

# Abstract

Pure copper represents one of the most attractive yet challenging materials to process by additive manufacturing (AM) due to its high thermal conductivity and strong reflectivity to conventional infrared lasers. This doctoral research addresses these challenges by integrating process optimisation, analytical and probabilistic modelling, and post-fabrication functionalisation aimed at environmental applications. Two different AM technologies were investigated in this thesis: powder bed fusion laser-based technology (PBF-LB/M) and vat photopolymerisation (VPP) based on copper precursors. The main goal was to establish reliable methodologies for producing controlled porosity pure copper parts with specific microstructure and superficial characteristics. A dimensionless framework based on the Buckingham  $\pi$ -theorem was developed to describe the physical behaviour of the PBF-LB/M process. By correlating process parameters with the thermophysical properties of copper, scale-independent groups were formulated to predict the conduction-to-keyhole transition, following the standard procedure used for laser welding. The model successfully identified a transition threshold at a normalised enthalpy of approximately 6 - 8. A regression model, based on the experimental campaign carried out on printed cubes, linked the relative density to the non-dimensional groups, achieving an  $R^2$  of 0.988. Monte Carlo simulations quantified the statistical uncertainty associated with the deterministic process for forecasting density based on knowledge of input parameters. An innovative methodology for the AM of pure copper was studied by applying the metal precursor route for exploiting another AM process: VPP. Hydrated copper sulphate ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ) was dispersed in a photocurable resin, enabling uniform curing by reducing the refractive index mismatch between phases. After printing, the composite was sintered and reduced in an  $\text{N}_2/\text{H}_2$  atmosphere at  $600^\circ\text{C}$ , resulting in fully metallic copper with controlled internal porosity. The efficiency of the reduction process has been evaluated to verify the applicability of the solution.

Samples sintered at 950°C exhibited homogeneous grain structures with an average grain size of 7.2 μm, while higher temperatures (1000°C) induced excessive coalescence and microcracking. The process demonstrated the feasibility of precursor-based VPP for metallic copper and established quantitative relationships between solid loading, sintering temperature, and densification kinetics. The application of pure copper AM and the main limitations associated with the process have been transformed into opportunities by demonstrating how typical AM surfaces and induced (or designed) porosity can be exploited for metal organic framework (MOF) functionalisation. Copper gyroid lattices with high surface-to-volume ratios were fabricated and used as substrates for the growth of HKUST-1 crystals. FESEM and XRD analyses confirmed the formation of uniform and adherent crystalline layers.