

Characterisation and parametric optimisation of L-PBF and DIW of WC-12wt%Co/Mo cemented carbides using response surface methodology

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ARTICLE INFO

Keywords:

Additive manufacturing
WC-Co-Mo cemented carbides
Laser-powder bed fusion
Direct-ink writing
Response surface methodology
Microstructure

ABSTRACT

In this study, WC-8.4Co-3.6Mo (wt%) cemented carbides were fabricated by laser powder bed fusion (L-PBF) and direct-ink writing (DIW). The effects of various processing parameter combinations on the consolidation of the alloys were investigated. A multi-objective response surface methodology (RSM) was employed to determine the optimal L-PBF and DIW processing parameters, utilising a fractional factorial design of experiment (DoE) approach. The RSM analysis included parameters such as scanning speed, laser power, hatch spacing, extrusion pressure and solid loading. Samples prepared by L-PBF showed alternating layers of coarse and fine WC grains, with the fine grains embedded in a binder melt pool. Increasing the laser energy density resulted in a gradual decomposition of the WC phase, accompanied by the loss of Co and the formation of η phases. For DIW, feedstock filaments with powder loading content between 89.4 and 92.4 wt% were prepared using a binder system composed of Pluronic F-127 and Dolapix CE-64. These filaments exhibited steady thermoplastic behaviour with controllable extrusion, yielding samples with a linear shrinkage of approximately 20 %. The results revealed that DIW-produced samples achieved a maximum hardness of 12.69 GPa and a relative density of 95 % under optimised conditions, specifically an extrusion pressure of 0.125 MPa and a solid loading of 92.4 wt%. For L-PBF, a maximum hardness of 12.60 GPa and a relative density of 99 % were obtained at an optimised scanning speed of 485 mm/s, laser power of 197 W and hatch spacing of 90 μm . These optimisation results derived from the regression models provided new parameter sets for further refinement and enhancement.

1. Introduction

Cemented carbides are commonly used as cutting tools for high-speed milling of metal components owing to their good combination of mechanical properties at elevated temperatures [1,2]. These cutting tools are primarily composed of tungsten carbide (WC) particles embedded in a ductile binder matrix typically consisting of Co, Ni and/or Fe [3]. Conventional liquid phase sintering (LPS) is typically used to fabricate these cemented carbides, which involves mixing, pressing, debinding and sintering. Shaping of the symmetrical green compacts should be simple and carried out prior to liquid phase sintering [4,5]. Additive manufacturing (AM) is used to fabricate complex components

that are gaining momentum in the marketplace [6,7]. Common AM techniques for fabricating cemented carbides include selective laser sintering (SLS), laser-powder bed fusion (L-PBF), 3D gel printing, and binder jetting [8]. However, the high temperatures involved in L-PBF tend to result in the formation of W_2C and $\text{W}_2\text{Co}_4\text{C}$ brittle phases in WC-Co cemented carbides [9,10] as well as the partial evaporation of the Co binder phase [11]. Additionally, the rapid heating and cooling processes may result in high residual thermal stresses and microstructural inhomogeneities [8,12]. Various studies have reported on the relationship between the L-PBF processing parameters and the properties of the fabricated WC-Co alloys [9,10]. Optimised L-PBF parameters have thus far yielded WC-Co components with a relative density of approximately

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<https://doi.org/10.1016/j.ijrmhm.2025.107056>

Received 15 October 2024; Received in revised form 5 January 2025; Accepted 6 January 2025

Available online 7 January 2025

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Table 1

Nominal chemical composition and properties of AM WC703 and Mo powders.

Materials	WC wt%	Co	Mo	Particle size (μm)	Purity (wt%)	Source
AM WC703	Bal.	11–13	–	5–25	>99	Global Tungsten and Powders, USA
Co	–	99.9	–	2	99.8	Sigma-Aldrich, USA
Mo	–	–	99.9	<20	99.9	Sigma-Aldrich, USA

98 %. However, the challenge of microcracking resulting in components with compromised mechanical properties persists [13,14]. Several strategies, including printing bed preheating [11] and post-heat treatments [14–17], have been explored to fabricate L-PBF WC-Co carbides with comparable properties to conventional sintering. Despite the extensive study on the processing of WC-Co based cemented carbides using L-PBF, commercial viability has not yet been reached.

Recently, sinter-based AM techniques have proliferated, combining AM shaping and conventional sintering steps [18]. Sinter-based AM techniques have been presented as an attractive alternative for fabricating industrially applicable components. Most of these sinter-based techniques involve the use of organic binders which are removed during consolidation, like in conventional LPS. Bose et al. [18] reported on the sinter-based AM processing of cemented carbides. Among these techniques, direct-ink writing (DIW) or robocasting has been deemed favourable owing to its versatility and low cost [18,19]. Despite the limited available literature on DIW of cemented carbides, it has been reported that a maximum relative density of 99.7 % and a mean microhardness of 1652 HV₃₀ was achieved when robocasting WC-8wt% Co parts [18] from a paste/ink with a solid loading of 45 vol%. According to these findings, the ink rheology has a substantial impact on the DIW of composite powders. Ink rheology is mainly affected by the powder particle size, solid loading as well as binder composition [20]. Given the limited literature on this process and the quest to fabricate high-strength cemented carbide parts, it is important to understand the interaction between the DIW processing parameters and how they affect the resultant material properties.

Numerical approaches have rapidly advanced to aid in understanding and optimising various AM processing parameters [21,22]. A factorial Design of Experiments (DoE) has become a valuable tool for analysing these parameter interactions [21,22]. In a full factorial DoE,

each possible combination of factor levels is replicated an equal number of times. Response Surface Methodology (RSM) is an optimisation technique that helps to refine design parameters to enhance process outcomes [23]. RSM combines DoE, regression analysis and optimisation algorithms to refine and optimise stochastic response variables. While RSM can utilise either full or fractional factorial DoE, full factorial experiments often demand a large number of experimental observations, especially when multiple factors are involved. This can be particularly challenging in AM processes, where numerous parameters contribute to the response. Therefore, a fractional factorial DoE is often advantageous, as it strategically reduces the number of experiments by focusing on key interactions, making the optimisation process more efficient [23].

Cemented carbides fabricated using L-PBF have been found to contain abnormal WC grains [24]. Molybdenum (Mo) has been reported to enhance wettability between the solid solution and the binder phase in WC-based alloys [25], and to suppress WC coarsening in conventional sintering [27]. The current study explores the incorporation of Mo into the binder phase for the fabrication of WC-Co-Mo using both L-PBF and DIW technologies. The addition of Mo was explored due to its desirable high-temperature properties, including thermal stability [26], which could potentially reduce binder evaporation during the L-PBF process. The workflow of both L-PBF and DIW processes, from feedstock preparation to the final sintered product, is also discussed. The printability, microstructure, and properties of the cemented carbides fabricated by L-PBF and DIW were analysed and compared. A RSM approach was adopted to examine and optimise the combined effects of parameters for both AM processes.

2. Experimental procedures

2.1. Feedstock powders

In this study, L-PBF and DIW of WC-based cemented carbides were investigated using WC-12wt%Co (GTP AM WC703) and molybdenum (Mo) powders, with properties listed in Table 1. Mo was added as 30 % of the total metal binder content, resulting in a composition of 3.6 wt% Mo and 8.4 wt% Co. Fig. 1 shows the morphology of the two powders, revealing that the Mo powder is finer than the AM WC703 powder. The WC-Co powder, produced by plasma spheroidization, consists of spherical particles, whereas the Mo powder, produced through spray drying followed by calcination and hydrogen reduction of molybdenum oxide (MoO₃/MoO₂), exhibits more irregularly shaped granules.

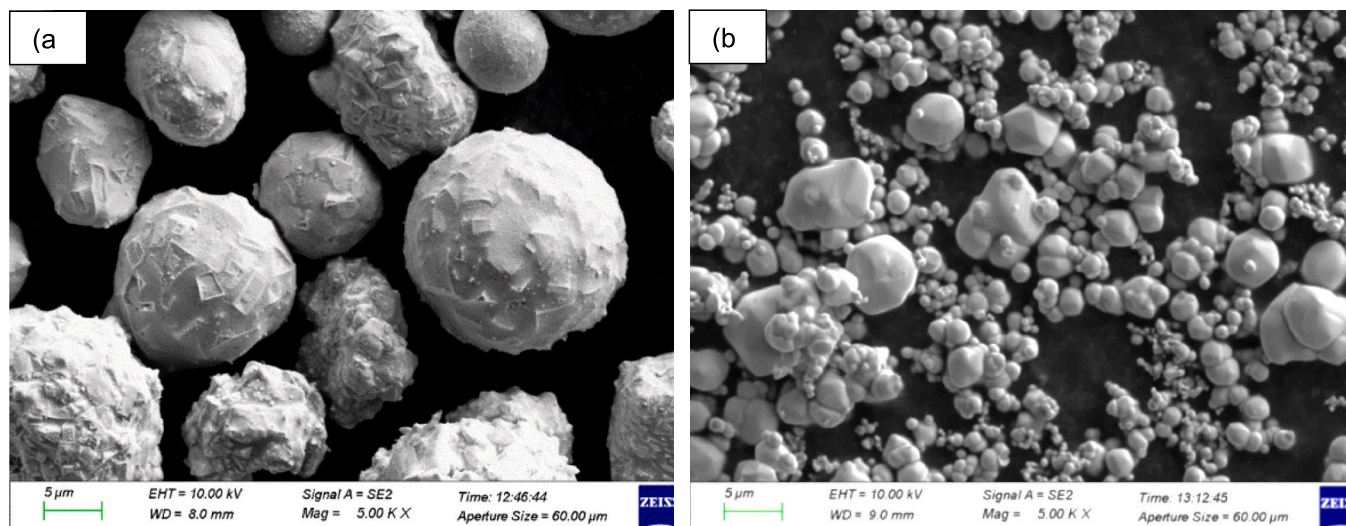


Fig. 1. Morphology of (a) AM WC703 (WC-12Co wt%) and (b) molybdenum (Mo) starting powders.

Table 2
Preliminary L-PBF processing parameters.

Parameter	Range
Laser power (W)	170–200
Scanning speed (mm/s)	450–570
Hatch spacing (μm)	40–50

Table 3
DIW processing parameters.

Parameter	Range
Extrusion pressure (MPa)	0.10–0.40
Paste solid loading (wt%)	89.4–92.4

2.2. Liquid phase sintering (LPS)

LPS was conducted using an Ultra Temp hot-isostatic press (HIP) furnace to consolidate the WC-3.6Mo-8.4Co (wt%) reference-grade powder. The green composite powder samples were initially heated under vacuum conditions at a rate of 2.4 °C/min up to 1200 °C. Argon purging was then performed at 0.37 MPa to mitigate cobalt loss. The heating process continued at a rate of 3.4 °C/min until the temperature reached 1410 °C. This temperature was maintained for 75 min, with hot-isostatic pressing applied at 4.4 MPa during the final 20 min. The furnace was subsequently cooled using water at a controlled rate of 3.4 °C/min.

2.3. Laser-powder bed fusion (L-PBF)

The Concept Laser Mlab 200R powder-bed machine was used for L-PBF processing, employing a continuous wave fibre laser with a maximum power of 200 W. The composite powder was processed on a sand-blasted 316 L stainless steel build plate. To maintain an oxygen content below 100 ppm, argon gas was purged into the printing chamber. Cuboid samples were fabricated without support structures, utilising an alternating raster (AR), rotated by 80° between each layer, and chess (CP) exposure patterns. A constant layer thickness of 30 μm was used. Table 2 outlines the preliminary parameters investigated, based on the capabilities of the Concept Laser Mlab and findings from previous studies [20,27]. These studies demonstrated advancements in achieving high densification and crack-free WC-Co alloys.

2.4. Direct-ink writing (DIW)

A RegenHU 3D-Discovery printer was used to fabricate green

compacts by DIW. Table 3 presents the processing parameters that were studied. The WC-12wt%Co/Mo inks were prepared using an aqueous solution of Pluronic F-127 and Dolapix CE-64. A gelling agent was created using a solution of 25 wt% Pluronic F-127 in 75 wt% distilled water. A dual asymmetric planetary centrifugal speedmixer was used to disperse the aqueous solution and powder mixture. The mixing process was repeated five times at speeds ranging from 1500 to 2100 rpm for 15 s per run. The resulting pastes were loaded into syringe cartridges and extruded through a 0.25 mm nozzle into filaments using a constant-pressure plunger to print the green compacts. The printing parameters included a constant 25 % overlap, a printing speed of 20 mm/s, a layer thickness of 46 μm , and a strand width of 67 μm . To prevent oxidation after printing, the compacts were dried in humidified polymer containers for 23 days. While this extended drying period represents a limitation of the DIW process compared to L-PBF, it was essential for preserving the structural integrity of the green body prior to debinding and sintering. Thermal debinding was conducted at 600 °C for 2 h in an Ar–5H₂ atmosphere, followed by vacuum sintering in a graphite furnace at 1410 °C and 1.8 MPa for 90 min.

2.5. Response surface methodology (RSM) optimisation

A multi-objective response surface methodology (RSM) was employed to optimise the AM processing parameters starting from a selected Design of Experiment (DoE). RSM is a mathematical and statistical tool used to analyse the relationships between input variables and response parameters [28,29]. Design-Expert 13.0.5 (Stat-Ease Inc., Minneapolis, USA) software was used to generate regression models and determine the interactions between the parameters. The process parameter ranges outlined in Tables 2 and 3 were derived from the fabrication of the WC-based cemented carbides reported in literature, considering various parameter combinations [11,18,30–33]. The suggested values provided by the equipment manufacturers fall within the specified parameter ranges. All parameters were set at four levels to enhance overall fabrication efficiency. The DoE calculations and analyses for this study were conducted using Design-Expert software. A

Table 5
ANOVA of density and hardness response surface regressions for L-PBF.

Parameter	Range	Density	Hardness
		p-values	p-values
Model	–	0.0257	0.2636
Laser power (W)	170–200	0.6187	0.6175
Scanning speed (mm·s ^{−1})	450–570	0.4602	0.4532
Hatch spacing (μm)	40–50	0.3763	0.5557

Table 4
Preliminary L-PBF experimental design matrix and measured responses.

Exp. Trial	Laser power W	Scanning speed mm/s	Hatch spacing μm	Layer thickness μm	VED* J/mm ³	Scanning strategy	Density g/cm ³	Hardness HV ₃₀
1	197	485	50	30	271	80° AR	13.83	996
2	184	450	50	30	273	80° AR	13.85	1039
3	180	565	50	30	212	80° AR	13.35	1151
4	189	458	50	30	275	80° AR	13.85	987
5	197	485	50	30	271	CP	13.86	1068
6	184	450	50	30	273	CP	13.57	1144
7	180	565	50	30	212	CP	13.69	942
8	189	458	50	30	275	CP	13.92	914
9	190	550	45	30	256	80° AR	13.87	961
10	180	568	45	30	235	80° AR	13.45	1080
11	185	450	45	30	305	80° AR	13.99	1094
12	197	485	45	30	301	80° AR	13.81	1113
13	190	550	40	30	288	80° AR	13.49	992
14	180	568	40	30	264	80° AR	13.30	852
15	185	450	40	30	343	80° AR	13.90	1122
16	197	485	40	30	338	80° AR	14.05	1096

* VED = Volumetric Energy Density; AR = Alternating Raster; CP = Chess Pattern.

fractional factorial DoE was employed to generate process parameter combinations for the RSM. The simultaneous contributions of two processing parameters to different responses were then demonstrated using RSM quadratic modelling.

2.6. Microstructure and mechanical property evaluation

To study the microstructures of the cemented carbides, scanning electron microscopy (JSM-7500F, JEOL) was utilised in conjunction

with an energy-dispersive X-ray spectroscopy system (Inca Penta FETx3, Oxford Instruments). Vickers microhardness (HV_{30}) tests were conducted on polished samples following standard metallographic preparation using a load of 30 kgf [34]. The average and standard deviation of the hardness values were calculated from five indentations taken at various locations on each sample. To analyse anisotropy in the AM-processed samples, microstructural and hardness measurements were performed on both vertical and horizontal cross-sections. The density of the samples was measured using the Archimedes method.

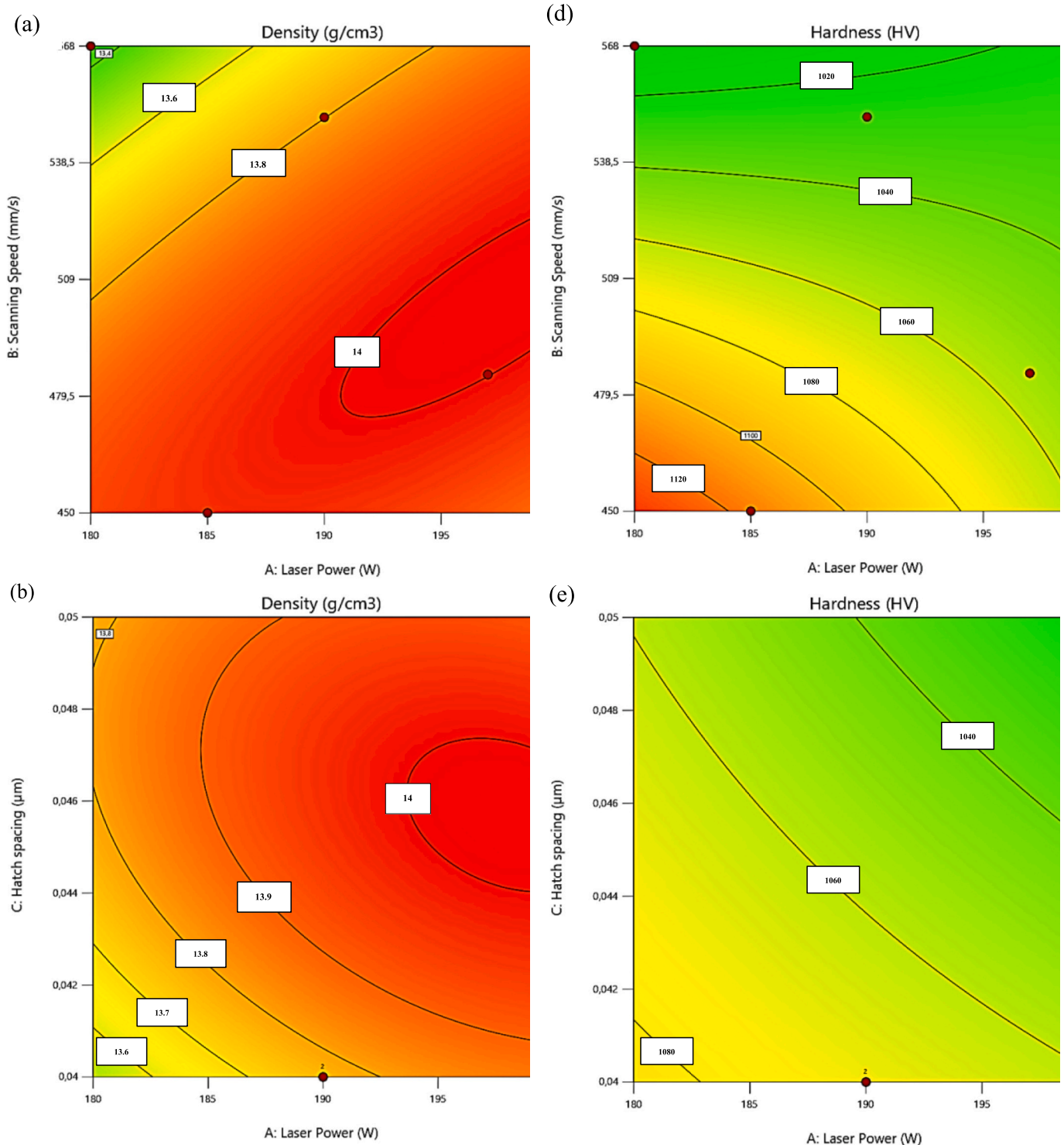


Fig. 2. Preliminary response surface plots of two-parameter combinations for (a - c) relative density and (d - f) hardness of WC-12Co/Mo compacts fabricated by L-PBF.

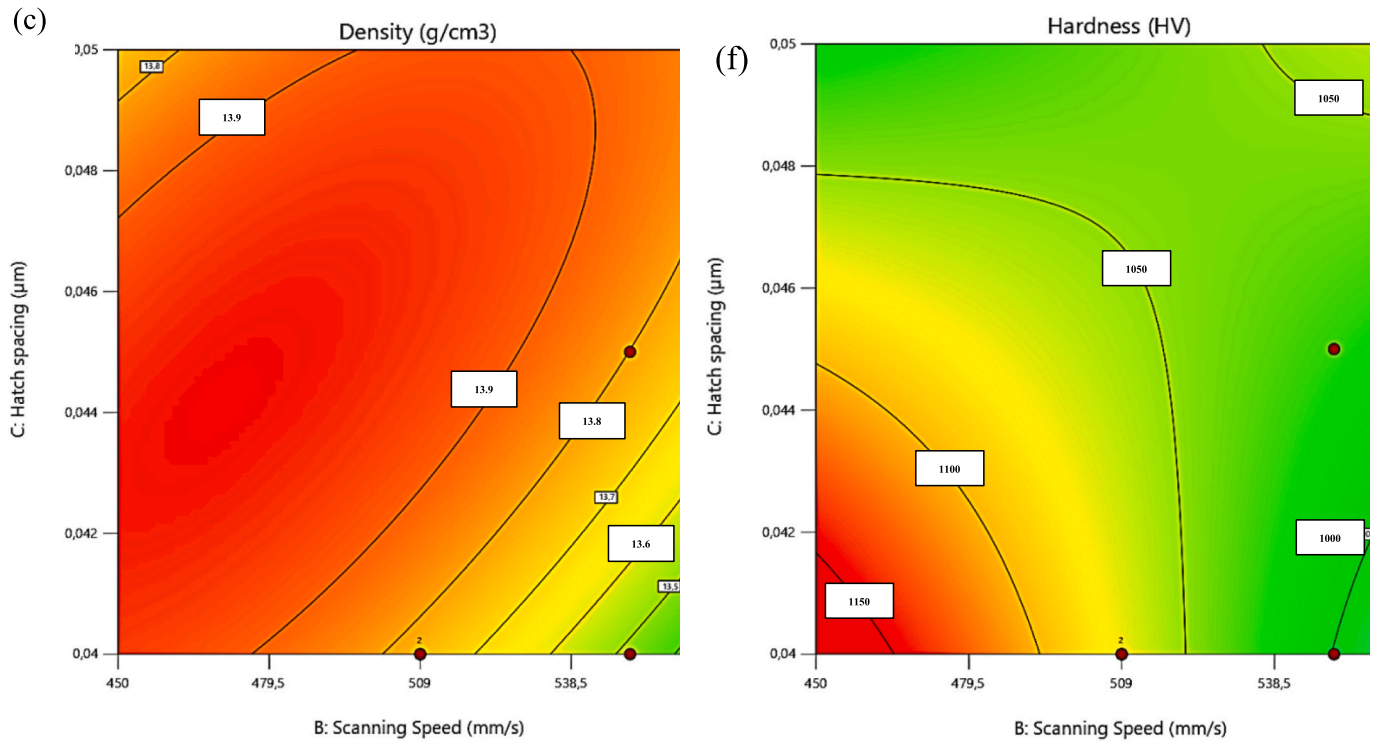


Fig. 2. (continued).

Table 6
DIW experimental design matrix and measured responses.

Exp. Trial	Extrusion pressure MPa	Solids loading wt%	Scanning strategy	Density g/cm ³	Hardness HV ₃₀
1	0.234	90.4	90° Bi-D*	12.87	1081
2	0.129	92.4	90° Bi-D	13.16	1027
3	0.285	90.4	90° Bi-D	13.25	1055
4	0.125	92.4	90° Bi-D	13.29	957
5	0.390	90.4	90° Bi-D	13.46	1044
6	0.310	91.4	90° Bi-D	13.46	1079
7	0.315	91.4	90° Bi-D	13.07	1041
8	0.205	89.4	90° Bi-D	13.26	1095
9	0.225	89.4	90° Bi-D	13.44	1095
10	0.380	89.4	90° Bi-D	13.18	1105
11	0.320	91.4	90° Bi-D	13.39	1094
12	0.205	89.4	90° Bi-D	13.33	1088
13	0.130	92.4	90° Bi-D	13.16	1026

90° Bi-D = Bi-directional with 90° rotation.

3. Results and discussion

3.1. Response surface methodology

Cemented carbides are used in high-wear applications that require a favourable combination of hardness, density and fracture toughness [1]. These properties are influenced by various factors, including metal binder content, carbide grain size and fabrication technique. For L-PBF, the fabrication of WC-12wt%Co/Mo cemented carbides was evaluated based on the laser power, hatch spacing and scanning speed. Table 4 shows the DoE matrix for L-PBF fabrication. A central composite design (CCD) was employed to prepare the data for statistical analysis using Design Expert software. Three independent variables (i.e. laser power, scanning speed and hatch spacing) were utilised in the L-PBF experimental design. For each respective fabrication technique, the coefficients of the properties were calculated using the quadratic model fitted to Eq. 1. Prior to regression, the parameter values were normalised

to minimise the effects of unexplained variability in the observed responses.

$$Y = \beta_0 + \sum_{i=1}^K \beta_i x_i + \sum_{i=1}^K \beta_{ii} x_i^2 + \sum_{i=1}^{n-1} \sum_{j=i+1}^n \beta_{ij} x_i^2 \beta_{ij} x_i x_j \quad (1)$$

where Y represents the output parameters (such as density, hardness, etc.), x_i denotes the input factors (i.e. hatch spacing, extrusion pressure, etc.), and β_i are the coefficients derived from the experimental results. The density and hardness results from the 16 runs detailed in Table 4 were utilised for the analysis. Normalised parameters were employed to formulate the response equations in Eqs. 2 and 3.

Table 5 presents the analysis of variance (ANOVA) results for the density and hardness results, with a 95 % confidence interval, for the L-PBF technique. The mathematical models in Eqs. 2 and 3 establish the relationship between the density and hardness responses and the input parameters: laser power (A), scanning speed (B) and hatch spacing (C). *P-values* less than 0.0500 indicate that the model terms are significant; however, in this case, there are no significant model terms related to density and hardness. No significant terms are denoted with respect to the hardness of the samples. Conversely, the model is significant with respect to density, with a *p-value* of 0.0257. This finding implies that density plays a significant role in the prediction model and should continue to be used as a key measure for the manufacturability of the alloys. Notably, the density of the fabricated samples was highly dependent on scanning speed. Therefore, subsequent fabrication and optimisation runs should focus on processing factors, specifically

Table 7
ANOVA of density and hardness response surface regressions for DIW.

Parameter	Range	Density <i>p-values</i>	Hardness <i>p-values</i>
Model	–	0.5992	0.0086
Extrusion pressure (MPa)	0.10–0.40	0.6173	0.3432
Solid loading (wt%)	89.40–92.40	0.6514	0.0118

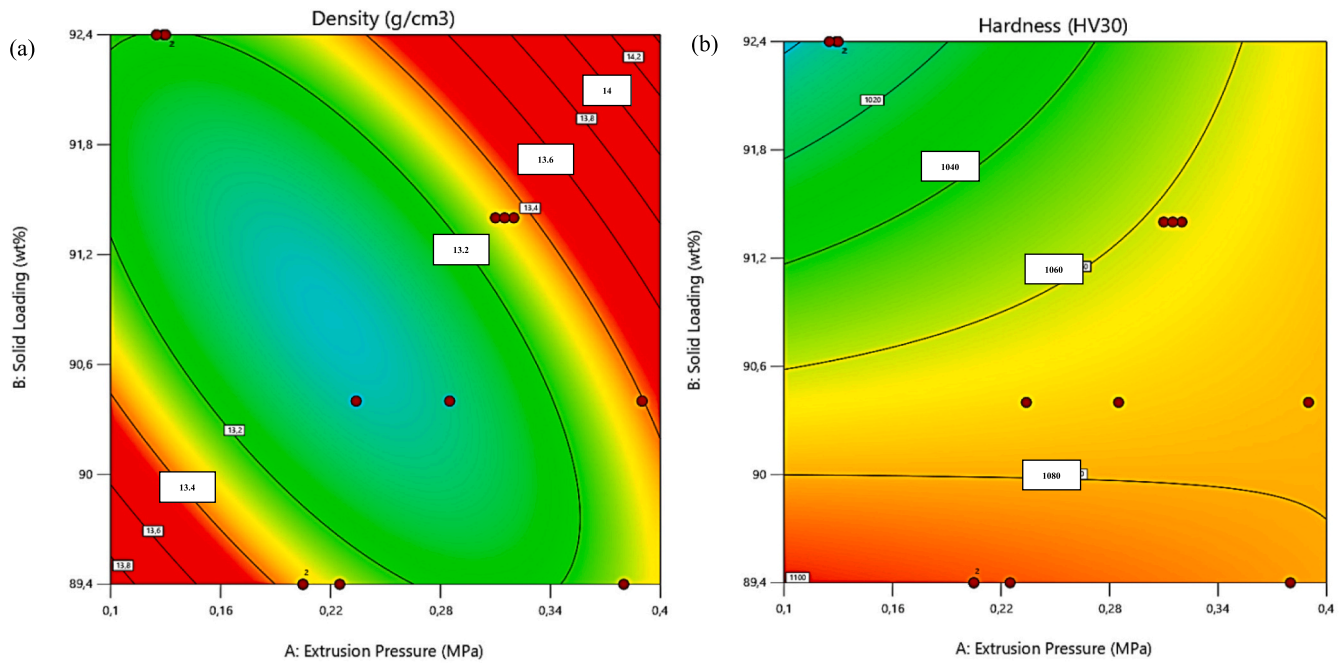


Fig. 3. Response surface plots of two-parameter combination for relative density and hardness during DIW.

scanning speed and hatch spacing, that significantly impact both the density and hardness of the WC-12wt%Co/Mo alloys.

$$\begin{aligned} \text{Density (g/cm}^3\text{)} = & 13.69 + 0.1171A - 0.1410B + 0.0757C + 0.1530AB \\ & - 0.0515AC + 0.1791BC - 0.0677A^2 - 0.1309B^2 \\ & - 0.1219C^2 \end{aligned} \quad (2)$$

$$\begin{aligned} \text{Hardness (HV}_{30}\text{)} = & 1055.54 - 15.60A - 40.63B - 16.41C + 24.44B \\ & - 4.29AC + 64.24BC \end{aligned} \quad (3)$$

Fig. 2 illustrates the response surface plots depicting the combined effect of laser power (A), scanning speed (B) and hatch spacing (C) on the density and hardness of the WC-12wt%Co/Mo alloys. Any convolution observed in the surface plot indicates how changes in one factor influence the behaviour of another. For instance, in Fig. 2 (a), the interaction between laser power and scanning speed reveals that density increases when the laser power is at its maximum and the scanning speed is within the range of 495 mm/s to 524 mm/s. This indicates that, within this scanning speed range, the laser delivers sufficient energy to consolidate the powder particles, while reducing Co evaporation. Conversely, a lower scanning speed combined with higher laser power leads to a decrease in density, as previously reported by Fries et al. [14].

A similar observation was noted regarding the interaction between A and C. Fig. 2 (c) demonstrates that increasing the scanning speed (B) while maintaining a very low hatch spacing (C) resulted in a decrease in density. This decrease led to the formation of pores, indicating that the overlap between the two laser scanning paths was not adequate. In contrast, the interactions between A-B and A-C resulted in minimal variations in hardness. However, the B-C interaction shown in Fig. 2 (f) indicates that reducing both parameters improves hardness due to the development of a more uniform and denser microstructure. This observation aligns with the response surface plot in Fig. 2 (c). Despite being layered, the refined microstructure typically enhances the hardness of the samples, a phenomenon attributed to the Hall-Petch effect. Conversely, increasing the scanning speed at lower hatch spacings decreases hardness due to the loose packing of the powder particles.

Additionally, a higher hatch spacing decreases hardness as it leads to insufficient overlap of neighbouring scan tracks, resulting in pore formation. Lowering the scanning speed and hatch spacing allows for extended exposure of the powder material to high temperatures due to prolonged interaction with the laser. This increased thermal input contributes to the formation of larger grains and the decarbonisation of WC grains, ultimately leading to reduced hardness [35,36].

A similar optimisation procedure was applied to DIW of the same material composition. The preliminary DIW experimental matrix is outlined in Table 6, which details the various combinations of parameters tested. This study investigated the impact of ink solid loading and extrusion pressure on the resultant part properties. Variations in responses to changes in the extrusion pressure (A) and solid loading (B) were simultaneously analysed using the RSM equations presented in Eqs. 4 and 5. The model's *p-value* is 0.0086, indicating that it is statistically significant and can reliably predict how changes in A and B influence the final part properties. In contrast, there are no significant terms concerning density, suggesting that solid loading and extrusion pressure do not significantly affect the density within the tested range. However, solid loading has a *p-value* of less than 0.050 for hardness, as shown in Table 7, indicating that it is a significant variable with respect to hardness alone. This finding aligns with similar results reported in literature [20,27]. The density and hardness were best modelled using cubic and linear equations, respectively.

$$\begin{aligned} \text{Density (g/cm}^3\text{)} = & 13.05 + 0.1646A + 0.1082B + 0.4473AB + 0.3816A^2 \\ & + 0.2800B^2 \end{aligned} \quad (4)$$

$$\text{Hardness (HV}_{30}\text{)} = 1062.71 + 13.58A - 28.12B + 23.28AB \quad (5)$$

Fig. 3 illustrates the response surface plots for the DIW technique. The effects of solid loading on relative density were most pronounced at both very low and very high extrusion pressures. As shown in Fig. 3 (a), increasing both the extrusion pressure and the solid loading resulted in the highest sample density. This outcome was expected, as a higher solid loading implies a greater availability of powder particles within a unit volume, necessitating increased extrusion pressure for effective consolidation. Higher extrusion pressure enhances particle packing and

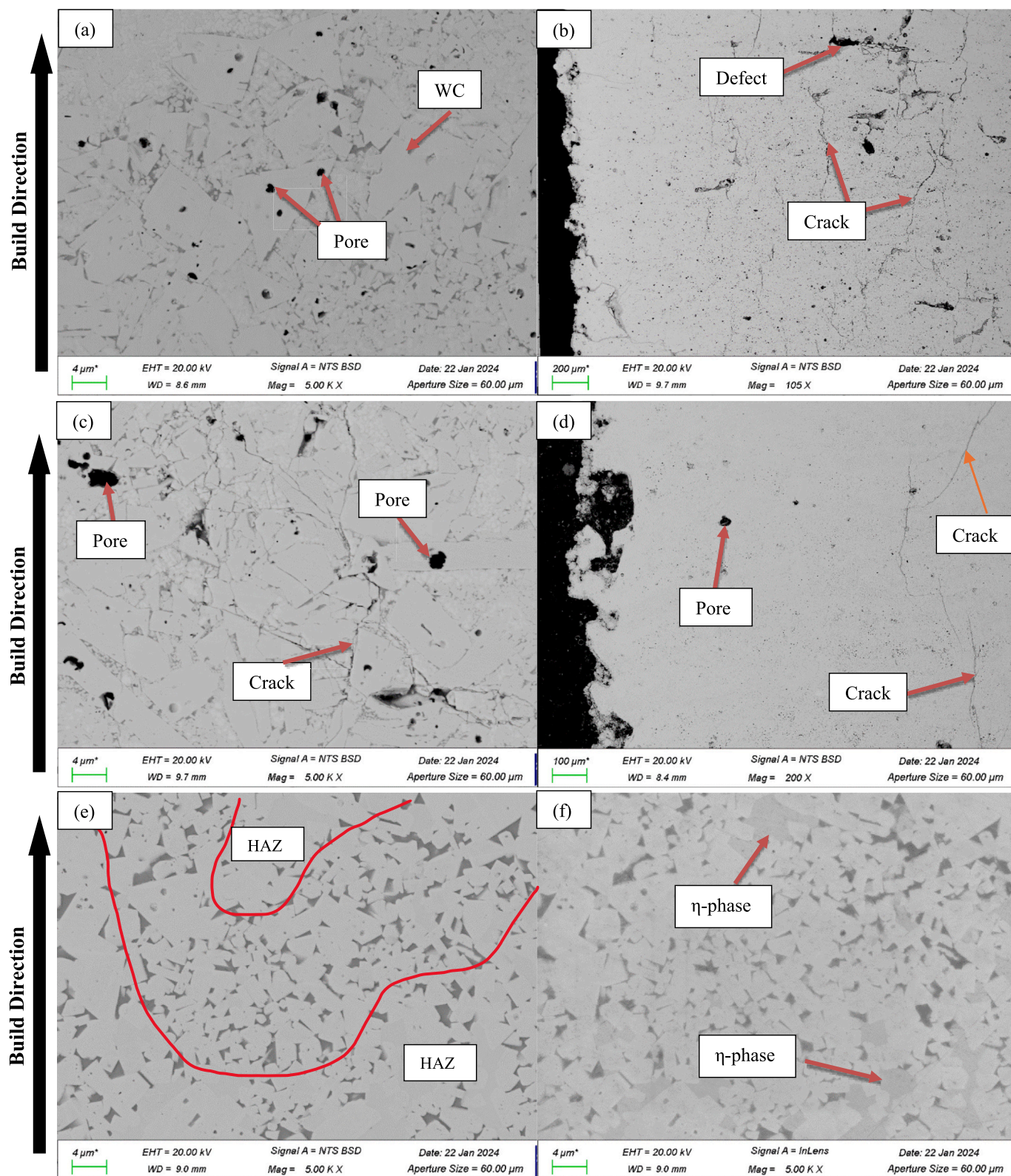


Fig. 4. SEM images of WC-12Co/Mo (wt%) fabricated by L-PBF using a VED of (a)-(b) 338 J/mm³, (b)-(c) 212 J/mm³, (c)-(d) 149 J/mm³.

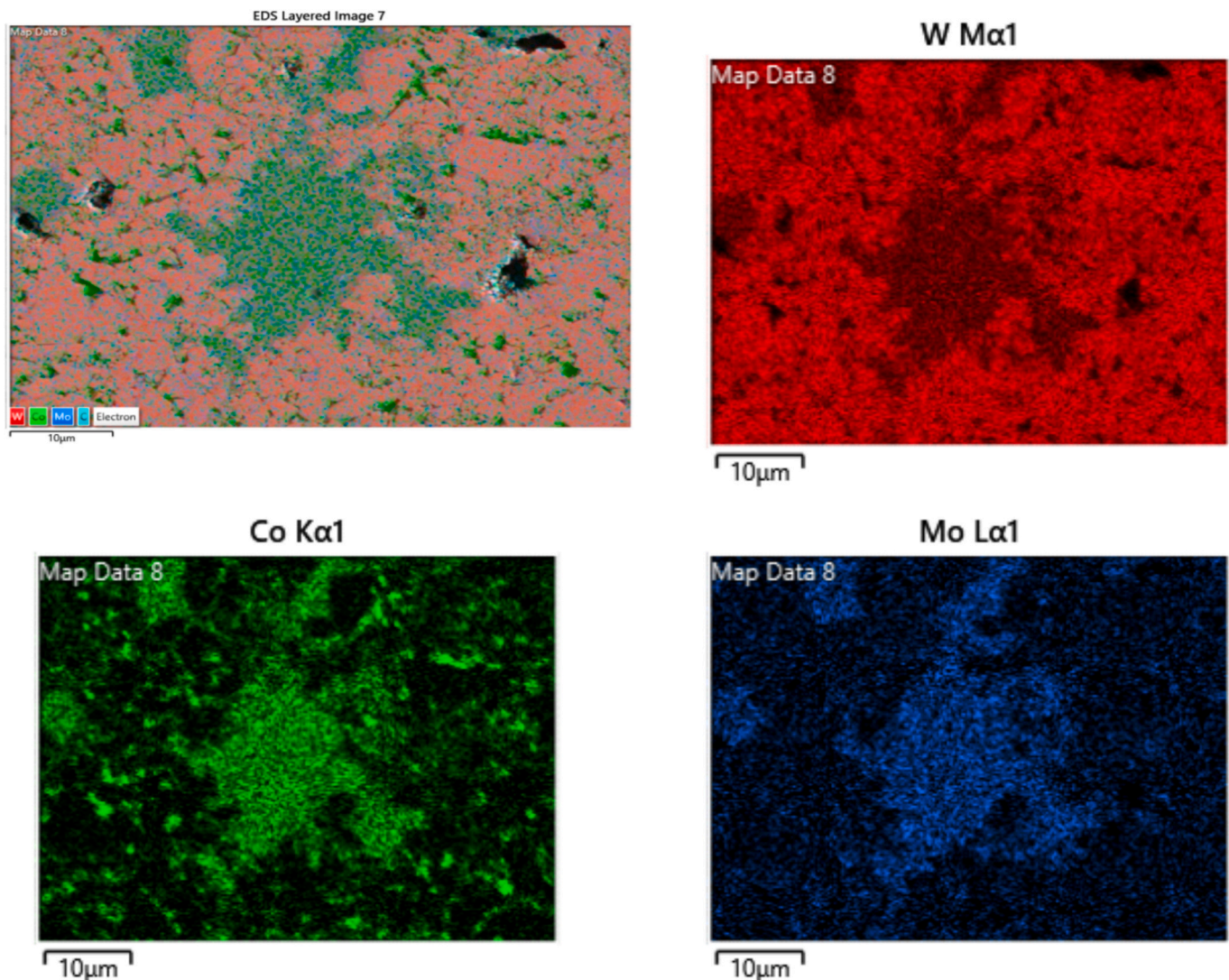


Fig. 5. SEM/EDS analysis of WC-12Co/Mo (wt%) fabricated by L-PBF using a VED of 338 J/mm³.

reduces the number of voids between the filaments, leading to a denser structure. Conversely, the lower density observed at moderate levels of extrusion pressure and solid loading can be attributed to suboptimal particle packing and the evaporation of the binding solution. This could lead to the formation of micro-voids within the printed samples, ultimately reducing the overall density.

Fig. 3 (b) shows that increasing the solid loading while maintaining low extrusion pressure results in significantly lower hardness values. This reduction can be attributed to the loose packing of powder particles at low extrusion pressures, which causes poor inter-filament bonding and a higher concentration of micro-voids between filaments. These voids and gaps compromise structural integrity, leading to reduced local hardness due to the lack of material continuity. In contrast, at higher extrusion pressures, the ink with increased solid loading achieves better filament fusion and particle consolidation, which minimises the number of voids. Therefore, optimising the extrusion pressure is crucial to ensuring that high solid loading is accompanied by sufficient densification and minimised void formation, ultimately improving both the density and hardness of the final part.

3.2. Microstructures and mechanical properties

Microstructural characteristics are critical to the performance of cemented carbides. Fig. 4 presents the microstructures of L-PBF-

processed cemented carbides at low magnification, fabricated using different energy densities. Samples produced at volume energy density (VED) levels exceeding 270 J/mm³ exhibited numerous microcracks and large pores, even though they achieved a relative density of approximately 97 %. Decreasing the hatch spacing (d_h) from 50 µm to 40 µm led to a further decrease in density, attributed to the significantly high temperatures in the melting zones, which caused evaporation of the Co-based binder. Fig. 4 (a) shows keyhole porosity, resulting from material evaporation and inert gas entrapment during solidification when high laser power and low scanning speed were employed [14].

High laser power combined with low scanning speed leads to a very high VED [31], which frequently results in excessive binder evaporation and the formation of undesirable carbide phases. In contrast, samples produced with lower VED (< 150 J/mm³) showed no apparent defects, apart from the formation of larger η -carbides. Fries et al. [11] reported similar findings when exploring the effect of post heat treatments on the microstructure of WC-12wt%Co fabricated by L-PBF. The localised presence of η -carbides is primarily due to concentrated heating at lower scanning speeds and high VED, which can influence carbide precipitation. These high-temperature thermal reactions, coupled with the uncontrolled environment of the printing chamber, make phase changes and carbon loss almost unavoidable [37]. The WC-Co-Mo samples fabricated using optimised L-PBF parameters, i.e. 80 W laser power, 560 mm/s, 100 µm hatch spacing, and 30 µm layer thickness, achieved a

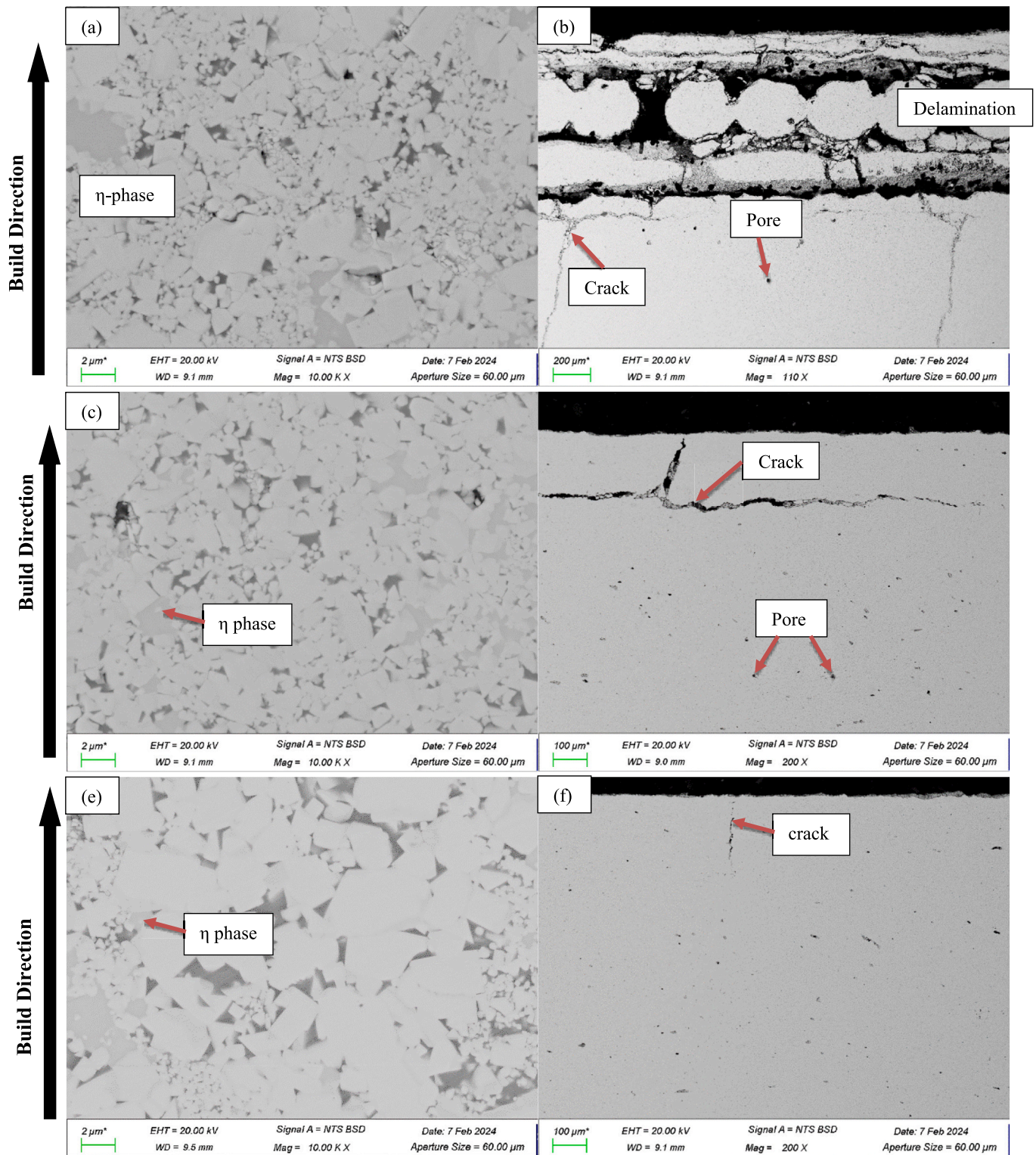


Fig. 6. WC-8.4Co-3.6Mo (wt%) fabricated by DIW using a solid loading of (a)-(b) 89.4 wt%, (c)-(d) 91.4 wt%, and (e)-(f) 92.4 wt%.

density of $14.48 \pm 0.03 \text{ g/cm}^3$, while the preliminary samples reached only $14.05 \pm 0.06 \text{ g/cm}^3$ density. In line with similar studies, the dense spherical granules shown in Fig. 1 played a significant role in enhancing the density of the SLM-processed carbides.

Anisotropy analysis of the SLM-processed samples was performed on the vertical cross-sections, corresponding to the building direction. Fig. 4 (e) illustrates a lamellar structure with alternating layers of fine WC grains embedded in a solidified melt pool. This structure can be

attributed to variations in sintering temperature and liquid phase sintering time during L-PBF. Since the power distribution within the laser beam follows a Gaussian function, as noted in [9], the sintering temperature is consistently higher at the upper portion of the powder layer. This leads to the formation of coarser WC grains in each alternating layer, thus creating the lamellar structure observed in Fig. 4 (e). Interestingly, between these coarser layers, smaller, more equiaxed WC grains are observed, potentially contributing to more uniform properties

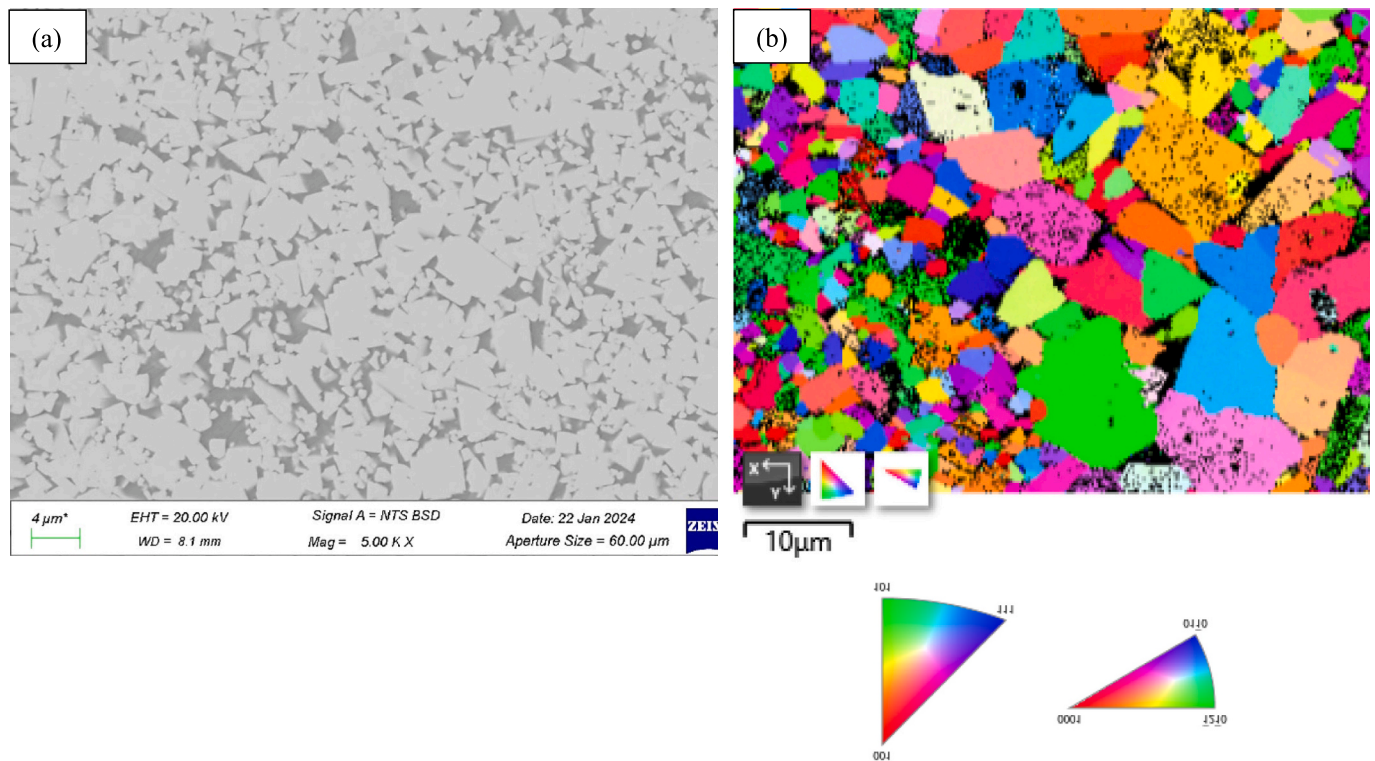


Fig. 7. Microstructure (a) and corresponding EBSD results (b) of WC-8.4Co-3.6Mo (wt%) fabricated by LPS.

along the layer. The layer thickness of the fine WC grains ranged from 18 and 24 μm, with the range increasing at higher VED levels. Reducing the layer thickness could, however, result in excessive evaporation of the Co binder [11]. Molybdenum (Mo) was primarily added to the WC-Co system to mitigate excessive evaporation of the Co binder by diffusing into the Co binder phase. During L-PBF, the coarse Mo particles dissolved into the Co binder under the elevated temperatures generated by the laser, forming a solid solution due to the high thermodynamic affinity of Mo for Co, as detailed by Lassner and Schubert [38]. The rapid nature of L-PBF results in partial dissolution of Mo in Co, thereby enhancing the binder phase through the formation of a Co—Mo matrix. Fig. 5 depicts the SEM/EDS analysis, showing the Co—Mo overlap within the binder phase. Given the sintering conditions inherent to L-PBF, Mo also interacted with WC grains to form complex carbides, such as (W,Mo)C. However, the rapid cooling rates in L-PBF may lead to the formation of trace amounts of (W,Mo)C carbides [25]. Consistent with prior studies on L-PBF processing of WC-xCo ($x = 6, 8, 10, 12$, and 20 wt %), no microstructural anisotropy was observed in the horizontal cross-sections.

Fig. 6 displays SEM images of WC-12Co/Mo (wt%) fabricated by DIW and subsequently sintered at 1410 °C, using different solid loadings. The sintered samples approached full density but exhibited microcracks in both transverse and longitudinal directions, as seen in Figs. 6 (b, d, and f). These cracks are likely a result of uncontrolled drying conditions. Compared to the L-PBF fabricated samples, the microstructures of the DIW ones featured a mixture of finer and coarser WC grains. The influence of solid loading on the sintered microstructure is evident. At a lower solid loading (89.4 wt%), the solvent evaporation caused numerous pores, which hindered complete sintering densification, see Fig. 6 (b). Furthermore, the added Mo showed limited interaction with WC grains within the AM WC703 powder agglomerates. The observation in Fig. 6 (e) indicates that coarse grained agglomerates are encased by finer WC grains, likely due to Mo's grain growth inhibition effect. This finding supports the assertion of a lower sinter activity with respect to Mo and internal powder materials in the AM WC703

agglomerates.

Delamination near the top of the parts was observed due to solvent evaporation during drying and debinding. Parts fabricated using 92.4 wt % solid loading ink exhibited approximately 20 % linear shrinkage. The higher solid loading contributed to the fabrication of high-density compacts and reduced the shrinkage during drying and sintering. This higher solid content (92.4 wt%) helped minimise crack and pore formation, as shown in Fig. 6 (f). Therefore, higher solid loading can be beneficial for achieving a homogeneous microstructure, as well as parts with high dimensional accuracy and density. Although paste rheology was not measured in this study, Fig. 6 (b) suggests that the paste exhibited shear-thinning behaviour, facilitating smooth extrusion and shape retention after deposition [18]. However, shape retention post-deposition may lead to anisotropy along the build direction, particularly in the upper layers. Developing an optimal paste formulation with a balanced combination of solids loading, particle size and binder composition is essential for fabricating fully dense cemented carbides.

During sintering, smaller WC grains dissolved in the binder phase and subsequently re-precipitated onto larger WC grains resulting in the larger carbide grains observed in Fig. 6 (e). The larger WC displayed a faceted shape with slightly rounded edges, while the smaller grains appeared almost spherical. The high sintering temperature (1410 °C) caused substantial dissolution of Mo into both the WC grains and the Co binder pools. Molybdenum was primarily located around the WC grains, as shown in Fig. 7, and the rounding of the WC edges can be attributed to the formation of a (W,Mo)C solid solution [25,26]. In general, the improved microstructure homogeneity in DIW-processed samples can be linked to the formation of a Co/Mo-liquid phase during sintering. Adequate bonding between layers is crucial for the mechanical integrity of the compacts. Residual porosity, likely due to incomplete particle packing or insufficient sintering, was present in most samples. The bonding strength is influenced by the deposition parameters, such as nozzle size, extrusion pressure, filament overlap and layer height [20,27]. According to the RSM plots in Fig. 3, lower extrusion pressures enhance the density and hardness of WC-12wt%Co/Mo alloys.

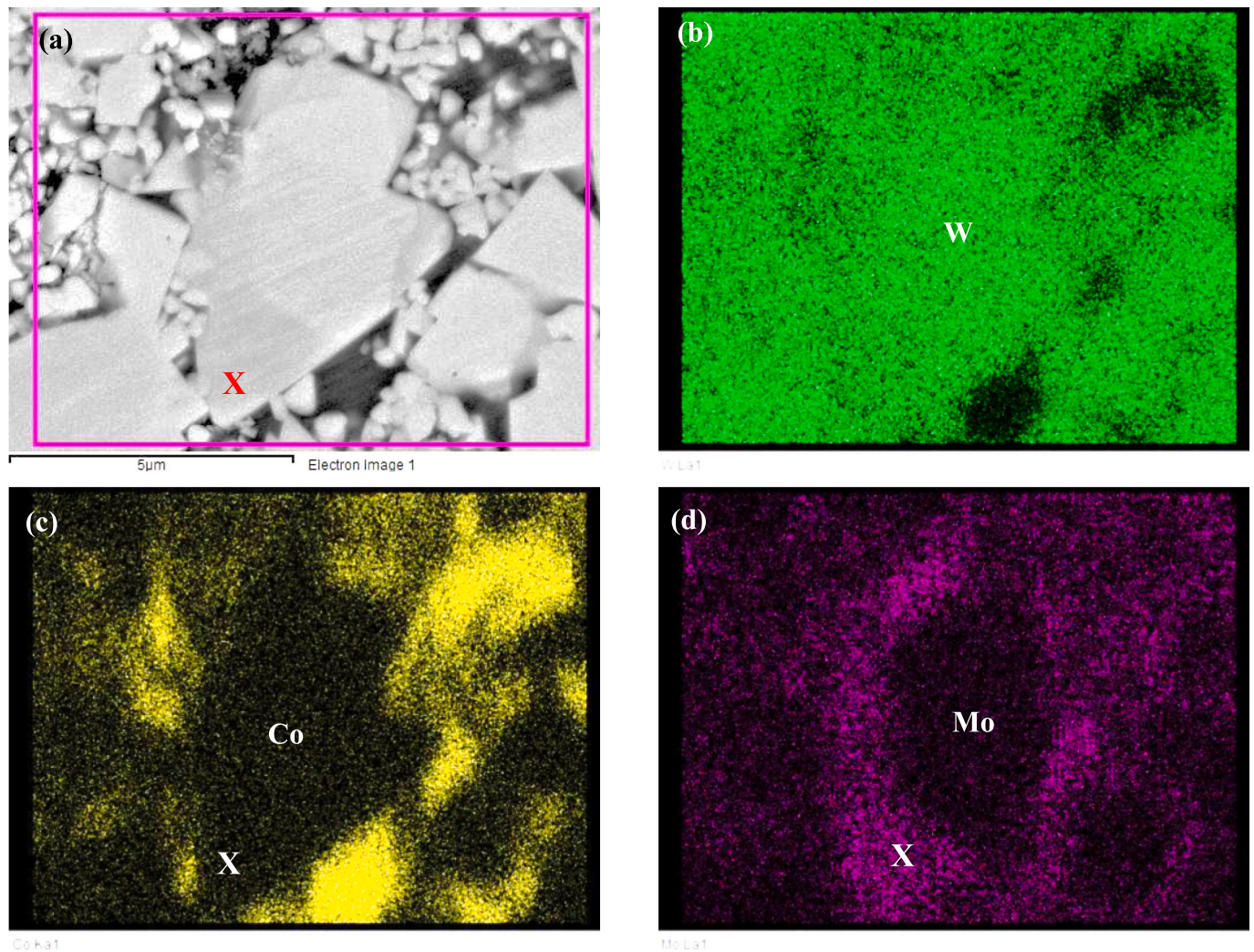


Fig. 8. Microstructure (a) and corresponding EDS elemental mappings (b) W, (c), Co and (d) Mo of WC-8.4Co-3.6Mo (wt%) cemented carbide processed by DIW.

Therefore, the starting powder material and the consolidation process of the green AM compacts produced by DIW may need to be reconfiguration to achieve optimal sintering outcomes. Micro-cracking, as seen in Fig. 6, likely results from differential shrinkage during the drying and debinding processes. To address these challenges, future research will focus on further optimising the DIW processing parameters and drying process conditions, as well as exploring the incorporation of carbon black to eliminate η phases.

Fig. 7 shows the microstructure of the reference WC-3.6Mo-8.4Co (wt%) sample fabricated via conventional LPS. The microstructure is characterised by a mix of large and small WC grains, with relatively well-distributed Co—Mo binder pools. This improved binder distribution is attributed to the capillary action of the liquid binder during the secondary rearrangement stage of LPS [34]. Although LPS resulted in better binder pool distribution compared to L-PBF and DIW, it also led to some grain growth due to the prolonged holding time at 1410 °C. However, the grain growth inhibition effect of Mo in (W,Mo)C solid solution was evident, as seen in the slight rounding of WC grains edges [25]. In contrast, during L-PBF processing, the temperature distribution in the binder phase reached high values, leading to momentary melting followed by rapid solidification. This resulted in inhomogeneous binder pool distribution, as shown in Fig. 4 (e). As depicted in Fig. 7 (b), the random orientation of WC grains in the LPS sample provides isotropic properties, making it suitable for a range of applications requiring good mechanical performance.

The grain orientation and microstructure play a significant role in determining the mechanical properties and performance of cemented carbides, which are essential in applications that require high hardness and wear resistance. The rapid cooling rates typical of L-PBF tend to yield a fine-grained microstructure with a strong texture [16]. However, the larger WC grains did not exhibit any preferred orientation, largely due to laser-induced re-melting that occurs as each subsequent powder layer is scanned during the build process. EBSD analysis of the L-PBF-fabricated samples, as depicted in Fig. 9, revealed no preferred crystallographic orientation, despite the directional solidification in the molten pools. The scanning strategy and high thermal gradients result in grain alignment along the heat flow direction, which often produces elongated, larger WC grains parallel to the build direction [39,40].

In contrast, the WC-12wt%Co/Mo samples fabricated by DIW (Fig. 8 (c)) exhibit a random grain orientation with a less pronounced texture compared to those produced by L-PBF. The uniform cooling and absence of strong directional solidification resulted in nearly equiaxed and randomly oriented WC grains, contributing to more isotropic mechanical properties. The average grain size of the samples fabricated by DIW is approximately 5.02 μm , as determined from imaging analysis. Fig. 8 illustrates the microstructure and corresponding elemental distribution of the WC-12wt%Co/Mo alloy produced by DIW. The analysis reveals three major phase contrasts corresponding to the W-rich region, the Co-rich region and the transition region that is Mo-rich. Notably, a phase enriched in W and Mo was observed at the edges of the WC grain, as

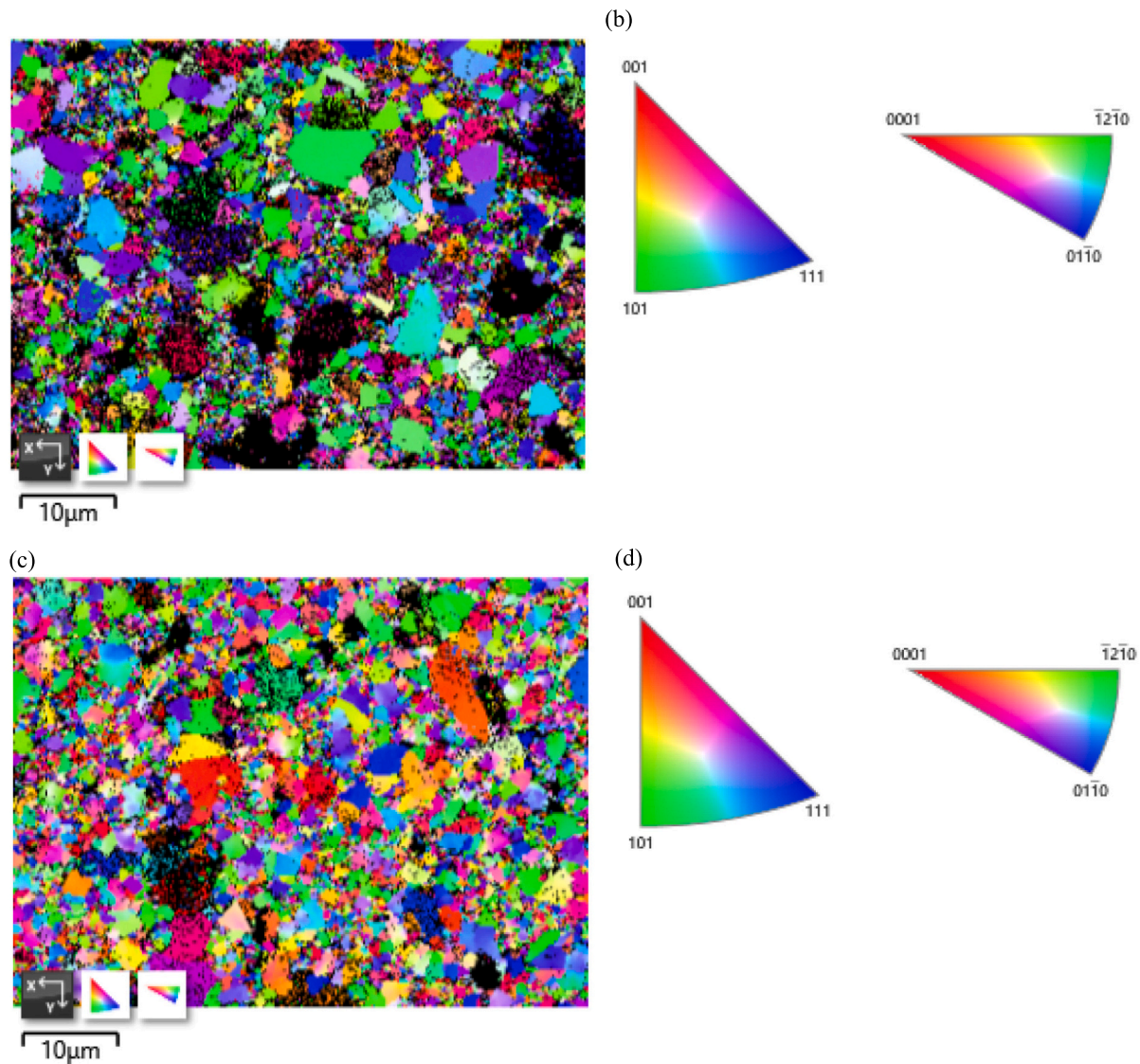


Fig. 9. EBSD results of WC-8.4Co-3.6Mo (wt%) fabricated by (a) L-PBF ($P = 197$ W, $v = 485$ mm/s, $h = 90$ μ m) and (b) DIW (92.4 wt% solid loading, 0.125 MPa), and respective inverse pole figures.

Table 8
Properties of the consolidated samples.

Properties	LPS	L-PBF	DIW
Density (g/cm ³)	14.33 $\pm$ 0.24	14.05 $\pm$ 0.06	13.74 $\pm$ 0.09
Hardness (GPa)	13.14 $\pm$ 0.09	12.60 $\pm$ 0.38	12.69 $\pm$ 0.11

indicated by the 'x'. This suggests that Mo has dissolved into WC to form a (W,Mo)C solid solution around the WC grains, potentially acting as a grain growth inhibitor [26,41]. Additionally, Mo also dissolved in the Co binder.

3.3. Hardness and density properties

Table 8 presents some of the properties obtained from the two fabrication techniques. The conventionally sintered LPS samples exhibited higher hardness than those fabricated by both L-PBF and DIW. This enhancement in hardness can be attributed to the optimal combination of sintering temperature and pressure, which facilitated effective sintering of the powder particles, resulting in fully dense samples [25].

Despite the differences in processing methods, the hardness values for samples produced by L-PBF and DIW were similar at their maximum. The hardness of the L-PBF samples was attributed to the optimised processing parameters, specifically tailored to the powder material, allowing sufficient sintering during the rapid laser melting and solidification process. Notably, the L-PBF samples had a lower residual Co content, as estimated from EBSD results, and exhibited larger, randomly oriented WC grains compared to those produced by DIW. Higher VED in L-PBF contributed to this lower residual Co content, promoting solid-state diffusion between WC grains and enhancing densification [14–17]. Both fabrication techniques produced similar density values; however, the residual Co content was higher in DIW, providing an additional binding phase between the WC grains. In contrast, the L-PBF technique experienced limited sintering and thermal shock due to the rapid processing speeds, which resulted in the formation of pores and cracks, as illustrated in Fig. 4. Consequently, the presence of a high number of microcracks in the L-PBF samples hindered the measurement of fracture toughness using the indentation method, as shown in Fig. 4 (b). This indicates the need for further optimisation of each fabrication process to tailor material properties for various industrial applications.

4. Conclusion

In this study, RSM was employed to determine and optimise the processing parameters for fabricating WC-8.4Co-3.6Mo (wt%) cemented carbides using PBF and DIW. Samples with the same composition were also fabricated via LPS for benchmarking purposes. The relative density and Vickers hardness of the samples served as key performance indicators, allowing for the assessment of the printability of WC-8.4Co-3.6Mo (wt%) cemented carbides via both techniques. The findings of the study are summarised as follows:

- 1) The RSM approach effectively identified key correlations between processing parameters and the density and hardness responses in both L-PBF and DIW through fractional factorial experiments. This highlights the utility of RSM in optimising complex fabrication processes for WC-Co/Mo cemented carbides.
- 2) Samples fabricated using WC-3.6Mo-8.4Co (wt%) via LPS exhibited superior hardness, outperforming those fabricated using L-PBF and DIW, owing to the well-distributed Co—Mo binder pools.
- 3) Samples fabricated by L-PBF exhibited alternating distributions of coarse and fine WC grained layers, with fine grains embedded in large binder melt pools, along with the formation of η phases. The RSM analysis suggests maintaining a medium-to-low volumetric energy density (VED) levels to minimise metallurgical defects such as microcracks and pores.
- 4) The optimisation process using the RSM resulted in L-PBF samples achieving a maximum hardness of 12.60 GPa and a relative density of 99 % at a scanning speed of 485 mm/s, a laser power of 197 W and a hatch spacing of 90 μm . However, the resultant microstructures still exhibited microcracks, pores and η phases.
- 5) In contrast, the microstructures obtained from DIW were more homogeneous, containing a mixture of fine and coarse WC grains, as well as dispersed η phases. Metallurgical defects, such as cracks and pores, were more pronounced at the top of the samples due to delamination and uncontrolled drying conditions. The presence of η phases in the starting powder presents the need for the addition of carbon black to mitigate the formation of undesirable phases. Additionally, magnetic measurements are recommended to provide valuable insights into carbon loss and WC grain growth in the cemented carbides.
- 6) A relative density of 95 % was achieved with an optimised extrusion pressure of 0.125 MPa and a solid loading of 92.4 wt% during DIW processing. The high solid loading introduces more powder particles in the ink, resulting in increased density and minimising the formation of cracks and pores. While a higher solid loading can be advantageous for reducing part shrinkage, care must be taken to avoid producing highly viscous ink that may be difficult to extrude and print reliably.

In conclusion, this RSM-based study demonstrated that the microstructural properties of L-PBF samples are highly sensitive to critical parameters, including laser power, scanning speed and hatch spacing. Additionally, for DIW, the research highlighted that the successful fabrication of fully dense cemented carbides is significantly influenced by ink formulation, extrusion parameters and drying conditions.

CRedit authorship contribution statement

Nthape P. Mphasha: Writing – review & editing, Writing – original draft, Visualization, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Rodney M. Genga:** Writing – review & editing, Supervision, Funding acquisition, Conceptualization. **Natasha Sacks:** Writing – review & editing, Validation, Supervision, Resources, Funding acquisition, Conceptualization. **Claudia Polese:** Writing – review & editing, Visualization, Supervision. **Jozef Vleugels:** Writing – review & editing, Validation, Supervision, Resources,

Conceptualization. **Shuigen Huang:** Supervision, Resources, Investigation, Conceptualization. **Xola Madyibi:** Software, Methodology, Investigation.

Declaration of competing interest

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

Acknowledgements

This research is supported by the National Research Foundation of South Africa (Grant No.: 129313), the DSI-NRF Centre of Excellence in Strong Materials (CoE-SM Grant No: 41292) and the Council for Scientific Industrial Research. We gratefully acknowledge the financial support of the scientific research fund of KU Leuven under project C2E/23/022 and KA/22/029. Opinions, findings and conclusions or recommendations expressed in this work are those of the authors and are not necessarily to be attributed to the funders.

Data availability

Data will be made available on request.

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