct contact between Cu and Gr is observed without any obvious interfacial gaps or reaction layer in the examined region. Fig. 6c and 6d show two adjacent Cu grains separated by a twin boundary, with the corresponding FFT and SAED patterns confirming the FCC (Face centered cubic) crystal structure of both grains. Low-magnification ADF-STEM image coupled with EELS elemental mapping (Fig. 6e) shows carbon localized along the inter-splat boundary, whereas Cu is absent from this region, directly confirming the localization of Gr at the interface. The oxygen map shows no preferential enrichment at the Cu–Gr interface, indicating that no detectable interfacial oxide layer formed during CS deposition. The carbon K-edge EELS spectrum exhibits the characteristic π^* (~ 285 eV) and σ^* (~ 292 eV) transitions of graphitic sp² carbon, indicating that the graphitic structure is largely retained after deposition.

It should be noted that TEM analysis is inherently local and representative of a small volume of the deposit. The thickness of Gr platelets is observed to vary throughout the deposit, consistent with the heterogeneous distribution of multilayer Gr nanoplatelets in the powder feed-stock [36]. While individual layer counting is not possible from the present HRTEM images, the multilayer graphitic nature of the platelets is confirmed by HRTEM. The random and heterogeneous Gr distribution throughout the Cu matrix is further reflected in the scatter of Raman spectroscopy measurements across multiple points, confirming local variations in Gr layer number, orientation, and defect density. The present TEM observations should therefore be interpreted as representative of the local Cu–Gr interfacial structure rather than a global average of the deposit microstructure.

These results collectively confirm: (i) Gr is preserved as 2H-graphite at inter-splat boundaries after CS deposition, retaining its graphitic sp² carbon structure without phase transformation or conversion to amorphous carbon; (ii) intimate mechanical contact is maintained at the Cu–Gr interface without visible gaps or delamination, governed by van der Waals interactions and mechanical interlocking.

3.2.1. As-sprayed Cu and Cu–Gr deposits

Fig. 7 shows the microstructural analysis using EBSD comparing pure Cu, Cu–Gr 800, and Cu–Gr 500 samples. The IPF maps display heterogeneous grain size with varied crystallographic orientations (represented by random colour distributions) for all samples. The presence of numerous dark spots in the IPF maps corresponds to points with low indexing confidence, typically associated with non-well bonded particles (porosity), surface imperfections, strain-induced lattice distortions, or secondary phase regions. In both Cu–Gr deposits, these dark features were more abundant and widely distributed along particle interfaces, likely corresponding to Gr-rich regions. Most of these areas coincide with regions where EDX mapping indicated a higher C concentration (Fig. 7a3–7c3). In addition, some of these dark regions may have resulted from poor Kikuchi pattern quality, which can occur in areas with large local strain gradients generated by the SPD during CS deposition and possibly intensified by the presence of Gr flakes. This is characteristic of materials subjected to SPD during high velocity impact, where extreme strain rates result in extensive dislocation generation. The accumulated dislocations act as a driving force for dynamic recrystallization (DRX), which produces new defect-free grains within the deposit [48,49]. For Cu, the dominant mechanism at regions of higher strain is continuous dynamic recrystallization (CDRX). In these areas, deformation is relatively homogeneous, and dislocation rearrangement along with sub-grain rotation dominates. This process leads to a gradual increase in misorientation, which is characteristic of CDRX. In contrast, at the centre of the particles, where the strain rate is lower, localized strain concentration can occur. This can promote grain boundary bulging and migration, which are features of discontinuous dynamic recrystallization (DDRX). As a result, larger grains can form in the particle interiors [37].

As these recrystallized grains grow, annealing twins are formed, a

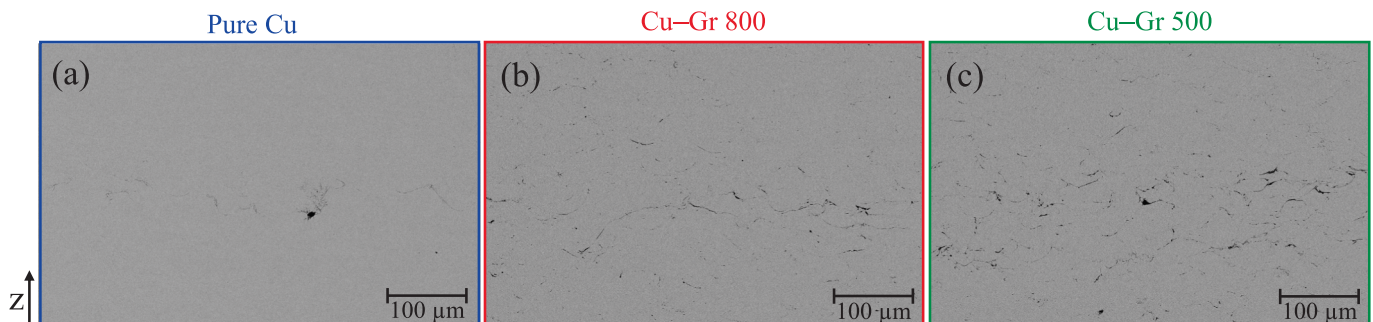
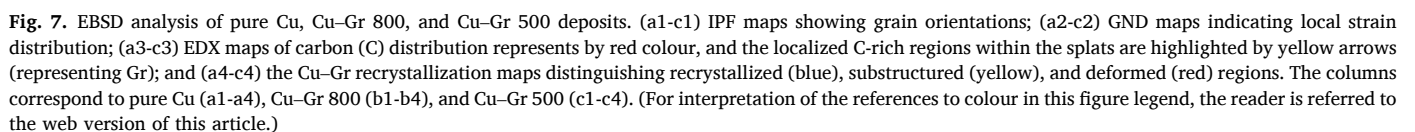
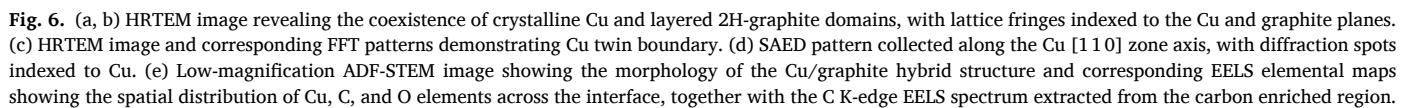


Fig. 5. SEM cross-section images of (a) pure Cu, (b) Cu–Gr 800 and (c) Cu–Gr 500 deposits.



characteristic feature of face-centered cubic metals such as Cu [37]. This confirms that recrystallization occurred despite the presence of Gr. Cu has a high stacking fault energy, and CDRX is favoured. The pure Cu sample exhibited more homogeneous structural features (Fig. 7a1), representing more equiaxed grains with well-defined annealing twins, indicative of recrystallization. In contrast, the Cu–Gr samples displayed relatively finer grains at the particle interfaces and a more heterogeneous microstructure.

The geometrically necessary dislocation (GND) maps (Fig. 7a2–7c2) further illustrate that the Cu–Gr deposits exhibit a markedly higher dislocation density (green and yellow regions) than the pure Cu deposit. This suggests increased lattice curvature and strain accumulation likely associated with constrained plastic flow around Gr particles. The higher dislocation density and heterogeneous distribution in Cu–Gr deposits indicate that Gr may act as an obstacle to dislocation motion, promoting dislocation tangling and storage within the Cu particles. These EBSD observations are consistent with the XRD analysis, which revealed broader diffraction for the Cu–Gr deposit (Fig. 4), confirming the presence of defects and lattice distortions in the Cu matrix.

The recrystallization fraction maps (Fig. 7a4–7c4) distinguish recrystallized (blue), substructured (yellow), and deformed (red) grains. Recrystallized grains exhibit low internal misorientation, indicating that most dislocations have been removed and the grains have achieved a nearly strain-free state, whereas substructured grains show moderate misorientation due to partial dislocation rearrangement, and finally the deformed grains have high internal misorientation reflecting high dislocation density and stored strain.

These EBSD maps reveal a high degree of DRX in the interior and interface of particles in pure Cu (Fig. 7a4), whereas in the Cu–Gr samples (Fig. 7b4 and 7c4), most grains were deformed with high internal misorientation. In Cu–Gr samples, recrystallization was predominantly observed in regions adjacent to the particle interfaces rich in Gr (Fig. 7b3 and 7c3), whereas the interiors of the particles largely retained their deformed microstructure with little evidence of recrystallization. This suggests that the addition of Gr locally influenced both DDRX and CDRX by modifying strain and heat distribution during impact. Gr is mostly located at the particle–particle interfaces; however, it influences not only the interfacial phenomena but also the microstructural evolution within the particle cores. The stiff Gr at the interface redistributes the impact strain, reducing the effective strain transmitted to the core. At the same time, the core experiences a lower local temperature due to the redistribution of heat by Gr at the interfaces. This behaviour can be attributed to the thermal heterogeneity generated by Gr, which exhibits a significantly higher thermal conductivity than Cu, introducing significant thermal gradients and local variations in heat dissipation at the Cu–Gr interfaces. While direct thermal modelling of Gr-containing CS particles remains an open direction for future simulation work, this interpretation is physically consistent with the well-established understanding that in CS, local temperature rise is a direct and coupled consequence of adiabatic plastic deformation. MD simulations of Cu–Gr particles in CS [31] demonstrate that Gr distribution significantly affects the plastic deformation state of the composite particle during impact. Since plastic deformation governs both local strain accumulation and adiabatic heat generation during CS deposition, a modified deformation state induced by Gr is expected to alter local strain and thermal distributions, consistent with the EBSD results obtained for the Cu–Gr deposits. Moreover, in the Cu–Gr deposits, the composite consists of Gr and Cu matrix, which have significantly different coefficients of thermal expansion (CTE). This CTE mismatch could further contribute to local thermal stresses and strain accumulation and microstructural changes during deposition. These effects are more pronounced in Cu–Gr 500, where the lower impact velocity (as shown in Fig. S2) and reduced temperature input result in a lower fraction of fully recrystallized grains compared with the Cu–Gr 800 composite, leading to a more heterogeneous microstructure. All the quantitative values extracted from the recrystallization fraction maps and GND density maps for all samples are

summarized in Fig. S5.

3.2.2. Effect of post deposition annealing

While the annealing response of pure Cu CS deposits has been extensively reported in the literature [42,50,51], the influence of embedded Gr on recovery, recrystallization, and microstructural evolution remains less understood. Here, we examine the effects of annealing at 500 °C for 1 h on Cu–Gr samples, emphasizing the role of Gr in grain growth, dislocation recovery, and boundary pinning.

The Raman spectroscopy and EBSD results of the annealed Cu–Gr samples are presented in Fig. 8a and 8b. For both Cu–Gr 800 and Cu–Gr 500, the characteristic D, G and 2D peaks confirm the presence of Gr after annealing. In addition, the average intensity ratio of the D to G peaks (I_D/I_G) is lower than in the as-sprayed condition, indicating a reduction in Gr defect density. This decrease can be attributed to the thermal activation of defect healing and relaxation mechanisms during annealing at 500 °C. Specifically, vacancies, edge defects, and local strain induced by the high-velocity CS impact can partially recombine or relax at elevated temperatures, resulting in a more ordered Gr lattice. As reported by Alyobi et al. [52], moderate thermal treatment can reduce defects in Gr. Notably, the decrease in average I_D/I_G indicates that the Gr flakes preserve their structural integrity and thermal stability during the 1 h annealing process, while also playing a significant role in the microstructural evolution of the Cu–Gr composite. Additionally, comparable average I_{2D}/I_G results for the as-sprayed and annealed samples suggest that no major change in Gr stacking state occurred during the annealing process.

Annealing induced partial recovery and recrystallization of the Cu matrix in both Cu–Gr 500 and Cu–Gr 800 samples. EBSD analysis (Fig. 8c–8c1 and 8d–8d1) revealed a reduction in local misorientation compared with as-sprayed condition (Fig. 7), indicating that stored dislocations partially rearranged and annihilated, while new high-angle boundaries formed in regions of high initial strain. Since the CS deposits already contain a high density of dislocations and exhibit a highly heterogeneous microstructure as a result of SPD and the presence of Gr, subsequent annealing can promote discontinuous static recrystallization (DSRX) in the Cu–Gr samples [53]. During this process, new strain-free grains nucleate preferentially in regions of high dislocation density and grow into the surrounding deformed Cu matrix, while the presence of Gr at particle interfaces influences grain boundary mobility and acts as a pinning agent [53]. Moreover, the grain size distribution of Cu–Gr 500 was comparable to that of Cu–Gr 800. The higher GND density in as-sprayed Cu–Gr 500 (explained in section 3.2.1) provides a larger driving force for recovery and recrystallization. During annealing, Gr no longer inhibits recrystallization nucleation within the Cu splats. Recovery and static recrystallization proceed in the splat interiors, reducing the GND density and raising the fully recrystallized fraction from 16.1 % to 59.1 % (Cu–Gr 800) and from 15.6 % to 74.3 % (Cu–Gr 500), with a corresponding decrease in the deformed fraction from 75.4 % to 7.4 % and from 77.8 % to 1.8 %, respectively. However, the mean grain diameter remains essentially unchanged (2.19 ± 1.13 to 2.29 ± 1.11 μm and 2.07 ± 1.03 to 2.33 ± 1.21 μm , Fig. S5e,f), indicating that the transformation is recovery-dominated and that grain growth is confined within the original particles by Gr-decorated inter-splat boundaries acting as Zener pinning sites [54]. As a result, the grain sizes of the Cu–Gr samples remain comparable to those in the as-sprayed condition, as shown in Fig. S5. This contrast highlights the different mechanisms governing microstructure refinement in CS deposition observed in as-sprayed samples (dynamic, time-limited) versus annealed (static, thermally relaxed) Cu–Gr composites.

3.3. Mechanical properties

Microhardness measurements revealed the highest hardness (112.83 ± 9.93 HV) for the Cu–Gr 500 sample and the lowest for pure Cu (80.18 ± 4.21). The enhanced hardness of the deposits originates from the

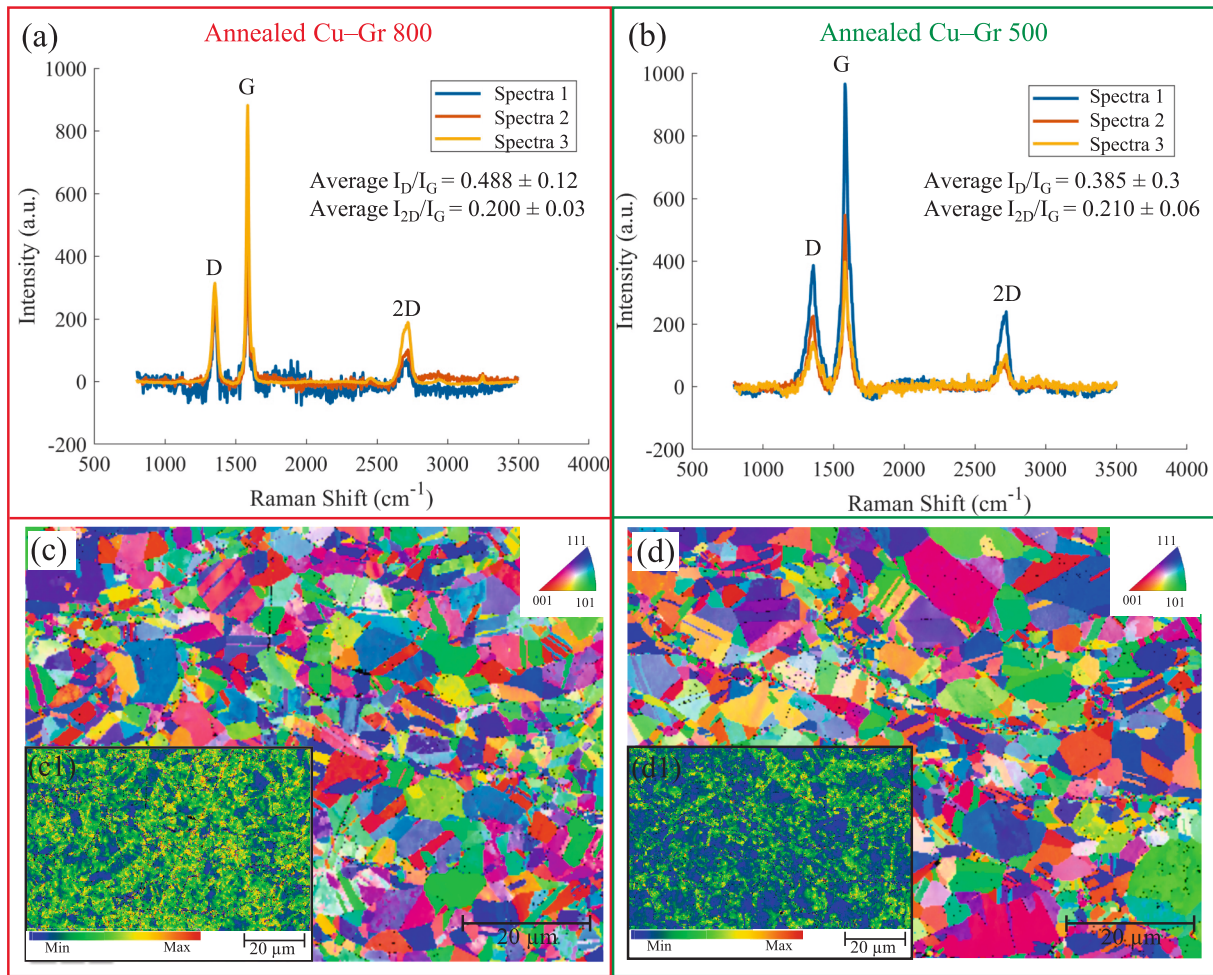


Fig. 8. Raman spectroscopy results of the annealed (a) Cu-Gr 800 and (b) Cu-Gr 500 deposits, showing the characteristic D, G, and 2D peaks of Gr and calculated average intensity ratios of I_D/I_G and I_{2D}/I_G , IPF maps of annealed (c) Cu-Gr 800 and (d) Cu-Gr 500 deposits, GND maps of annealed (c1) Cu-Gr 800 and (d1) Cu-Gr 500 deposits.

deformation of the particles upon impact, which promotes extensive dislocation generation and significant grain refinement [55]. In general, due to Cu's low-to-medium stacking fault energy, thermal softening through recrystallization becomes dominant at high temperatures, resulting in a reduction in hardness [37]. The enhanced hardness of the composite deposits compared to pure Cu one, can be ascribed to the presence of Gr, which not only promotes dislocation resistance but also contributes through its intrinsically high strength. For all samples, the microhardness data, as reported in Table 3, exhibited a trend consistent

Table 3
Microhardness (HV 0.1), UTS, and strain to failure of as-sprayed Cu and Cu-Gr samples.

Sample ID	Microhardness (HV 0.1)	UTS (MPa)	Strain to failure (%)
AS pure Cu	80.18 ± 4.21	174.01 ± 20.46	1.19 ± 0.26
AS Cu-Gr 800	86.91 ± 2.90	121.96 ± 2.24	0.75 ± 0.04
AS Cu-Gr 500	112.83 ± 9.93	125.15 ± 11.71	0.34 ± 0.07
Annealed pure Cu	65.22 ± 3.87	191.62 ± 0.75	14.02 ± 3.25
Annealed Cu-Gr 800	65.55 ± 1.26	98.15 ± 3.92	0.77 ± 0.08
Annealed Cu-Gr 500	67.3 ± 1.45	55.7 ± 4.15	0.27 ± 0.01

with the dislocation densities observed in the EBSD analysis, indicating dislocation hardening as the dominant hardening mechanism.

Tensile stress-strain data shown in Fig. 9a demonstrate a clear dependence of mechanical behaviour on both the process temperature and the addition of Gr. The results in terms of ultimate tensile strength (UTS) and strain to failure are reported in Table 3.

Pure Cu samples exhibited the highest tensile strength and ductility, whereas the Cu-Gr 500 series exhibited the lowest strain to failure value. The presence of Gr at the interfaces between Cu particles could have hindered metallurgical bonding; therefore, an improvement in ductility was not achieved. Cu-Gr 800 sample demonstrated higher strain to failure, indicating that the elevated process temperature enhanced the metallurgical bonding. Strengthening in the composites is generally attributed to grain refinement, dislocation strengthening, and load transfer to the Gr phase [56,57]. Both Cu-Gr samples exhibited increased GND density, indicating enhanced dislocation storage. However, despite the higher GND density, the composite deposits exhibited lower tensile strength than pure Cu samples, suggesting that the negative impact of Gr outweighed its dislocation strengthening benefits. The dominant strengthening mechanisms in CS composites include DRX-induced grain refinement and load transfer strengthening arising from the interaction between the matrix and the reinforcement; thus, the interfacial bonding between Gr and metal matrix becomes very crucial. In the composite deposits, the presence of Gr at particle interfaces impeded Cu-Cu bonding, reducing interfacial contact and limiting load transfer. These weak interfaces acted as stress concentrators, facilitating

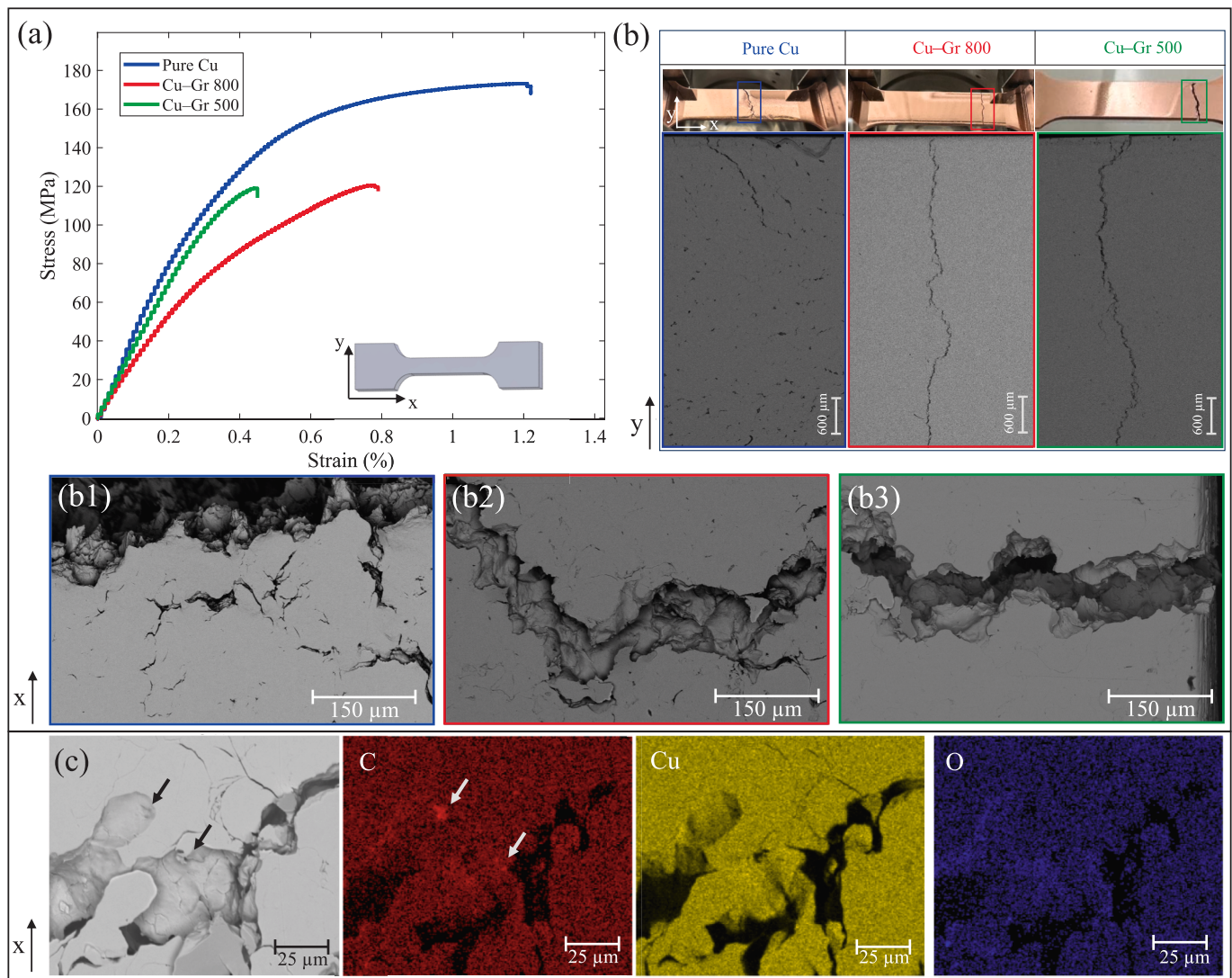


Fig. 9. (a) Representative tensile stress–strain curves of as-sprayed pure Cu, Cu–Gr 800, and Cu–Gr 500 samples (inset: schematic of the tensile specimen). (b) Optical images of fractured samples and the corresponding regions analysed by in-situ SEM during tensile testing. (b1–b3) In-situ SEM lateral view images of Cu, Cu–Gr 800, and Cu–Gr 500 samples showing differences in fracture paths. (c) BSE image and EDX maps of the lateral view of fracture path in the Cu–Gr 500 sample showing particle separation and elemental distribution of C (Gr), Cu, and O, highlighting the presence of Gr at particle interfaces.

early crack initiation and premature failure, and diminishing the strengthening potential of Gr. A comparable behaviour has been observed in composites consolidated by spark plasma sintering and vacuum infiltration under through-plane tensile testing [56].

In-situ SEM observations during tensile testing (Fig. 9) also confirmed distinct failure characteristics between pure Cu and Cu–Gr samples. Both Cu–Gr samples exhibited relatively fast and straight crack propagation, whereas the pure Cu samples showed more tortuous fracture surfaces with evident secondary microcracks connections as shown in Fig. 9b and 9b1–9b3. The presence of Gr at the particle interfaces contributed to low strain to failure due to localized strain accumulation and weak bonding regions, especially in the Cu–Gr 500 sample, where lower deposition temperature limited plastic flow and diffusion leading to slightly higher porosity. In contrast, the Cu–Gr 800 sample exhibited better inter-particle bonding and higher density, consistent with its higher ductility observed in the stress–strain results. Fig. 9c demonstrates how the presence of Gr at particle interfaces plays a pivotal role in determining the fracture path within the Cu–Gr 500 sample. In-situ EDX mapping revealed that Gr acts as a stress concentrator, which directs crack propagation along the Gr-rich regions.

The fracture surface morphologies of all the samples were closely

related to the morphology of the initial particles (Fig. 10). The spherical Cu particles in the pure Cu deposit promoted extensive plastic deformation, resulting in a more ductile behaviour confirmed with the presence of dimples on the fracture surface. Conversely, the irregular and flaky morphology of the Cu–Gr feedstock resulted in brittle fracture in composite deposits, leading to the formation of layered, torn features on the fracture surface.

The as-sprayed pure Cu deposit exhibited a mixed ductile–brittle fracture morphology characterized by equiaxed dimples and particle separation, suggesting effective particle deformation and stronger interparticle bonding compared to the Cu–Gr samples. Cu–Gr fracture surfaces, on the other hand, showed pronounced layered tearing and interlamellar delamination characteristics of the brittle fracture; the high-magnification SEM view (Fig. 10d) and EDX result confirmed C enrichment at the interfaces (Spectrum 1), identifying Gr-rich zones, which promoted interfacial decohesion, producing a brittle fracture mode.

Tensile test data after annealing are also reported in Table 3. After annealing, pure Cu samples showed a clear improvement in mechanical performance, exhibiting enhanced ductility and a more uniform plastic deformation behaviour (Fig. 11a). This improvement can be attributed

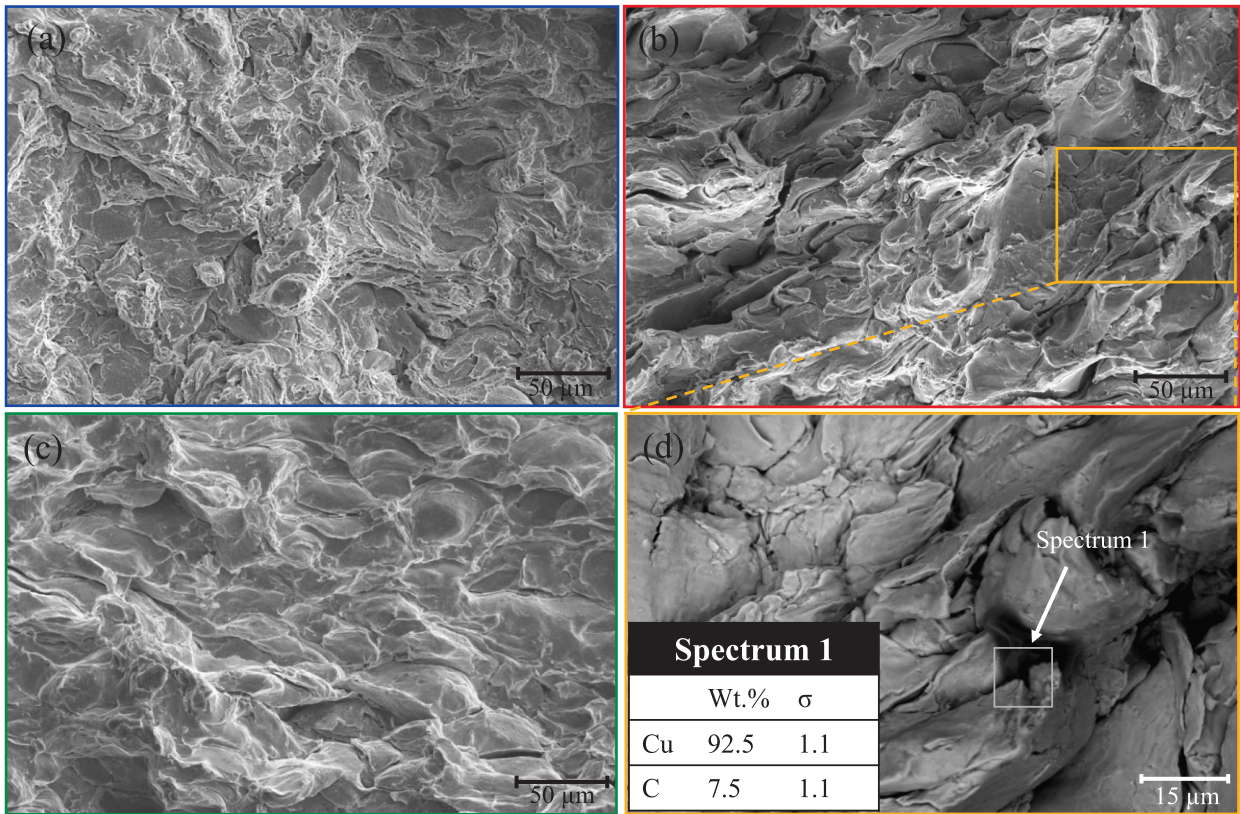


Fig. 10. SEM-BSE and EDX images show fracture surface morphologies of as-sprayed (a) pure Cu, (b) Cu-Gr 800, and (c) Cu-Gr 500 deposit, a magnified view of a selected area (d), with a corresponding localized elemental composition analysis (inset).

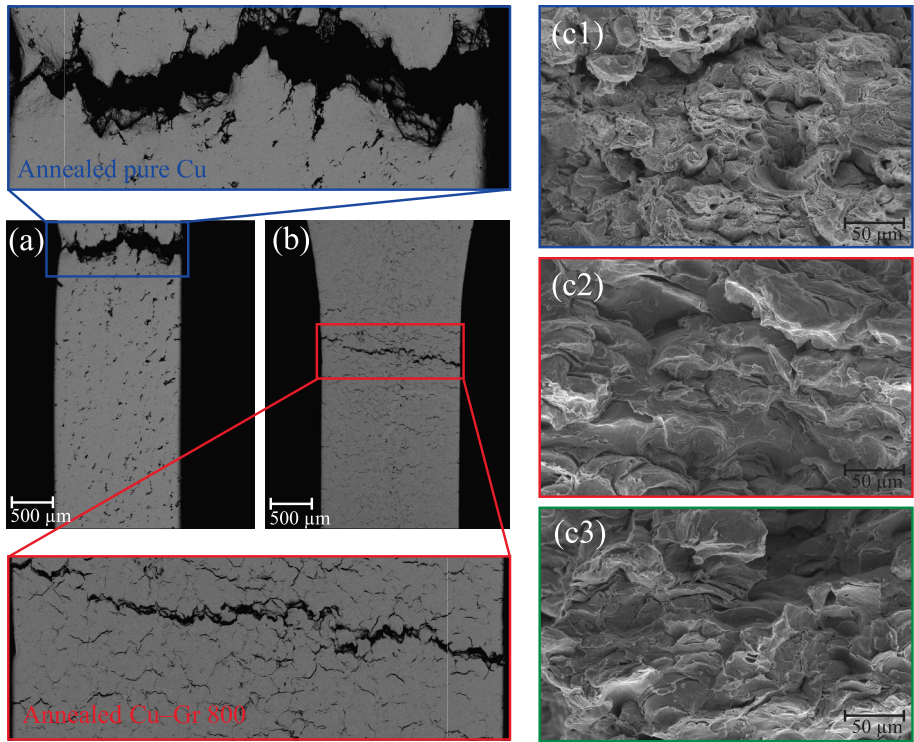


Fig. 11. In situ SEM images showing the lateral view of the crack path on annealed: (a) pure Cu and (b) Cu-Gr 800 tensile samples with the corresponding higher magnification. SEM images of the fracture surfaces: (c1) Cu, (c2) Cu-Gr 800, and (c3) Cu-Gr 500.

to enhanced interparticle diffusion bonding, which strengthens Cu-Cu interfaces and allows more efficient load transfer across the deposit. In

contrast, the Cu-Gr samples showed a reduction in tensile strength after annealing while maintaining strain-to-failure values comparable to

those of their corresponding as-sprayed samples. This behaviour is likely due to recovery and recrystallization in the Cu matrix during heat treatment that leads to reduced strength as shown in Fig. 8. While annealing promotes interparticle diffusion bonding in pure Cu, the presence of Gr at particle interfaces in Cu–Gr composites keep acting as a diffusion barrier, limiting metallurgical bonding. As a result, interfacial debonding remains the dominant failure mechanism, leading to reduced tensile strength and no significant ductility improvement after heat treatment. The reduction in tensile strength is more pronounced in the Cu–Gr 500 sample than in the Cu–Gr 800 deposit. This behavior can be attributed to the initially lower deposit density of Cu–Gr 500, which results in a reduced number of effective metallic interparticle contact points and a higher sensitivity to interfacial effects. In contrast, Cu–Gr 800 retains a more continuous metallic network that better preserves mechanical integrity after heat treatment. SEM observations of the fracture surfaces reveal a fully brittle fracture behaviour for the Cu–Gr samples (Fig. 11c2 and 11c3), whereas the pure Cu sample (Fig. 11c1) exhibited a ductile fracture mode characterized by well-defined dimples, which was further confirmed by the extensive plastic deformation observed during in-situ SEM observations (Fig. 11a), whereas the Cu–Gr samples exhibited a rapid and straight fracture dominated by particle–particle separation (Fig. 11b).

In addition, other microstructural factors may contribute to the reduced tensile performance, including residual porosity, imperfect Cu–Gr interfacial bonding, and stress concentration around Gr-rich regions, which can occur due to the large mismatch in CTE between Cu and Gr. This may have led to the development of residual stresses during thermal treatment, potentially weakening the Cu–Gr interface and negatively affecting the overall deposit strength. These effects can limit efficient load transfer from the Cu matrix to Gr and promote premature failure. Therefore, although Gr provides local strengthening effects that increase hardness, its influence on tensile properties depends critically on its dispersion, interfacial bonding, and the overall integrity of the CS microstructure.

3.4. Thermal and electrical conductivity results

The TC and EC data of the deposits are presented in Fig. 12. TC of Cu–Gr 800 (319 ± 3.2 W/mK) closely matches that of pure Cu (323.9 ± 7.3 W/mK), while that of Cu–Gr 500 is much lower (243.1 ± 8.5 W/mK), indicating the role of higher deposition temperature in enhancing bonding and reduced interfacial resistance, despite the slightly higher defect in Gr (See Table 2). Since other parameters, such as grain boundaries and additional phonon-scattering sources, are similar

between the two Cu–Gr composite deposits, interfacial quality, porosity and dislocation density are considered to be the dominant factors governing the observed differences in TC. However, despite the incorporation of highly conductive Gr, the TC of the Cu–Gr 800 still did not exceed that of pure Cu, indicating that interfacial scattering and microstructural defects continue to limit heat transport within the composite deposits.

Increasing the TC of Cu–Gr composites has also been reported as challenging in the literature for different consolidation techniques. Previous studies identified two critical factors for enhancing TC in Cu–Gr composites: (i) strong interfacial bonding between Cu and Gr, which facilitates efficient phonon transfer, and (ii) preferential alignment of Gr flakes along the heat flow direction, which enables the exploitation of Gr's intrinsically high in-plane TC [58,59]. Lee et al. [6] reported a significant decrease in in-plane TC even with a 20° misalignment of 2D phase, and this anisotropic behaviour was reported to become more pronounced when more than 0.5 wt% of Gr was added. Ke Chu et al. [60] demonstrated that high TC in Cu–Gr composites can be achieved by using a high Gr content (30 vol%) and aligning these Gr layers through a complex processing route involving vortex mixing, vacuum infiltration, and subsequent consolidation via spark plasma sintering. In contrast, random Gr distribution resulted in a significantly lower TC (264 W/m·K). Similar trends have been reported in other studies [61,62]. Achieving Gr alignment in CS composites is particularly challenging due to the random particle trajectories during high velocity impact and deposition.

In addition, the EC of both Cu–Gr deposits were lower than that of pure Cu. As shown in Fig. 12, the EC was measured to be 56.22 MS/m for Cu, while Cu–Gr 800 and Cu–Gr 500 exhibited 43.40 and 37.18 MS/m, respectively. Although a direct comparison between TC and EC is not entirely fair, since TC was measured in-plane, whereas EC was measured through-plane, the distinct thermal and electrical transport behaviours in Cu–Gr composites can be attributed to the different sensitivities of phonons and electrons in relation to microstructural features. Furthermore, in Gr, heat is predominantly carried by phonons, whereas EC is mainly governed by electrons [9]. In TC, the situation becomes more complex due to phonon-electron coupling especially in the presence of strains introduced during fabrication processes [63], such as ball milling and CS deposition.

We hypothesize that in the Cu–Gr composites, phonon-dominated heat transfer remains relatively efficient because Gr provides additional high-conductivity pathways, and phonons can cross the Cu–Gr interfaces when the interfacial bonding is sufficiently strong like in the case of Cu–Gr 800. Although defects, grain boundaries, and agglomeration of Gr flakes introduce phonon scattering, the overall reduction in

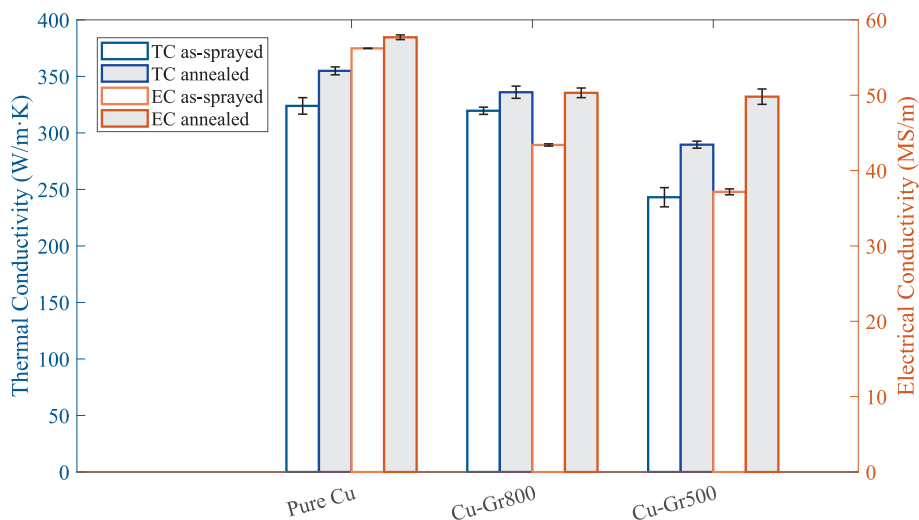


Fig. 12. Dual-axis bar chart showing TC (W/m·K, left axis) and EC (MS/m, right axis) for as-sprayed and annealed series of pure Cu, Cu–Gr 800 and Cu–Gr 500.

thermal transport is modest for Cu–Gr 800, allowing the composite to retain a TC comparable to that of pure Cu. In contrast, EC is strongly affected by microstructural disruptions, where electrons experience significant scattering at Cu–Gr interfaces, voids, dislocations, and poorly bonded regions.

After annealing, both TC and EC of the pure Cu and Cu–Gr composites increased compared to the as-sprayed condition, as shown in Fig. 12. The results indicate that annealing effectively reduced lattice defects and dislocation density, improving phonon and electron transport within the Cu matrix. In the Gr-reinforced samples, particularly Cu–Gr 500, this behaviour may be associated with the microstructural recovery of the Cu matrix and improved interparticle bonding due to heat treatment, which reduces the defect density and electron scattering. In addition, annealing may improve the interfacial contact between Gr flakes and the Cu matrix, contributing to enhanced transport properties. As a result, the synergistic effect of defect reduction and improved Cu–Gr interactions yield the high TC and EC gains in the pure Cu and Cu–Gr deposits.

To contextualize the TC and EC values obtained in this study, we compared our results with those reported for Cu–Gr composites produced by other AM techniques, such as L-PBF, although comparable data are extremely limited. To date, only one recent study has comprehensively investigated TC of Cu–Gr composites fabricated using AM (specifically L-PBF) [64], which limits direct comparisons but underscores the significance of our findings. Zhang et al. [64], showed that the highest TC was achieved with 0.075 wt% Gr nanosheets in L-PBF samples, while increasing the Gr content to 0.1 wt% caused a significant reduction in thermal conductivity. It should also be noted that their study was conducted using Cu alloys (CuCrZr) rather than pure Cu, and processing Cu via L-PBF presents inherent challenges due to its high reflectivity and high TC.

To compare our EC results with the work of Zhang et al., we convert our measured MS/m values to IACS (international annealed Cu standard) using the standard reference (100 % IACS $\approx$ 58 MS/m). Accordingly, our Cu–Gr 800 and Cu–Gr 500 samples exhibit an EC of approximately 74.82 IACS and 63.8 IACS for as-sprayed and 86.8 % IACS and 85.9 % IACS for annealed, respectively. In contrast, the L-PBF study reports 32.5 % IACS for the as-built sample and 73 % IACS after annealing for a Cu–Gr alloy with 0.075 wt% Gr nanosheets. Similar to EC, TC data shown in Fig. 13 clearly exhibit higher values for the CSAM samples than for L-PBF, in both as-built and annealed conditions. This highlights the effectiveness of CSAM in producing Cu–Gr composites with superior electrical and thermal performance compared to the

existing beam-based AM methods.

Conclusions

In this study, Cu 1 wt% Gr composite deposits were successfully fabricated via cold spray additive manufacturing to investigate the influence of Gr on microstructural features and functional properties of the manufactured 2DMMCs. The effects of Gr incorporation were evaluated by comparing Cu–Gr and pure Cu deposits under identical deposition conditions, while the influence of gas temperature was assessed by comparing the Cu–Gr deposits produced at 500 °C and 800 °C. The evolution of the microstructure was examined in both as-sprayed and annealed conditions, and the resulting mechanical, thermal, and electrical properties were evaluated to establish clear structure–property–process relationships. Key findings are summarized as follows:

1. Ball milled Cu–Gr powder feedstock was successfully deposited by using CSAM with relatively high density and good quality. While the presence of Gr did not significantly reduce the relative density at 800 °C, it slightly reduced the DE and increased the surface roughness. In contrast, lower gas temperature (Cu–Gr 500) led to lower density, higher microstructural heterogeneity, and elevated GND density, despite leading to fewer Gr defects according to Raman spectroscopy. These factors collectively resulted in reduced mechanical, thermal, and electrical performance compared to Cu–Gr 800, highlighting that lower gas temperature compromises deposits consolidation, influences matrix microstructural features, and leads to lower overall performance.
2. In terms of microstructural evolution during the high-strain-rate particle impacts, Gr locally altered strain and heat distribution, promoting heterogeneous microstructures compared to the pure Cu deposits. The presence of Gr also enhanced the particle-level hardening mechanisms and influenced grain refinement by altering DRX, highlighting its dual role as reinforcement and microstructural modifier.
3. Cu–Gr 800 achieved the best overall performance, with thermal conductivity values comparable to pure Cu and increased micro-hardness. Both Cu–Gr samples showed lower ductility and tensile strength due to Gr acting as stress concentration points. Electrical conductivity was slightly reduced across all Cu–Gr deposits due to random Gr distribution, interparticle bonding limitations, and microstructural defects. These results emphasize that optimized

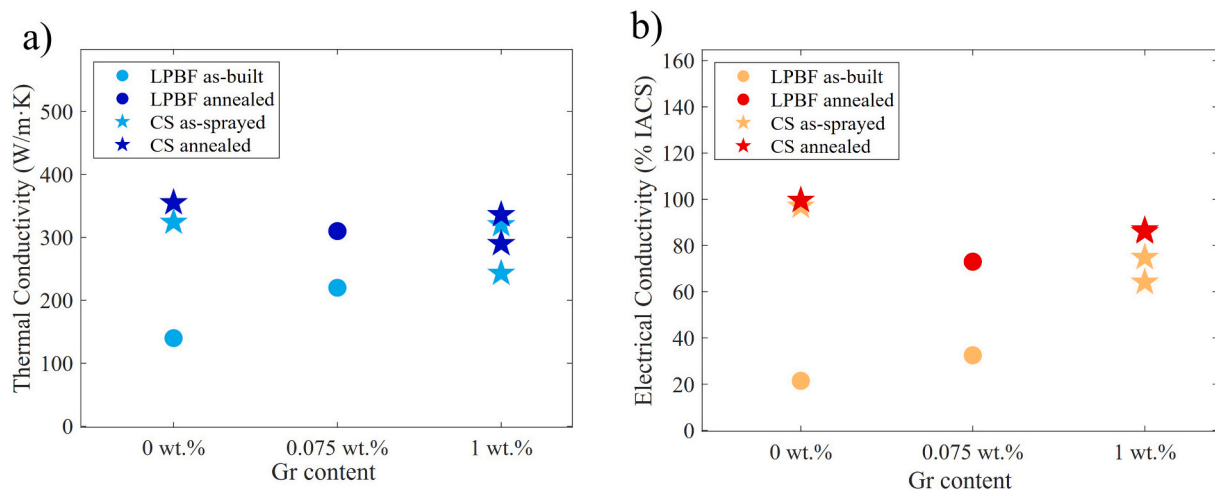


Fig. 13. Comparison of TC and EC of Cu and Cu–Gr composites. (a) Scatter plot of TC for as-built and annealed L-PBF samples (indicated by circles) [64] and CSAM samples (indicated by stars). (b) Scatter plot of EC for the same samples. Different colours indicate as-built (light colours) and annealed (dark colours) conditions. Multiple points for 1 wt% Gr correspond to different CSAM samples (Cu–Gr 800 and Cu–Gr 500).

powder preparation, CSAM parameters selections, and Gr incorporation are essential for balancing the strength and conductivity.

4. Post-deposition annealing was found to partially recover microstructural defects, reduce GND, and promote recrystallization, thus improving thermal and electrical properties. Mechanical properties, however, remain limited due to the Gr-induced stress concentrations.
5. A comparison with the available literature on other AM techniques for Cu–Gr composites suggests that CSAM deposits exhibit improved electrical and thermal properties. These findings highlight CSAM as a promising, low-temperature and scalable processing route for fabricating Cu–Gr 2DMMCs, providing a foundation for future optimization and functional applications.

Several challenges remain to be addressed to fully unlock the potential of CSAM for scalable manufacturing of Cu–Gr 2DMMCs. The weak van der Waals Cu–Gr interface is the principal factor limiting load transfer efficiency. Interfacial engineering strategies, including controlled interfacial oxidation to promote Cu–O–C bonding and chemical functionalization of the Gr surface with Cu-wettable groups, represent a promising route towards enhanced adhesion of the Cu–Gr composites.

Moreover, the random and heterogeneous distribution of Gr in CS deposits limits the exploitation of its exceptional in-plane properties and results in non-uniform deposit behavior. The irregular morphology of the ball-milled Cu–Gr feedstock influences the particle impact dynamics and, consequently, the Gr distribution during deposition. Future work should explore alternative powder preparation routes or ball-milling parameters to achieve a more uniform Gr distribution and improved deposit properties.

CRedit authorship contribution statement

Fatemeh Zarei: Writing – original draft, Visualization, Validation, Methodology, Investigation, Formal analysis. **Amir Ardeshtari Lordejani:** Writing – review & editing, Validation, Methodology, Investigation, Formal analysis. **Hyunjong Lee:** Writing – original draft, Validation, Methodology, Investigation, Formal analysis. **Siyuan Ruan:** Methodology, Investigation. **Apostolos Koutsoukakis:** Writing – review & editing, Methodology, Investigation, Formal analysis. **Xuyun Guo:** Formal analysis, Investigation, Writing – review & editing. **Davoud Jafari:** Writing – review & editing, Supervision, Resources. **Shuo Yin:** Supervision, Resources. **Valeria Nicolosi:** Supervision, Resources. **Sergi Dosta:** Methodology. **Wessel W. Wits:** Writing – review & editing, Supervision, Resources. **Rocco Lupoi:** Supervision, Resources. **Mario Guagliano:** Writing – review & editing, Supervision, Resources. **Sara Bagherifard:** Writing – review & editing, Supervision, Resources, Project administration, Methodology.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgement

The research leading to these results has received funding from the European Union's Horizon Europe Research and Innovation Program under grant agreement No. 101046835 (ThermoDust).

S.B. and M.G. acknowledge ERC-CoG ArchIDep funding from the European Research Council (ERC) under grant agreement n. 101044228. Views and opinions expressed are, however, those of the authors only and do not necessarily reflect those of the European Union or the European Research Council Executive Agency. Neither the European Union nor the granting authority can be held responsible for them. V.N. and X.G. wish to thank the support of the Research Ireland-

funded AMBER Research Centre and the Research Ireland Frontiers for the Future award (Grant Nos. 12/RC/2278_P2 and 20/FFP-A/8950, respectively). Meanwhile, V.N. and X.G. wish to thank SEAI (Award Number 24/RDD/01107) for their support. Furthermore, V.N. and X.G. wish to thank the Advanced Microscopy Laboratory (AML) in CRANN for the provision of their facilities and Clive Downing for assisting in the non-routine maintenance of the microscopes.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.matdes.2026.116929>.

Data availability

No data was used for the research described in the article.

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