

***IN-SITU* ALLOYING BY DIRECT ENERGY DEPOSITION FOR HIGH-THROUGHPUT SCREENING OF RCCA/RHEAs COMPOSITIONS**

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*“Remember to look up at the stars and not down at your feet.
Try to make sense about what makes the universe exist. Be curious.
And however difficult life may seem, there is always something you can do,
and succeed at. It matters that you don’t just give up.”*

Stephen Hawking

ABSTRACT

Combustion processes in systems for the aeronautic and aerospace sector would be more efficient if a higher service temperature could be used; however, this increase is not possible due to the Ni-based superalloys' intrinsic constraints. Yet, High Entropy Refractory Alloys (RHEAs) have been developed, presenting the potential to surpass them.

In this dissertation, the *in-situ* alloying by Direct Energy Deposition (DED), combined with thermodynamical simulations (CALPHAD), is presented as a high-throughput screening methodology to gather immense new information on RHEAs based on the MoNbTaWV system. Furthermore, the relationship between process parameters, alloy composition, and structure was established.

To fulfil these objectives, the following procedure was employed: simulation-assisted design for RCCA/RHEAs by first principles calculations and CALPHAD simulations; powders characterisation; MoNbTaW parts production by Direct Energy Deposition (optimisation through Response Surface Methodologies (RSM) and characterisation); and *in-situ* alloying for high-throughput of RCCA/RHEAs. The characterisation of all samples produced was assessed through optical microscopy (OM) and scanning electron microscopy with energy dispersive spectroscopy (SEM/EDS); moreover, electron backscatter diffraction (EBSD) and X-ray diffraction (XRD) were also used for specific samples characterisation. Additionally, the microhardness evolution was assessed with increasing V content for all samples.

The CALPHAD simulations show that the addition of V and Ti to the base system allows a single-phase BCC structure to be kept. On the other hand, the formation of intermetallic structures is observed for Al, Cr, and Zr additions. For the DED set-up available, it was concluded by the RSM that the optimal parameters for the MoNbTaW deposition were 1800 W laser power, 300 mm/min relative surface speed, and 12.5 g/min feed rate. Experimentally, it was observed that most of the V additions allow to sustain the MoNbTaW BCC single-phase structure; however, due to the high melting range, the structure presents an increasing heterogeneity with the V content increase. It was also observed that a biphasic structure is present for addition superior to 40 at%. Regarding the hardness evolution, it is verified that a 25 at% of V increase promotes a strengthening higher than 40%. Based on these results, it was attainable to qualify DED as a RHEAs screening technology and expand the practical knowledge of RCCAs/RHEAs, thus accelerating the potential application of these alloys in aerospace applications.

Keywords: CALPHAD; Direct Energy Deposition; MoNbTaW; RCCAs; RHEAs.

RESUMO

Os processos de combustão em sistemas para o sector aeronáutico e aeroespacial seriam mais eficientes se fosse viável utilizar uma temperatura de serviço mais elevada. No entanto, este aumento não é possível devido às limitações intrínsecas das superligas de níquel. De forma a colmatar estas limitações, as ligas refratárias de alta entropia (RHEAs) têm surgido com o potencial de ultrapassar as superligas de níquel comumente utilizadas.

Nesta dissertação, a adição *in-situ* de elementos por Deposição Direta de Energia (DED), combinada com simulações termodinâmicas (CALPHAD), é apresentada como uma metodologia de triagem de alto rendimento para reunir novas informações relativas às RHEAs com base no sistema MoNbTaWV. Adicionalmente, a relação entre os parâmetros do processo, a composição e a estrutura das ligas foi estabelecida.

Com vista a atingir estes objetivos, foi adotado o seguinte procedimento: design de RCCA/RHEAs assistido por simulação por cálculos termodinâmicos e simulações CALPHAD; caracterização de pós; produção de peças de MoNbTaW por DED (otimização através de RSM e caracterização); e adição *in-situ* de V como ferramenta de triagem de elevado rendimento de RCCA/RHEAs. A caracterização de todas as amostras produzidas foi avaliada através de microscopia ótica (MO) e microscopia eletrónica de varrimento com espectroscopia de energia dispersiva (SEM/EDS). A difração por retrodifusão de elétrons (EBSD) e a difração de raios-X (XRD) foram também utilizadas para a caracterização de algumas amostras. Por fim, influência do teor de V na microdureza foi avaliada em todas as amostras.

As simulações CALPHAD mostram que a adição de V e Ti ao sistema base permitem a conservação de uma estrutura monofásica BCC. Por outro lado, a formação de compostos intermetálicos é observada para as adições de Al, Cr e Zr. Para o set-up de DED disponível, concluiu-se que os parâmetros ótimos para a deposição da liga MoNbTaW são 1800 W de potência laser, 300 mm/min de velocidade relativa da superfície e 12,5 g/min. Experimentalmente, observou-se que a maioria das adições de V permite conservar a estrutura monofásica BCC do sistema MoNbTaW; no entanto, devido à elevada gama de fusão, a estrutura apresenta uma heterogeneidade crescente à medida que o teor de V aumenta. Observou-se ainda a presença de uma estrutura bifásica para teores superiores a 40 at% de V. No que concerne à variação da dureza, verifica-se que a adição atômica de 25% de V promove um endurecimento superior a 40% quando comparado com a liga MoNbTaW. Com base nestes resultados, foi possível qualificar o DED como uma tecnologia de rastreio de RHEAs e expandir o conhecimento prático dos RCCAs/RHEAs, acelerando assim uma potencial aplicação destas ligas em aplicações aeroespaciais.

Palavras-chave: CALPHAD; Deposição Direta de Energia; MoNbTaW; RCCAs/RHEAs.

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LIST OF ABBREVIATIONS

Al	Aluminium
AM	Additive Manufacturing
BCC	Body-Centred Cubic Structure
CALPHAD	Calculation of Phase Diagrams
CTE	Coefficient of Thermal Expansion
CCAs	Complex Concentrated Alloys
Cr	Chromium
DED	Direct Energy Deposition
DOE	Design of Experiments
EBSD	Electron Backscatter Diffraction
EDS	Energy Dispersive Spectroscopy
FCC	Face-Centred Cubic Structure
FR	Feed Rate
HAZ	Heat Affected Zone
HCP	Hexagonal Closest Packed
HEAs	High-Entropy Alloys
HT	High Temperature
INC	Inconel
LMD	Laser Melting Deposition
LP	Laser Power
Mo	Molybdenum
Nb	Niobium
OM	Optical Microscopy
PSD	Particle Size Distribution
RCCAs	Refractory Complex Concentrated Alloys
RHEAs	Refractory High-Entropy Alloys
RT	Room Temperature
SEM	Scanning Electrons Microscopy
T _m	Absolute Melting Temperature

Ta	Tantalum
Ti	Titanium
V	Vanadium
W	Tungsten
XRD	X-Ray Diffraction
Zr	Zirconium

LIST OF SYMBOLS

δ	Average atomic size mismatch
$\delta \chi_{\text{Allen}}$	Allens' electronegativity difference in a multicomponent alloy
Ad	Area of the built above the substrate
As	Area of the built below the substrate
d ₅₀	Average particle size
ΔS_{conf}	Configurational entropy variation
S _w	Cumulative distribution slope
ρ	Density
ΔG_{mix}	Gibbs free energy of mixing
J	Joules
kWh	Kilowatt per hour
μm	Micrometres
mm	Millimetres
N	Newtons
Ω	Ratio between Entropy and Enthalpy
ν	Relative Scanning Speed
VEC	Valence electron concentration
W	Watts
Θ	Wettability angle

01 INTRODUCTION

Conventional methods of developing useful engineering alloys have involved the combination of a principal element, such as Cu, Fe, or Al, with other elements, which may be found in small or considerable quantities. This approach, known as alloy synthesis, has propelled civilizations' technological progress and shaped our daily lives. By combining different elements, the alloy design concept has enabled remarkable advancements in various fields, from infrastructure and transportation to consumer products and medical devices. The strategic manipulation of alloy compositions has opened a world of possibilities, allowing the development of materials with tailored properties and enhanced performance characteristics that have significantly impacted on our modern society [1-2].

Stepping out of conventional thinking, the concept of High-Entropy Alloys (HEAs) was first reported by two independent researchers, Brian Cantor and Jien-Wei Yeh, at the beginning of the 20th century. These early publications attracted the interest of several researchers due to the characteristics of the developed alloys, mainly: their exceptional mechanical, thermal, magnetic, and corrosion-resistant properties. Therefore, the idea of combining multiple elements opened new avenues for alloy design, allowing scientists to explore uncharted territories of material properties [2].

From all the diverse groups of HEAs, Refractory High-Entropy Alloys (RHEAs) and Refractory Complex Concentrated Alloys (RCCAs) have presented interesting characteristics for their application in combustion process components. Ni-based superalloys are commonly used for high-temperature applications, such as jet engines and propulsion systems. Although these alloys show excellent chemical-mechanical behaviour, their melting point limits the maximum application service to temperatures around 1000 °C. As an attempt to increase the service temperature and resultant system efficiency increase, due to less fuel consumption and less CO₂ emissions. RHEAs and RCCAs have been presented as an alternative to the state-of-art nickel-based superalloys since they present high-temperature properties alongside a higher melting temperature, therefore, allowing an increase of the service temperature [3-4].

Several RHEA/RCCAs system have been reported in the literature [3], such as MoNbTaW, HfNbTaTiZr, NbTiVZr and AlMo_{0.5}NbTa_{0.5}TiZr. However, numerous obstacles related to the design, development, and industrialization of these alloys need to be surpassed to further develop new alloys. Unlike conventional alloys, the toughest challenge is alloy identification and selection, among the vast possible combinations, which depend on the type, number, and content of each element [3].

To surpass these obstacles, many alloy design strategies have been developed. The high-throughput alloy design integrated with computation and experimentation has been reported as one of the most influential and effective design strategies. This strategy can

be divided into three main blocks: (1) Phase prediction calculations/simulations; (2) Production; and (3) Microstructural and mechanical characterisation [5].

In the scope of this work, the strategy beforementioned was adapted to the goal of the LiRAs project (In-Situ alloying by Laser Cladding for high-throughput screening of RCCAs compositions as alternative to Nickel Superalloys), where first principle calculations and CALculation of PHase Diagrams (CALPHAD) methodologies were used for the selection of promising RHEA/RCCAs that would present a single-phase structure, and Direct Energy Deposition (DED)¹ was used for high-throughput screening by *in-situ* alloying. Figure 1 shows a schematic representation of the strategy adopted.

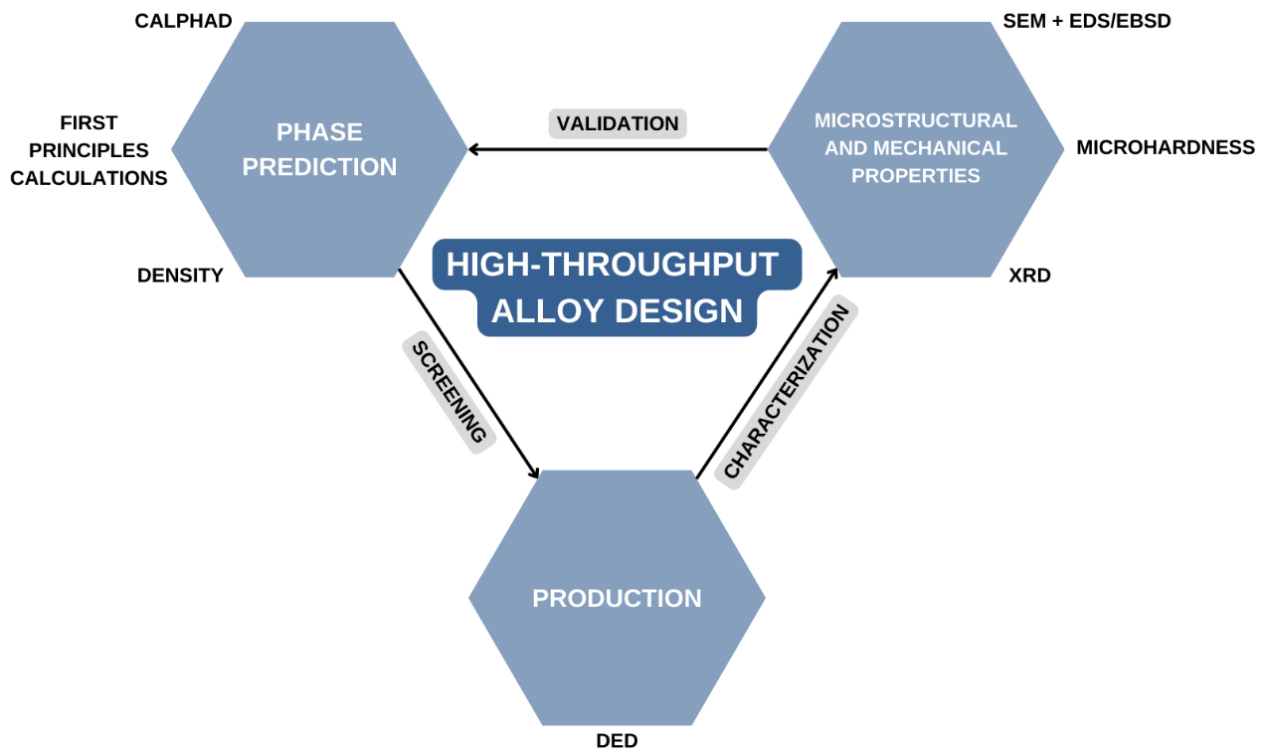


Figure 1: Schematic of a high-throughput alloy design and development strategy integrating high-throughput computation and experimentation.

Therefore, the present master dissertation was developed with the aim to: identify and develop new promising alloys based on RCCA/RHEAs; qualify the DED technology as a tool for high-throughput screening of RCCA/RHEAs; develop property/characteristic maps at room temperature (RT) of the developed alloys through microstructural, chemical, and mechanical characterisation; and to establish a relationship between simulation-based development approaches and experimental research data.

¹LC and DED are two Laser Melting Deposition (LMD) technologies, differing mainly in the deposition strategy. LC is a technology used for coating production, while DED is an Additive Manufacturing (AM) technology, where the component construction is done layer-by-layer. Given that the compositionally graded parts were constructed layer-by-layer, it was decided that the selected manufacturing technology would be referred to as DED.

The present document was written and structured into five chapters:

- Chapter 1 (the present chapter) presents the overall motivation, goals and framework of the LiRAs project and this dissertation.
- Chapter 2 depicts the most relevant literature, where topics related to HEAs (definition, thermodynamical calculations, microstructural and mechanical properties) are described, and content related to the selected manufacturing process.
- Chapter 3 presents the materials and methods used to fulfil of the project goals.
- Chapter 4 describes to results and discussion of all the activities developed, alongside some procedures with a more iterative character that were performed to optimise the *in-situ* alloying process based on the results.
- Finally, Chapter 5 summarizes the conclusions drawn from the work carried out and mentions future work perspectives that could be conducted to enrich this present work.

This dissertation also resulted in three accepted conference submissions for: poster presentation to the SPM - MATERIALS 2023 (Appendix 1); oral presentation to the Euro PM2023, which also resulted in a conference paper submission indexed by Scopus (Appendix 2), and an oral presentation to FEMS EUROMAT 2023 (Appendix 3).

02 LITERATURE REVIEW

High-Entropy Alloys (HEAs) can be classified according to their composition or configurational entropy. Turning to the first criteria, HEAs are normally defined as alloys that present at least five elements, with atomic percentages comprehended between 5 and 35 % [2]. However, they can also contain minor elements, with a mole fraction of less than 3.5% [6].

Yet, the description above does not explain the title "high-entropy alloys", so it is necessary to consider the total mixing entropy, where configurational entropy (ΔS_{conf}) predominates over the other three contributors, magnetic dipole, vibrational and electronic randomness, to classify an alloy as part of this group [1-2]. Boltzmann's equation may be used to express the system configurational entropy:

$$\Delta S_{conf} = -k \ln(w) \quad (1)$$

Where k is Boltzmann's constant, w is the number of possibilities that the available energy can be mixed or shared between system particles. Employing Equation 1, considering the molecularly configurable entropy for solid solution formation with n element and mole fraction x_i , it is possible to obtain the following expression:

$$\Delta S_{conf} = R \sum_{i=1}^n x_i \ln x_i \quad (2)$$

Through Equation 2, it is possible to divide materials and alloys currently used into three distinct groups according to their configurational entropy: Conventional alloys, such as steels and Al-alloys, are presented as low-entropy alloys ($\Delta S_{conf} < 1R$); Superalloys and Bulk Metallic Glasses (BMG) reported as medium-entropy alloys ($1R < \Delta S_{conf} < 1.5R$); and HEAs ($\Delta S_{conf} > 1.5R$), where this criterion does not limit the minimum five elements required for alloys to belong to this family [1,7].

The **high-entropy effect** plays a significant role in stabilising a solid solution against the intermetallic compounds, resulting in a less complex microstructure than the anticipated brittle heterogeneous structure. This behaviour can be explained thermodynamically by the Gibbs free energy of mixing (ΔG_{mix}); however, it will be further depicted alongside other thermodynamical parameters for phase prediction in point 2.2 of this chapter [1,7-8].

In addition to the high configurational entropy observed in HEAs, three other **core effects** (sluggish diffusion effect, severe lattice distortion effect, and cocktail effect) have been identified, which explain the superior properties of HEAs when comparing them to the conventional alloys [4].

Since the multi-element matrix of each solid solution in HEAs is an overall matrix, each atom will be bordered by different elements, leading to stress and a **severe lattice distortion** [8]. Furthermore, the different atomic sizes, binding energies, and crystal structure patterns between constituent elements will promote a more significant lattice distortion (Figure 2) since the nonsymmetric neighbouring atoms will affect the atomic position [2].

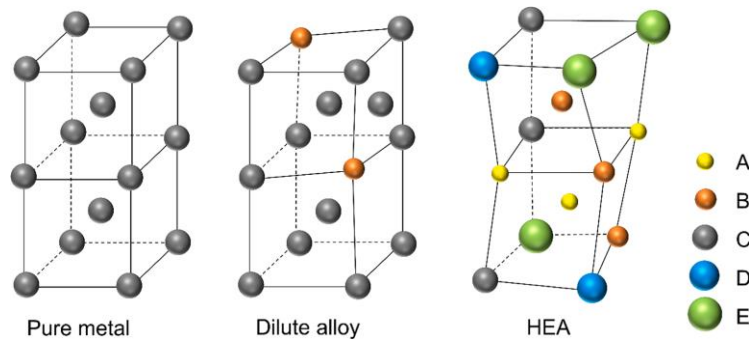


Figure 2: Schematic diagram showing the severely distorted lattice [5].

HEAs are often considered random and/or organised solid solutions, and their matrix can be considered a whole phase. As a result, an atom's diffusion in a whole-solute matrix differs significantly from the conventional alloy matrix. During diffusion, a vacancy is wrapped in the whole-solute matrix, tussled by different atoms, as explained by the **sluggish diffusion effect**. HEAs are believed to have higher activation energy and slower diffusion because of the increased variance in lattice potential energy across lattice sites [9]. As a result of this effect, HEAs tend to present exceptional high-temperature stability and strength and superior oxidation resistance [10-11].

Finally, these alloys can present one or multiple phases, depending on the composition and processing. The overall characteristics will be derived from the constituent phases' total contributions, depending on each phase's size, shape, distribution, phase borders, and attributes [9]. In addition, each phase behaves as a multicomponent solid solution whose characteristics are derived from the fundamental properties of components (**cocktail effect**), as determined by the mixing rule and from the mutual interchange of the elements present and the extreme lattice distortion. This includes anything from an atomic-scale multicomponent effect to a microscale multiphase effect [9,12].

As beforementioned, the HEA field has evolved rapidly and is no longer confined to single-phase solid solution microstructures, englobing multiphase structures, disordered solid solutions, amorphous phases, intermetallic, etc. [13]. Thus, the categorisation of these alloys has become a necessity. This could be achieved by considering several characteristics, such as mechanical and non-mechanical properties, microstructure, and composition of the alloys [5]. This study will analyse RHEAs and RCCAs in further detail since they have been emphasised as two families with the potential for high-temperature applications.

2.1 Refractory High-Entropy and Refractory Complex Concentrated Alloys

The terms RCCAs and RHEAs may be confused; however, currently, RCCAs can be defined as alloys containing between four to nine refractory elements, which present a multiple-phase structure with possible intermetallic components. On the other hand, RHEAs can be presented as single-phase alloys with a high configurational entropy [14].

The microstructural characteristics strongly control the materials' mechanical performance, thus being necessary to proceed to a correct alloy design in terms of composition to obtain exciting properties for a particular application [5]. RHEAs tend to present higher ductility and better high-temperature stability compared to RCCAs. In addition, multi-phase structures increase oxidation problems at high temperatures when more chemically distinct phases are present. Although, certain phases, such as the Laves phase, can significantly reduce room temperature (RT) ductility while increasing high temperature (HT) strength and improving RHEA oxidation resistance [3]. Therefore, ongoing research is still needed to develop new alloys that are both strong and ductile at RT and HT [5].

RHEAs/RCCAs usually present a brittle behaviour at RT due to the properties of its constituent elements and the possible segregation of impurities in the grain boundaries. However, a brittle-to-ductile transition is observed when loaded at higher temperatures due to electronic structure changes that induce the transition of elastic instability modes from tensile to shear failure [15].

Although RCCAs and RHEAs are both composed of refractory elements, the wide variety of compositions and microstructures possibly results in a significant range of reported values for the yield stress (σ_Y) and specific yield stress (σ_Y/ρ) at a specific temperature [3,13]. Figure 3 shows the variation of these two properties with the temperature increase. Due to the wide gap to fill in Figure 3, it becomes more and more relevant to the application of screening strategies, as the one proposed in this work on the MoNbTaW system allows a more efficient characterisation in a more significant number of simultaneous compositions.

The characterisation of RCCA/RHEAs at temperatures above 1200 °C is scarce, but the pioneering work of Senkov et al. [16] proved the capability of these materials under critical temperatures. They showed that the RHEAs MoNbTaW and MoNbTaWV present an increase of their plastic strain from 2% and 1.5%, respectively, to 10-15%, with an associated compressive strength of 421-506 MPa and 656-735 MPa, at temperatures up to 1600 °C. The high-temperature resistance of HEAs, similar to the Ni-superalloys, can also be explained by the slow elements' diffusion, which is related to the high melting temperature (T_m). The high-temperature softening occurs at $0.6T_m$, so this phenomenon is expected to be delayed with the increase of the T_m of the alloy in question, thus leading to better performance than certain nickel superalloys [16].

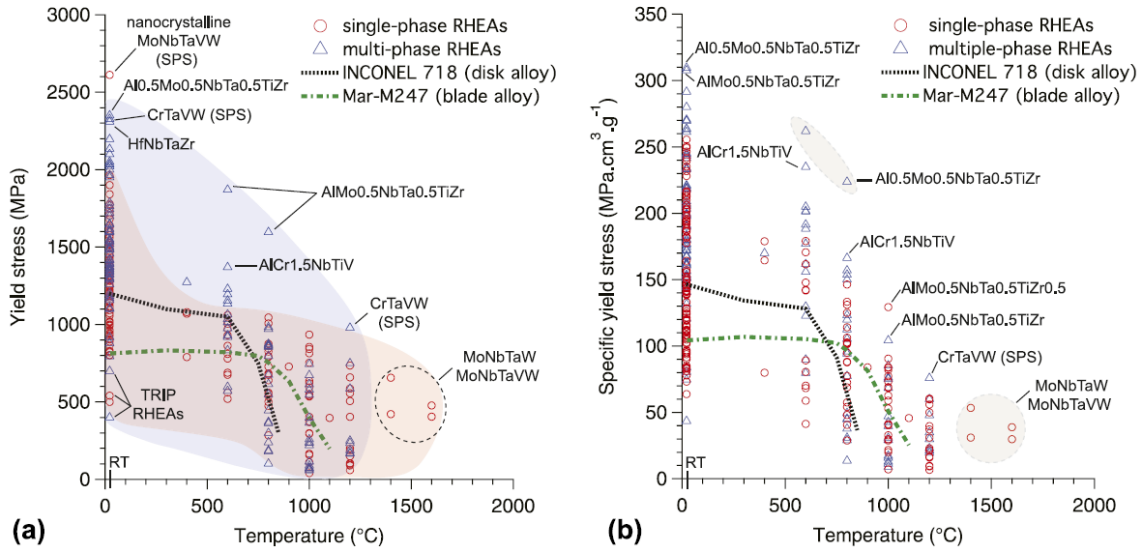


Figure 3: Temperature dependence of (a) yield stress and (b) specific yield stress for RHEAs and two representative Ni-based superalloys, Inconel 718 and Mar-M247 [3].

Nevertheless, RT properties can also be altered by alloying, for example, using group IV elements (Ti, Hf, and Zr) that lead to an increase in ductility. Han et al. [17] observed that the addition of Ti led to the improvement of the plastic strain to values above 10% and the increase of the σ_Y to 1343 and 1515 MPa, during compression, for the equimolar MoNbTaTiW and MoNbTaTiVW systems, respectively. Thus, the Ti additions enhanced the strength and ductility of the system previously reported by Senkov et al. [16], possibly due to the segregation of Ti and Nb, which are more ductile metals, in interdendritic regions.

Li et al. [18] studied the *in-situ* alloying of the MoNbTaWZr system and found that the additions of Zr lead to a strength and compressive strain improvement at RT when compared with the initial MoNbTaW system, from 1157 to 2340 MPa, and 1.7 to 17%, respectively, despite presenting two disordered body-centred cubic (BCC) phases (Figure 4).

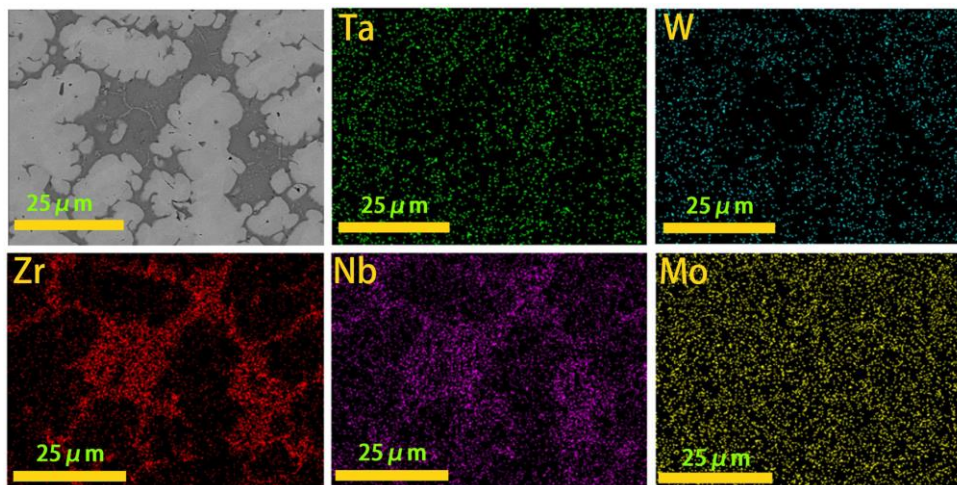


Figure 4: SEM/EDS mapping of Zr, Nb, Mo, Ta, and W elements in the ZrMoNbTaW alloy [18].

Although there is a clear focus on improving yield strength and ductility, alloying strategies can also be used to improve other properties, such as corrosion resistance. Al and Cr are two great examples of elements that could improve corrosion resistance due to the formation of adherent and protective films, as already observed in conventional alloys [19]. Regarding the effects of Al additions to the MoNbTaW system, it has yet to be discovered the precise effects due to the lack of publications on this topic. However, even though Cr can maintain the single-solid solution in the MoNbTaVWCr_x (with $x \leq 2$), the formation of Cr₂O₃ was not observed [20].

As it is possible to observe from the works described before, simply adding an element to a well-known system can lead to major changes in characteristics, utterly distinct from the background knowledge related to the conventional alloys. Hence, powerful predictive approaches based on thermodynamic parameters and experimentation have been developed to predict the microstructural and mechanical characteristics without unnecessary use of resources and time.

2.2 Thermodynamical Concepts for Phase Prediction in HEAs

Predicting solid solution stability in HEA has long been a topic of considerable interest in the HEA community, and it is critically important in terms of directing future HEA research for certain application-driven alloy designs. Assuming that the involvement of the kinetic factor is not considered, the Gibbs free energy controls thermodynamically the phase formation, being the final microstructure controlled by the relation between mixing enthalpy (ΔH_{mix}) and mixing entropy (ΔS_{mix}) [1,7-8].:

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix} \quad (3)$$

From Equation 3 is possible to conclude that a higher number of elements and higher temperatures can decrease the free energy of the mixture by increasing the last term of the equation to promote the formation of a stable solid solution over an intermetallic with lower configurable entropy [1,7-8]. Due to the higher mixing entropy, the Gibbs phase rule (Equation 4) will not be observed:

$$P + F = C + 1 \quad (4)$$

where P is the maximum number of phases, F is the degrees of freedom, and C is the number of components. Thus, it suggests that this effect favours the solid solution formation with simple structures and fewer components since the increased entropy of the multi-element composition is predicted to stabilize the microstructure [2,21-23].

However, other factors must be considered in the phase formation prediction. Hume-Rothery (HR) rules state that solid solutions are achievable when [2]:

- The size difference between the solute and solvent atoms is smaller than 15% and for complete solubility must be lower than 8%;

- Extended solid solubility is achieved when the crystal structures of the two elements are the same;
- Solubility is extended when the solvent and solute have the same valency;
- To prevent the formation of intermetallic compounds, the electronegativity of the two elements should be similar.

Contrary to conventional alloys, HEAs do not present a base/principal element, so the average atomic size mismatch parameter (δ) was created allowing the definition of the solid solution topological instability for multicomponent alloys:

$$\delta = \sqrt{\sum_{i=1}^n x_i \left(1 - \frac{r_i}{r}\right)^2} \quad (5)$$

where x_i and r_i represent the atomic fraction and atomic radius of each element i , respectively [24].

As beforementioned, forming a solid solution also requires that the elements have similar electronegativity and electron concentration. Allens' electronegativity difference in a multicomponent alloy ($\delta\chi^{Allen}$) can be defined as:

$$\delta\chi^{Allen} = \sqrt{\sum_{i=1}^n x_i \left(1 - \frac{\chi_i^A}{\chi^A}\right)^2} \quad (6)$$

where χ^A corresponds to the average Allen's electronegativity of the alloy, and χ_i^A to Allen's electronegativity of the i^{th} component [24].

Regarding electron concentration, it can be expressed by two distinct concepts: the average number of itinerant electrons per atom (e/a), and valence electron concentration (VEC). Both parameters have a clear effect on the structure; however, the e/a used for HEAs containing transition metals is highly controversial so, for convenience, only VEC is considered regarding the phase stability [25]. VEC can be defined by the following equation:

$$VEC = \sum_{i=1}^n c_i (VEC)_i \quad (7)$$

where $(VEC)_i$ is the VEC for each element. It has been observed that HEAs solid solutions present a BCC structure for $VEC \leq 6.87$, face-centred cubic (FCC) structures for $VEC \geq 8$, and in between it will be possible to observe a mixture of both structure phases [25].

Yang and Zhang [26] have proposed a new parameter, Ω , which considers the combined effects of ΔH_{mix} and ΔS_{mix} on the stability of a multicomponent solid solution:

$$\Omega = \frac{T_m \Delta S_{mix}}{|\Delta H_{mix}|} \quad (8)$$

$$T_m = \sum_{i=1}^n x_i (T_m)_i \quad (9)$$

Where T_m is the average melting temperature of the n -element alloy and T_i is the melting point of component i of the alloy [2].

Considering the different parameters stated above, several experimentations were conducted in an attempt to establish range values and correlations for the microstructure prediction. For example, Poletti and Battezzati [27], using Allen's scale, showed that the combination of $1\% < \delta < 6\%$, and $3 > \delta \chi_{Allen} < 6$ will lead to a solid solution without the presence of intermetallic phases. On the other hand, by studying the phase formation of different multicomponent alloys with the parameters Ω and δ , to form solid solution HEAs a $\Omega \geq 1.1$ and $\delta \leq 6.6\%$ need to be verified [2]. Thus, through the realization of the previous calculations and through the application of the conditions described by several authors, it will be possible to obtain a better compression of the type of structure that will be obtained before the effective production of the alloy.

Nevertheless, the determination and quantification of specific components, such as intermetallic, becomes impossible by this methodology; thus, other methodologies have been developed and will be described in the following chapter.

2.3 Simulation-assisted Design for RHEAs/RCCAs

Apart from thermodynamical calculations based on the first principles, phase diagrams serve as guidelines for materials design and process optimisation since they represent the first step to property speculation. However, the methodology is highly time-consuming and expensive when it is intended to obtain diagrams of ternary and higher-order systems over wide ranges of compositions and temperatures, as in the case of HEAs. The **CALPHAD** methodology stands as an alternative to this practical method (Figure 5).

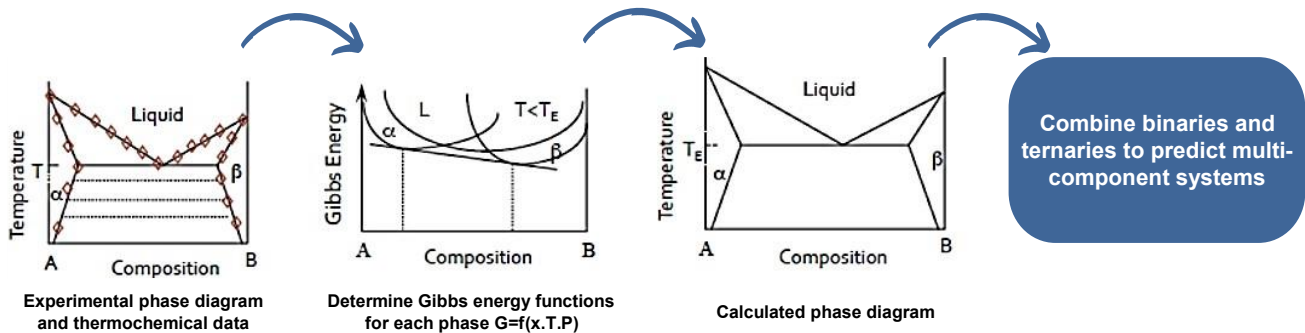


Figure 5: CALPHAD Methodology. Adapted from [28].

This phenomenological route initiates with the practical data acquisition of lower-order systems, binaries, and ternaries, or by “first principles” total energy information and phase equilibrium data. After selecting the thermodynamical models for each phase present in each lower-order system previously calculated, it is possible to obtain higher-order systems phase diagrams by extrapolation. The calculated multicomponent phase diagrams must be verified through standard experiments; however, the amount of experimentative effort involved is insignificant compared to the traditional approach [2,29].

Currently, a few databases are available for the specific study of HEAs, one of which is the TCHEA6 database integrated into Thermo-Calc software. The most recent version of the TCHEA6 database has 310 binary systems and 201 ternary systems assessed to the full range of compositions and temperatures, being left-out 301 ternaries for the same assessment. It is also important to mention that 515 solution and intermetallic phases are modelled in this version [28].

This approach, alone or combined with thermodynamic calculations, has already been proven effective and valuable for developing HEAs [30-32]. For example, Gao et al. [33] proposed the combination of first-principles calculations (i.e., enthalpy of mixing, atomic size mismatch, electronegativity difference, among others) with the CALPHAD approach for the design of innovative RHEAs. A total of sixteen equimolar alloys, ranging from quinary to enneadic systems, were designed. Afterwards, two alloys were experimentally verified by X-ray diffraction (XRD), energy-dispersive spectroscopic (EDS) and scanning electron microscopic (SEM). From this work, the key findings were: (1) empirical calculations are helpful for this type of alloy design; however, competing phase formations are not considered; and (2) CALPHAD provided a reliable thermodynamic database and proved an efficient tool in searching for new single-phase HEAs, precisely six new single-phase systems.

Nonetheless, every study focused on predicting the microstructural characteristics of the design alloys mentions the urgent need to assess if the simulated results are observed upon the alloy fabrication for proper optimisation of the model used in these methods.

2.4 Production Routes

Several routes can be utilized to produce HEAs. However, for RHEAs the high melting point is presented as an obstacle for their manufacturing. Four different processing routes have been highlighted in the literature as the most promising and capable of manufacturing these alloys: Casting processes [34-35], Coating processes (from thin coats obtained by CVD/PVD technologies to thicker ones produced by Laser Cladding) [36], Powder Metallurgy processes [37-41], and AM processes [42-44]. Since DED has presented a growing interest in both academic and industrial community and was the consolidation route chosen, this technology will be discussed in more detail.

2.4.1 Direct Energy Deposition (DED)

DED is a laser technology which has been used for some years as AM technology, enabling attractive design freedom [45-46]. In this process, a high-energy laser beam produces a melt pool by melting the filling material (powder and/or wire), which allows a particular part to be constructed layer by layer. Figure 6 shows a schematic representation of a powder DED nozzle and its most essential components [47-48].

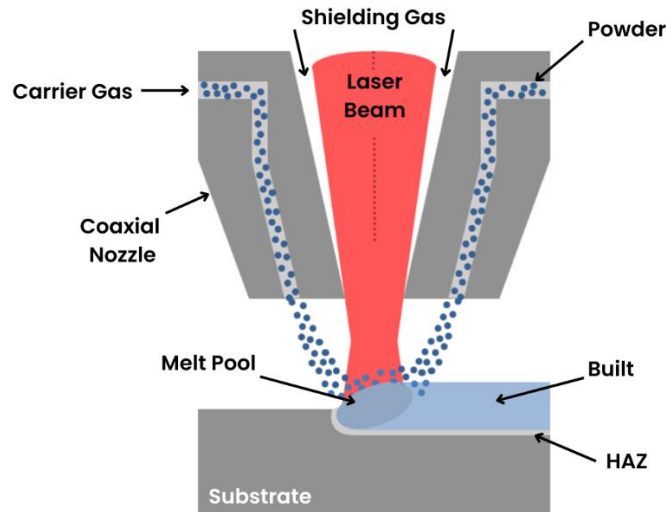


Figure 6: Schematic representation of powder DED equipment, adapted from [46].

Usually, a coaxial nozzle feeds the material into the previously mentioned melt pool, the material carried by an inert gas, enabling its flow. In the melt, high surface stress gradients occur, thus creating shear stresses at the surface of the liquid [49]. Shear stress at the free surface causes a high-velocity flow at the free surface, Marangoni-currents, which spreads to a thin surface layer due to fluid friction, and a much slower reverse flow in bulk [50].

The Marangoni-currents promote an intense mixing of the molten metal, leading to a uniform distribution of alloying elements from the molten substrate over the bead cross-section. As the material solidifies on the substrate, the DED equipment moves according to a particular path, creating a layer. Afterwards, the nozzle increases its height relative to the substrate, and the bead is formed, generating other layers until the desired part is finished [50].

In terms of the laser used by DED systems, it can be used several types of lasers, being the most commonly used the CO₂ lasers, the high-power diode lasers (HPDL), the neodymium: yttrium-aluminium-garnet (Nd:YAG) lasers, and the ytterbium fibre (Yb) lasers. The selection of the laser must be done considering the absorptivity of the materials at a specific wavelength. When the maximum absorptivity is observed for the laser wavelength, it will be possible to minimize the energy reflection losses, to guarantee a proper energy distribution, and to produce/repair parts [51].

Laser-deposited materials undergo a complex thermal path characterised by rapid solidification, rapid cooling, extreme temperature differences and repetitive heating and cooling cycles. As a result, microstructures are formed out of equilibrium, and there are noticeable structural differences between layers and even within individual layers. Furthermore, the microstructure and final properties are intricately linked to numerous process parameters that must be optimised based on the specific material. Process parameters are strongly influenced by material properties such as T_m , thermal conductivity, and laser absorption capacity, and this applies to each alloy [51].

There are several parameters to control in DED, although laser power, laser spot size, relative surface speed, and feed rate can be considered the most important to produce a part with the intended quality and characteristics [46,52].

Laser power, measured in Watts [W], translates the energy applied to the materials involved in the process, leading to the melting and formation of the intended structures. The selection of the laser power must be realised carefully, because when too high will lead to an increase in the dilution, and when too low can lead to a lack of fusion and adhesion to the substrate [46,52].

Laser spot size, measured in millimetres [mm], corresponds to the laser beam diameter and is inversely proportional to the energy density of the process [53].

Relative surface speed, usually measured in [mm/s], refers to the nozzle velocity. Since this parameter defines the time that the printing head stays at each point, it is possible to state that it will define several geometrical characteristics of the beads due to the restriction of energy applied and filling material deposited and the process productivity [52].

Lastly, **feed rate** represents the delivered quantity of raw material (powder and/or wire) into the melting pool in a particular period [52].

Nevertheless, these four parameters control can typically be completed by calculating several comparison parameters that allow for comparison between different DED systems, simplifying the parametrisation process, or even the process's energetic efficiency.

The power and energy density (Equation 10 and 11) correlates the laser power (LP) with the laser spot size (φ) and the two previous parameters with the relative surface speed (v) [54]:

$$\text{Power density } \left(W/mm^2 \right) = \frac{LP [W]}{\varphi [mm]} \quad (10)$$

$$\text{Energy density } \left(J/mm^2 \right) = \frac{P [W]}{v \left[\frac{mm}{s} \right] \times \varphi [mm]} \quad (11)$$

Given that the above process parameters are interdependent, it is possible to define new process parameters as combinations of existing ones or adjust the parameters from setup to setup. In this way, the value of such a function can then be varied linearly, which involves adjusting multiple parameters simultaneously, facilitating the optimisation of a particular DED process.

Another extremely important parameter, normally specific to each material, is energy efficiency (Equation 12) which correlates the laser power (LP) with the feed rate (FR) [55]:

$$\text{Energy efficiency } \left(\text{kg/kWh} \right) = \frac{FR \left[\frac{\text{g}}{\text{min}} \right] \times 60}{LP [W]} \quad (12)$$

From this parameter, it is possible to directly evaluate the efficiency of the process since it can obtain the material quantity that is being deposited concerning a specific unit of supplied energy. All the beforementioned parameters must be controlled and adjusted to manufacture a specific material or part with the best quality and characteristics according to the desired application [55].

Regarding the material's properties, several should be considered before the parameterization of a process window; however, T_m and melting range, laser absorptivity, thermal conductivity, and thermal coefficient of thermal expansion (CTE) are highlighted. The first two properties will determine the strategy of deposition and process window since they define the total energy input needed to prevent porosity and lack of fusion and the probability of increased microsegregation, solidification cracking, and non-uniform properties, respectively. The thermal conductivity and CTE will mainly condition the built quality, more especially the adherence, consolidation, thermal distortion, and even cracking [51].

After the production/repair of a part, it is vital to understand and quantify the efficiency and accuracy of the process in terms of the built geometrical and dimensional characteristics. Regarding this evaluation, track height and width, dilution ratio and wettability angle are the most commonly used; therefore, they will be described in the following sections [51].

More general geometrical characteristics of the built can be used as indicators of the built quality or efficiency, but also can indirectly serve as indicators of heat dissipation throughout the deposition. Tracks' height and width evaluation can be helpful in terms of process efficiency since if a single track presents a high height and width, fewer tracks will be needed to construct a particular part. However, it is mandatory to ensure the tracks' quality. On the other hand, the presence of thin single tracks with thin walls hampered the dispersion of heat from the molten area, resulting in elevated temperatures during construction and reduced cooling rates. Consequently, this has a direct impact on the microstructure and ultimate characteristics of the final product [51].

As mentioned, DED guarantees an excellent metallurgical bond; however, this effect leads to a heat-affected zone (HAZ) in the deposited-substrate interface and a mixing zone between these two materials. An exaggerated heat delivery increased the dilution zone, lowering the process yield since a large amount of material will be spent to ensure the bond and not promote the desired deposition. Therefore, the dilution ration evaluation is critical to ensure the intended bond and yield of the process. The dilution can be obtained by the ratio between the area of the bead below (A_s) the substrate and the total area (A_s and A_d), as observed in Equation 13 and the schematic representation in Figure 7 [56].

$$Dilution (\%) = \frac{A_s}{A_s + A_d} \times 100 \quad (13)$$

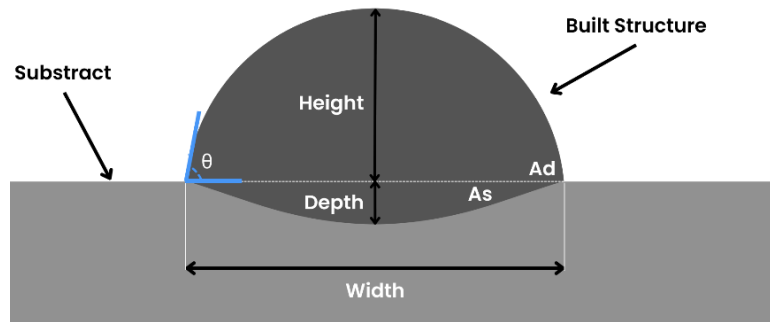


Figure 7: Schematic printed track during the DED process and significant dimensions, adapted from [56].

The dilution percentage can be controlled mainly by the laser power, relative scanning speed, and feeding rate. With the increase of the last two parameters mentioned above, the dilution will decrease since there will be less interaction between the laser and the materials being melted or because there will be a greater quantity of material to be deposited, respectively. In terms of the laser power, with its' increasing, the dilution will tend to increase due to the excessive heat delivered [57].

The wettability angle (θ) represents a quality indicator for plans and volumes constructions. The characteristic can be obtained by measuring the angle between the track and the substrate, as shown in Figure 7. For higher angles, the tendency to form defects when building more complex structures will increase since it will be more challenging to obtain a good bonding between tracks [58].

Despite the possibility to build and repair parts, DED presents an attractive feature since this type of technology can process several materials at once, making it possible to mix powders, wires with powders or even different wires. This characteristic enables DED to be used as a process capable of realizing *in-situ* mixing of materials, leading to, for example, functionally graded materials. The production of materials with varying compositions adds an extra level of intricacy, as each point along the gradient represents a distinct alloy with its unique set of properties. Consequently, achieving successful laser deposition of gradients may necessitate adjusting process parameters in a composition-specific manner for each build job [51].

2.4.1.1 DED as a tool for high-throughput screening of HEAs

After identifying the optimal process parameters, implementing laser deposition for gradient components is uncomplicated. There are two approaches for handling powders: (1) Pre-blending and loading, where powders can be pre-mixed together and loaded separately for each composition step; or by (2) multiple feeders, where a system can be equipped with multiple powder hoppers and feeders, allowing for the *in-situ* mixing of different powder types in varying quantities for each layer. Both approaches enable the creation of compositionally graded materials by controlling the powder mixing and deposition process in a sequential manner [51].

Due to this fact, DED, and similar technologies, such as LC, have already been proven to be effective methods for screening processes of several materials, such as CCAs and HEAs. Li et al. [59] showed the suitability of LC to produce RHEAs based on the system $W_xNbMoTa$ with x varying from 0, 0.16, 0.33, and 0.53. Regarding the microstructural characteristics, it was possible to observe that any of the W concentrations studied would lead to a single-phase solid solution of the BCC structure as observed by the SEM and XRD analysis presented in Figure 8a and 8b, respectively.

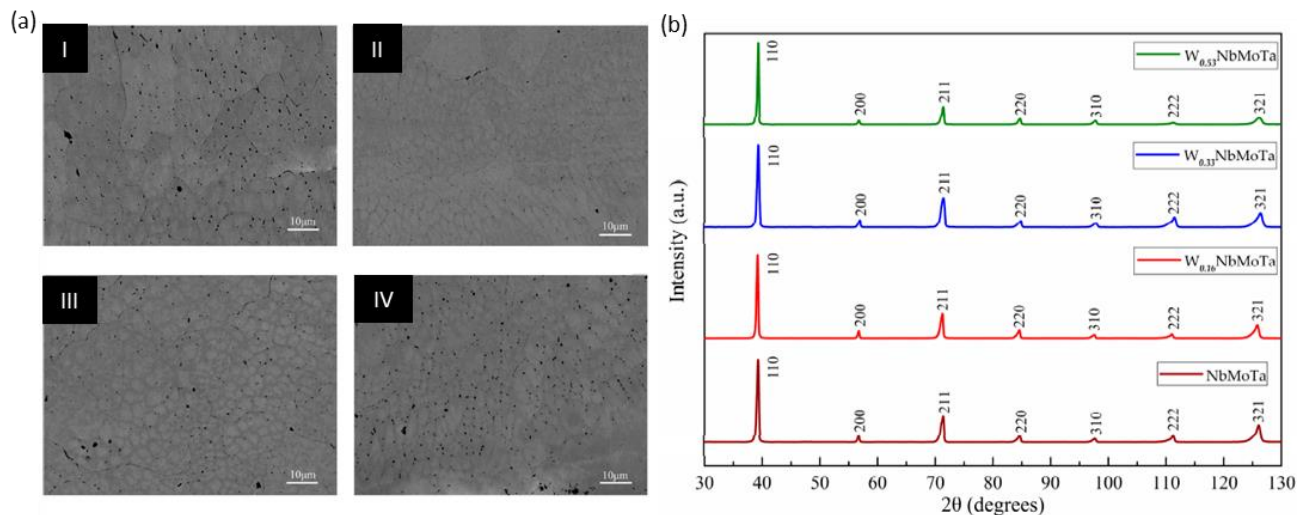


Figure 8: (a) Microstructure of the $W_xNbMoTa$ RHEAs: (I) NbMoTa; (II) $W_{0.16}NbMoTa$; (III) $W_{0.33}NbMoTa$; (IV) $W_{0.53}NbMoTa$; (b) X-ray diffraction (XRD) patterns of the $W_xNbMoTa$ [59].

Kuczyk et al. [60] reported the alloy design and microstructure evolution of the *in-situ* alloying of the CoCrFeNi alloy with Al through LMD. Based on the results presented, it is possible to conclude that LMD techniques are compelling and reliable for the screening of HEAs, resorting to a considerably low number of resources when compared to methods like casting. On the other hand, it was possible to confirm that these types of processes lead to a non-equilibrium solidification; however, the equilibrium structures could be achieved by means of heat treatments. Although CALPHAD simulations were used in this work, this type of methodology can be used more effectively, as it was used in the following work.

Vary et al. [61] also proved the suitability of DED for producing perform *in-situ* alloying for the high throughput of different HEAs. It was showed the advantages of using the CALPHAD methodology for accelerating and predicting the microstructural properties of these alloys. The combination of CALPHAD simulations with Python post-treatment of the acquired data made it possible to study more than 10000 compositions of CrFeNiMoTi system. Afterwards, with the possibility of *in-situ* alloying, composition gradients were deposited, obtaining “all-in-one” samples (Figure 9) that allowed the intended characterisation while reducing the number of samples, time consumed in the sample’s preparation and decreasing the raw materials used.

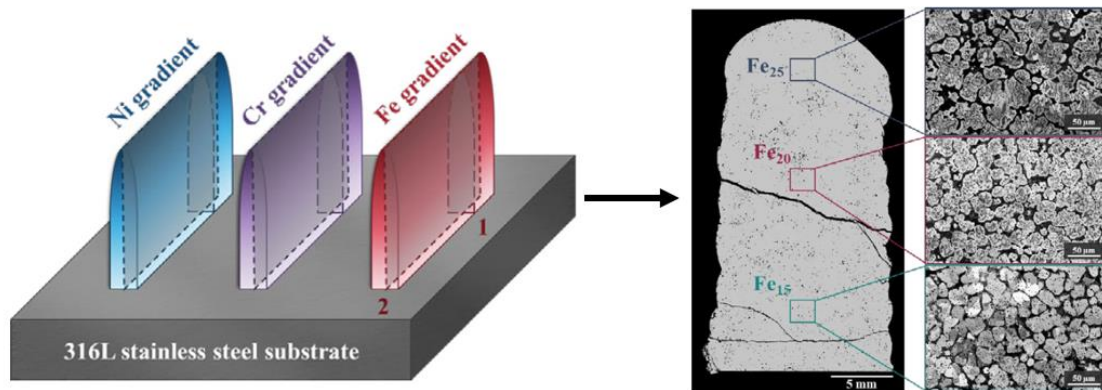


Figure 9: Example of the methodology used for high-throughput screening of HEAs by DED, adapted from [61].

03 MATERIALS AND METHODS

In this chapter, the practical procedures conducted are described. Figure 10 depicts the main tasks executed during the practical work developed in this dissertation, being therefore divided into the following groups: (1) simulation-assisted design for RCCA/RHEAs; (2) Powders characterisation; (3) MoNbTaW parts production by DED (optimisation and characterisation); and (4) *in-situ* alloying for high-throughput of RCCA/RHEAs.

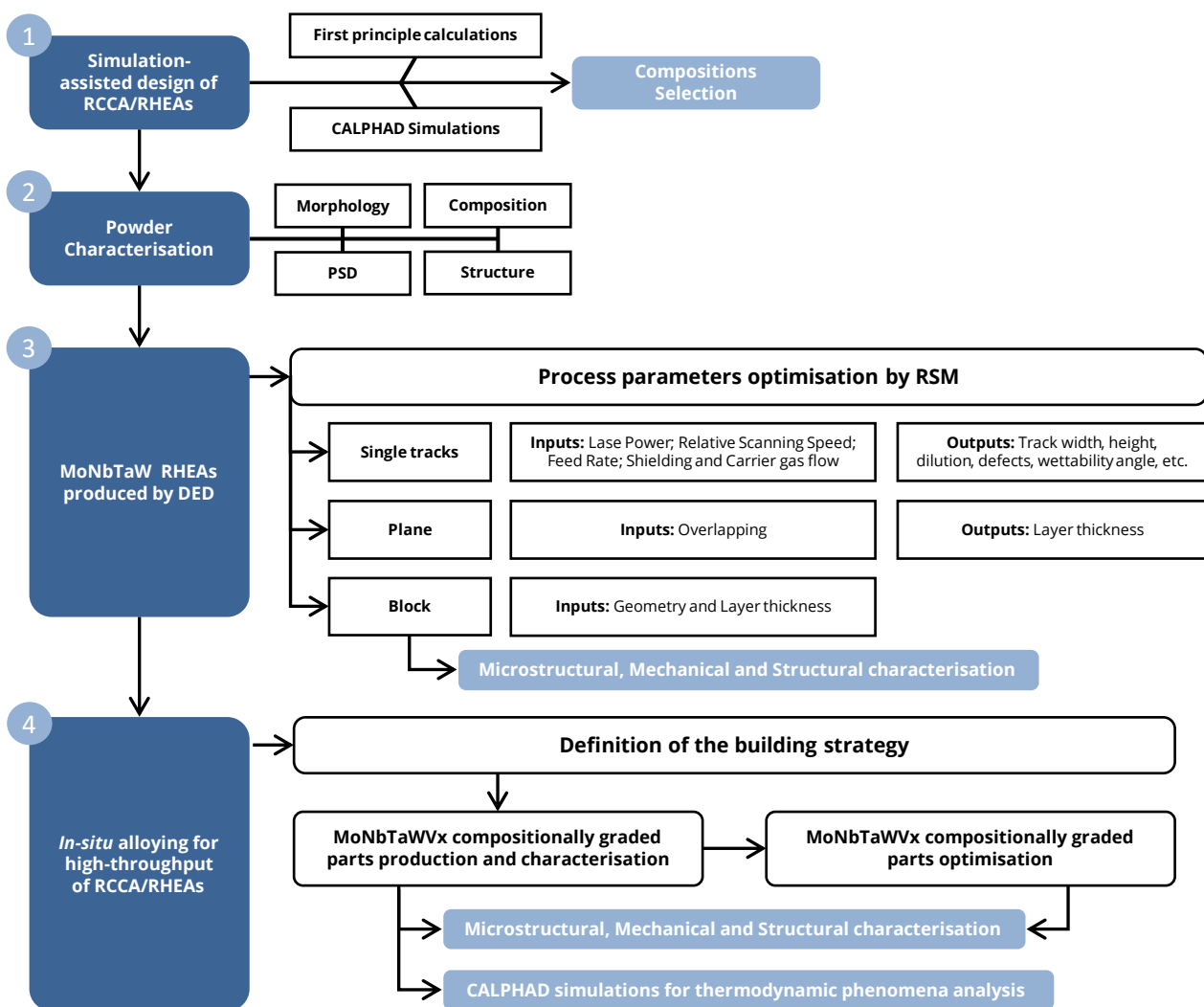


Figure 10: Overview of the experimental procedure.

3.1 Simulation-assisted design of RCCA/RHEAs

Initially, first principles calculations were performed, according to the thermodynamical parameters described in chapter 2.2, using the High-Entropy Alloys Predicting Software (HEAPS) [24]. In Table 1 the most relevant elements properties used for the phase prediction calculations are shown.

Table 1: Relevant elements properties used for the phase prediction calculations [24].

Element	Nb	Mo	W	Ta	V	Ti	Cr	Al	Zr
Atomic Radius (pm)	142.9	136.2	136.7	143	131.6	146.2	124.9	143.2	160.3
Melting point (K)	2750	2896	3695	3290	2183	1941	2180	933	2128
Allen electronegativity (-)	1.41	1.47	1.47	1.34	1.53	1.38	1.65	1.61	1.32
VEC (-)	5	6	6	5	5	4	6	3	4
Atomic Weight (g·mol ⁻¹)	92.91	95.95	183.84	180.95	50.94	47.87	52	26.98	91.22
Density (g·cm ⁻³)	8.58	10.23	19.41	16.68	6.12	4.5	7.19	2.7	6.51

Afterwards, equilibrium and non-equilibrium thermodynamical simulations were performed through the Thermo-Calc Software, version 2023a, with TCHEA6 High Entropy Alloys database. Equilibrium simulations were executed with the Material-to-Material function, obtaining pseudo-binary phase diagrams for the system MoNbTaWX (X = Al, Ti, V, Cr, and Zr). In terms of the non-equilibrium simulations, *Scheil* with Solute Trapping model was used since it is the most appropriate for AM processes such as DED, concerning the alloys compositions (MoNbTaW)_{100-a}X_a (X= Al, Ti, V, Cr, and Zr), with *a* ranging from 0 to 50% with a 5 at% step.

3.2 Materials

MoNbTaW alloy powders (45-150 µm) were purchased from TANI OBIS (TANI OBIS GmbH, Goslar, Germany), and V powders (45-150 µm) from AEM (Advanced Engineering Materials Limited, Hunan, China). Both as-received powder batches were characterised through scanning electron microscopy with energy dispersive spectroscopy (SEM/EDS), using a FEI Quanta 400 FEG ESEM with an EDAX Genesis X4M EDS. The particle size distribution (PSD) was also measured through laser diffraction by means of a Beckman Coulter LS230 (Beckman Coulter Inc., California, USA) with a measuring range of 0.04 to 2000 µm using PIDS (polarisation intensity differential scattering) technology. X-ray diffraction (XRD) was used to identify the phase structure of both powders. These analyses were conducted in a SmartLab SE X-ray diffractometer (Rigaku), in transmission mode, equipped with D/teX Ultra 250 is a 1D silicon strip detector and using Cu K_α radiation (λ= 1.54060 Å), that presented a Bragg-Brentano geometry. The acquisition was carried out within 2θ range from 30 - 140°, with a step size of 0.02° and an acquisition time of 5°/min.

It is also important to mention that a SAE 316L stainless steel (SS) substrate, provided by Ramada Aços (Ramada Aços e Indústrias, SA, Aveiro, Portugal), was used for all the depositions realised in the scope of this dissertation.

3.3 DED setup

To produce all the samples analysed during this dissertation, a DED setup (Figure 11) mounted and fully operating at INEGI was used. The setup used during the execution of the present work consisted of a Coherent Highlight FL3000 fibre laser (Coherent, Santa Clara, CA, USA), capable of delivering power of up to 3 kW and a laser spot size of

2.1 mm and a KUKA 6 axis robot (KUKA, Augsburg, Germany), paired with a COAX12V6 nozzle (Fraunhofer IWS, Dresden, Germany). Two Fraunhofer IWS powder splitters and a Fraunhofer E-MAqS system were also mounted. Argon (purity $\geq 99.99\%$) was used as shielding and carrier gas.

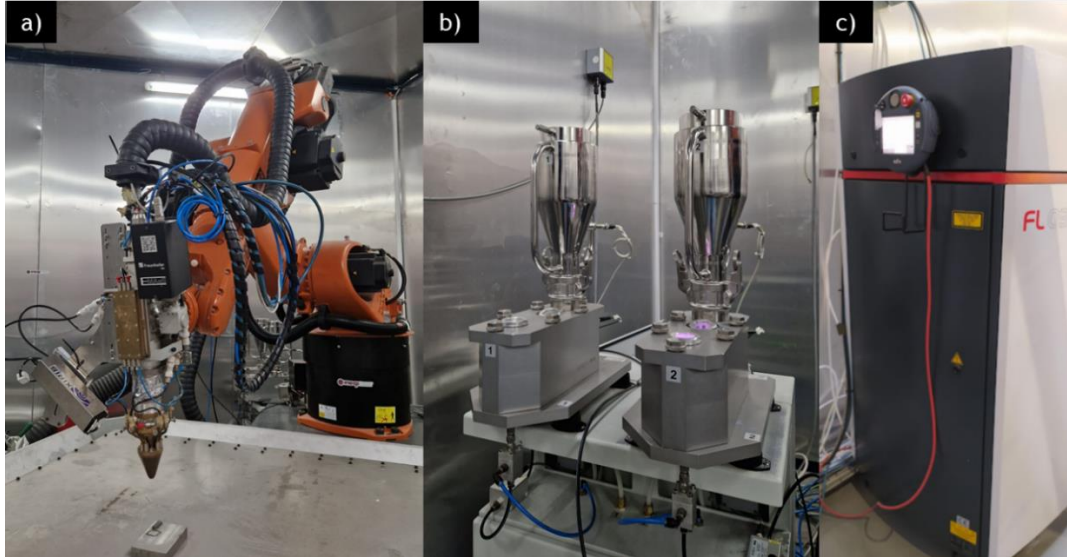


Figure 11: DED setup used for the depositions: (a) KUKA 6-axis robotic arm mounted with the COAX12V6 nozzle, powder splitter, and E-MAqS system; (b) powder feeders; (c) fibre laser.

3.3.1 Process Parameters Optimisation

Due to the lack of literature on the processing of the base RHEA under study, the process parameters window studied was built around the optimal process parameters selected for Inconel 718 in a previous study using the same DED setup. Since one of the goals of the LiRAs project is to develop novel material for high-temperature applications similar to the Inconel 718, it was considered a valid reference point for these parameters, which were: LP: 1800 W; v : 1600 mm/min FR= 25 g/min. Although the MoNbTaW base system presents almost double the melting temperature of the Inconel 718, some adjustments were made to ensure the melting of the powders and the quality of the builds. The parameters optimisation focused on the LP (W), v (mm/min) and FR (g/min), which were varied at three levels, as shown in Table 2, producing a total of twenty-seven ($3^3=27$) single tracks with 20 mm of length.

Table 2: Design of Experiments Levels used in the MoNbTaW single tracks optimisation

	Limits of the Design of Experiments		
Laser Power (W)	2000	2500	2700
Relative scanning speed (mm/min)	300	500	700
Feed Rate (g/min)	10.0	12.5	15.0

Besides the parameter adjustments, other strategies were adopted to ensure the MoNbTaW powder's total melting. The respective adjustments were the increase of the working distance from 13 mm to 14 mm (when comparing with the working distance used for the Inconel 718), the decrease of the carrier gas flow rate, and the increase of the

shield gas flow rate. The first two strategies were realised to increase the time the powders would contact the laser. Regarding the last one, this was used to minimise the oxidation problems that could occur since there was not an inert atmosphere during the depositions.

3.3.1.1 Cross-section geometrical characteristics analyses of single tracks

To assess the geometrical characteristics of each track deposited, all tracks were cut transversally and polished using silicon carbide abrasive paper, according to the following sequence: 400 - 800 - 1000 - 4000 mesh. Afterwards, polishing was finished with the resource to 1 μm diamond suspension and 0.03 μm colloidal silica. The cross-section images were obtained by resorting to a digital microscope from Leica, model LEICA DVM6, using the software *LasLeica*, allowing the measurement of the geometrical characteristics, such as deposit geometry (height, depth, wettability angle, and width), dilution (%), etc., through the software Image J (version 1.51, Wayne Ras-band, National Institutes of Health, Bethesda, MD, EUA). These measurements were used as inputs for the process parameters optimisation.

3.3.2 Samples production

With the optimal process conditions, ten samples, with varying layers composed of two single tracks each, were built with a zigzag printing strategy, using an overlapping of 40%. Due to the iterative character of the work developed, the deposition characteristics of the blocks produced will be duly presented before their characterisation. Regarding the samples with compositional gradients, the feeding parameters of each powder (MoNbTaW and V) were set to prefetch the optimal amount of g/min obtained after optimisation.

3.4 Microstructural characterisation

Regarding the microstructural characterisation, the cross-section of all the samples built were mounted through cold mounting with epoxy resin and were grinded and polished using silicon carbide abrasive paper, according to the following sequence: 400 - 800 - 1000 - 4000 mesh. Afterwards, polishing was finished with the resource to 1 μm diamond suspension and 0.03 μm colloidal silica with minor addiction of NH_3 and H_2O_2 .

The microstructure characterisation was, initially realised by OM for a more general understanding of the obtained structure, where all the specimens were previously etched for 40 seconds with an HCl , HNO_3 , and HF [2:1:2] solution. Afterwards, a more in-depth analysis was accomplished by SEM with an EDS detector, using the same equipment aforementioned. Electron backscatter diffraction (EBSD) analysis has been used to assist the phase identification of the first sample produced with the EDAX-TSL OIM EBSD (EDAX Inc. (Ametek), Mahwah, NJ, EUA) detector.

3.5 Structural characterisation

The structural analysis of all the compositionally graded and MoNbTaW specimens was accomplished through the beforementioned XRD equipment, with an acquisition carried out within 2θ range from $30 - 140^\circ$, with a step size of 0.02° and an acquisition time of $5^\circ/\text{min}$. Two approaches were used for a more general or targeted analysis of the graded specimen's characterisation. The area analysed in each approach was possible due to the positioning variation of the specimens, thus varying the zone where the beam would interact with the sample under study. Figure 12 is presented a schematic representation of the setup used.

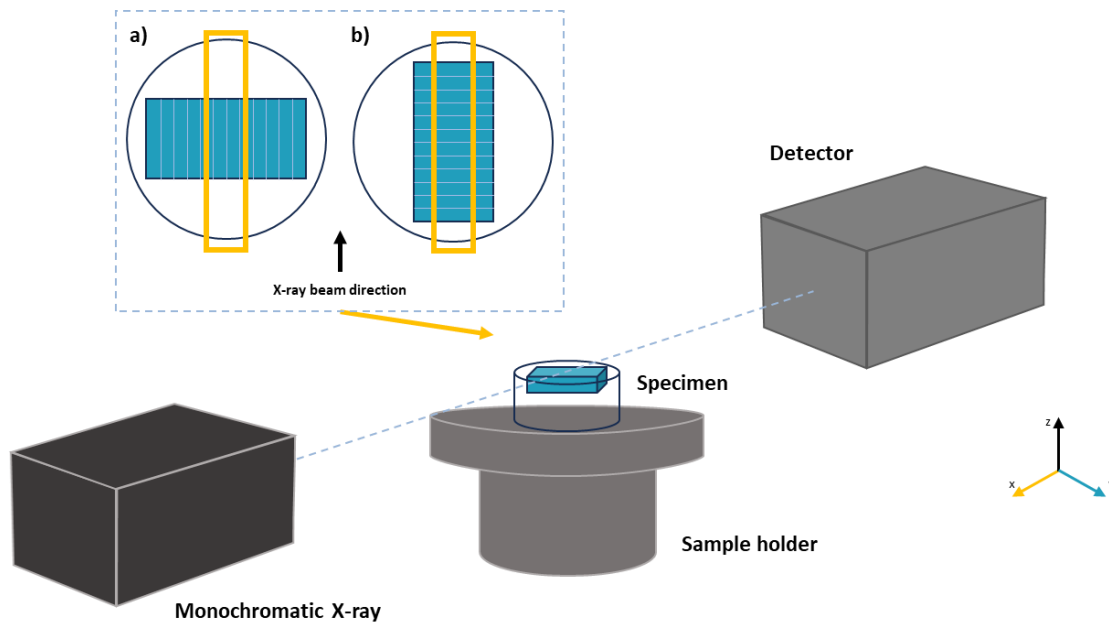


Figure 12: X-ray diffraction setup (not to scale): (a) position for a targeted analysis; (b) position for a global analysis.

3.6 Microhardness characterisation

The mechanical characterisation was performed by a FALCON 400 micro/macro-Vickers hardness tester (INNOVATEST). All measurements were performed according to the ISO 6507-1:2005 standard, where 10-15 indentations were made in each built sample, with a nominal test force of 9.807 N (HV 1) applied for 15 seconds. For the hardness profile, the same conditions were utilised, passing through the entire length of the specimens, maintaining a distance between indentations of $300\text{ }\mu\text{m}$.

Finally, as the entire work developed presents an iterative character, some briefer procedures will be described in full detail during the presentation and discussion of results to facilitate the understanding of the overall thrust of this work.

04 RESULTS PRESENTATION AND DISCUSSION

As described in Figure 10, the results will be divided in an identical way as the experimental procedures were subdivided, therefore presenting the following sub-chapters: (1) simulation-assisted design for RCCA/RHEAs; (2) powders characterisation; (3) MoNbTaW parts production by DED (optimisation and characterisation); and (4) *in-situ* alloying for high-throughput of RCCA/RHEAs.

4.1 Simulation-assisted design of RCCA/RHEAs

In this chapter, the phase calculations prediction and simulation-assisted design for RHEAs/RCCAs using the CALPHAD methodology are presented, for the system MoNbTaWX (X = Al, Ti, V, Zr, Cr), as a tentative to combine the results by these methodologies to access which of the beforementioned elements will lead to a single-phase structure when added to the base alloy. This structure is selected due to its capability of presenting promising properties for high-temperature applications, as described in sub-chapter 2.1.

4.1.1 First principles calculations for phase prediction

Initially, the combination of the average atomic size mismatch parameter (δ), Allens' electronegativity ($\delta\chi_{Allen}$), valence electron concentration (VEC), and the ratio between entropy and enthalpy (Ω) were used for the phase calculations prediction. For each thermodynamical parameter and their evolution with the addition of a certain element to the MoNbTaW system can be seen in Figure 13 and Figure 14. As mentioned in chapter 2.4, to obtain a single solid solution free of intermetallic phases it is necessary to correspond to several conditions. As stated by Poletti and Battezzati [27], the combination of $1\% < \delta < 6\%$, and $3\% > \delta\chi_{Allen} < 6\%$ is necessary to obtain the intended structure. On the other hand, Yang and Zhang [26] proposed that a solid solution is obtained when $\Omega \geq 1.1$ and $\delta \leq 6.6\%$.

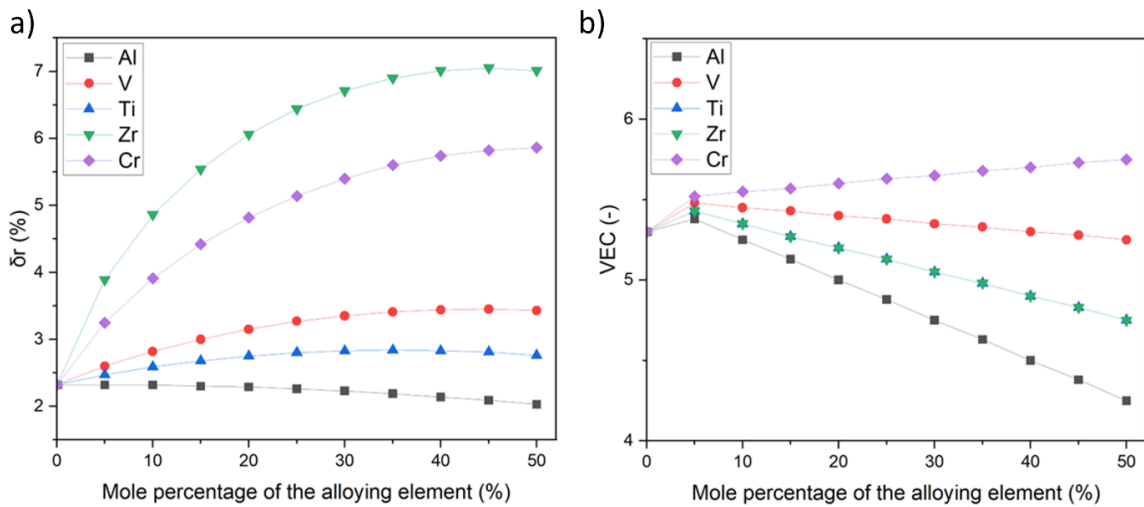


Figure 13: Solid Solution parameters related to the MoNbTaW-based RHEA/RCCAs: (a) atomic size mismatch; (b) Valence electron concentration (VEC).

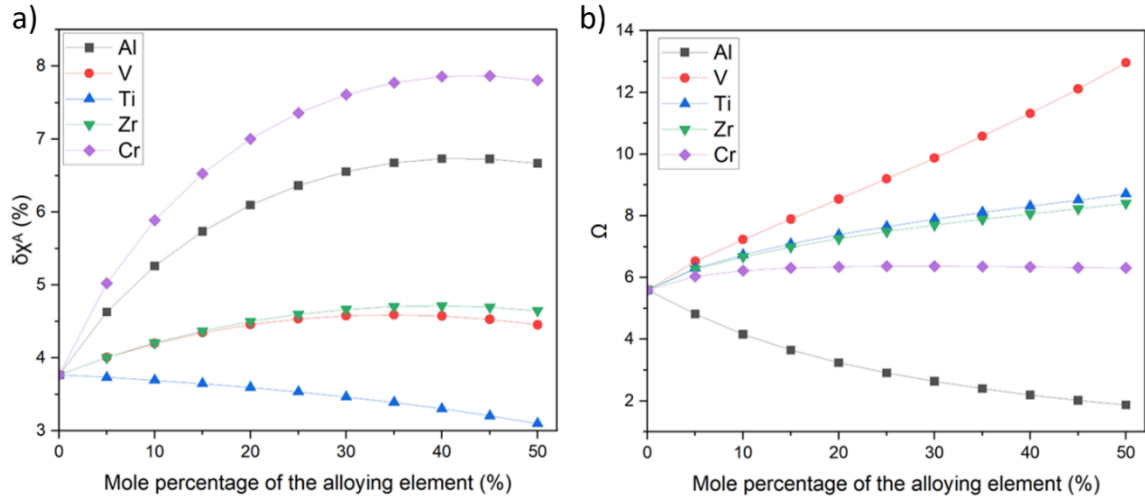


Figure 14: Solid Solution parameters related to the MoNbTaW-based RHEA/RCCAs: (a) Allens' electronegativity; (b) Ratio between Entropy and Enthalpy.

Assuming these two conditions, it is possible to conclude that only the systems MoNbTaWV and MoNbTaWTi present a single solid solution for every composition studied. Regarding the remained systems, this type of structure is only observed for additions inferior to 20 at% of Al, Zr, and Cr. In terms of the principal structure, since every alloy studied presents a VEC inferior to 6.87, it is possible to expect a BCC structure.

Although the type of alloy's microstructure is a crucial factor for the alloy selection, there are other factors of interest to consider, namely its T_m and ρ , extremely relevant properties when applied in aerospace industry systems. The influence of the studied alloying elements on the previous properties is presented in Figure 15.

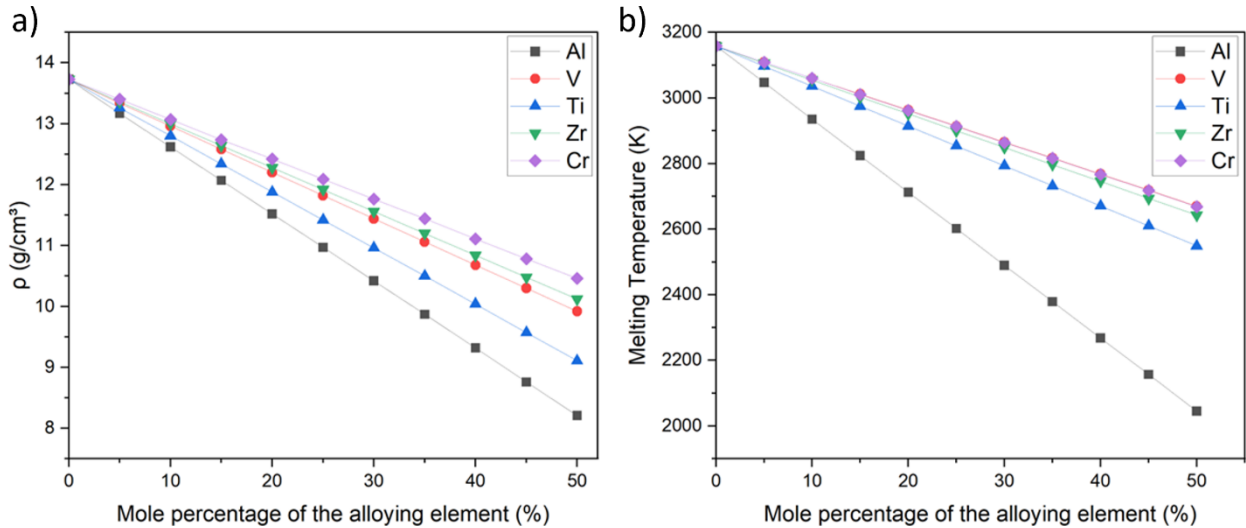


Figure 15: Influence of the proposed alloying elements on the (a) density and (b) melting point.

Al is the element that shows the most significant influence in both density and melting temperature. Even though the MoNbTaWAl system does not present a single-phase structure, its interest in reducing the density of the initial quaternary system cannot be disregarded. In terms of the T_m , despite its decrease, it is well above the T_m of Ni-alloys currently used in the applications in question, thus being a candidate of interest study.

However, it is crucial to consider that since the field of HEAs covers a wide range of compositions, these parameters were only established based on a particular set of alloys, making it difficult to predict if a particular system will behave similarly [2]. So, to enrich the beforementioned results, the CALPHAD methodology was used to evaluate the type and quantity of possible intermetallic structures that could be observed and confirm the previous results in sub-chapter 4.1.1.

4.1.2 CALPHAD simulations of pseudo-binary diagrams

CALPHAD simulations were performed, assuming an equilibrium cooling rate and allowing the construction of pseudo-binary phase diagrams for the systems of interest. For multicomponent phase diagrams, two-dimensional sections are usually plotted with some compositional variables held constant to facilitate their comprehension. In this case, the relation between the Mo, Nb, Ta, and W was kept constant, only varying their proportion to the added alloying element. It is also relevant to mention that in a quinary system, an invariant reaction involves a total of five reactants and products. For example, the reaction $\alpha \rightarrow \beta + \gamma + \delta + \theta$ is a clearly “eutectic type” invariant reaction. However, in these multicomponent systems, the classification can be quite difficult since the construction of *liquidus* surfaces was not possible the reaction classification. Yet, these diagrams can be used as valuable tools for the alloying effect evaluation [62].

In an early stage, the quaternary system MoNbTaW was studied to verify if the results would be identical to the literature [16], and, as expected, the system presented a single solid solution with a BCC structure (Figure 16) with a melting temperature of 3158 K (2885 °C), as also observed in the first principles calculations (Figure 14b).

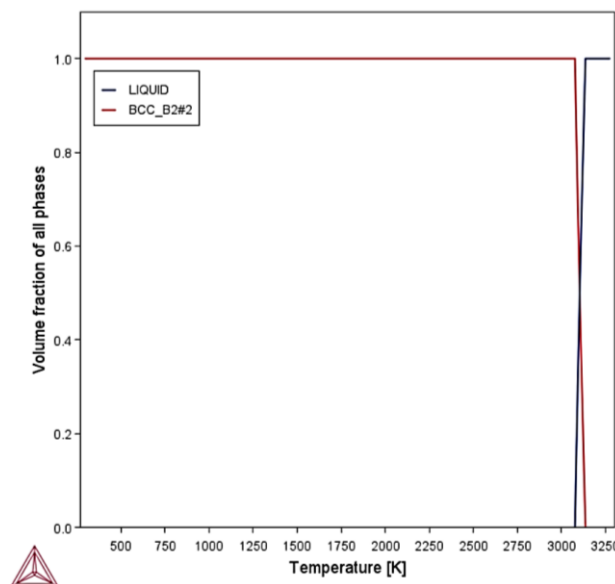


Figure 16: Mole fraction of equilibrium phases at various temperatures in the MoNbTaW equiatomic alloy.

Regarding the MoNbTaWV and MoNbTaWTi, in contrast to the results related to the phase prediction calculation, neither system presents a single solid solution structure. In Figure 17a, it is possible to observe that V leads to the formation of a miscibility gap for temperatures inferior to 1250 K (977 °C), thus forming a two-phase structure of two solid solutions with a BCC_B2 structure [63]. Ti (Figure 17b) has a similar effect as V; however, for lower temperatures, it is possible to verify the formation of a two or three-phase structure with a Hexagonal close packed (HCP) or BCC_B2 structure. Yet, both systems present a vast single solid solution domain for higher temperatures, the main structure of interest, thus becoming promising for high-temperature applications.

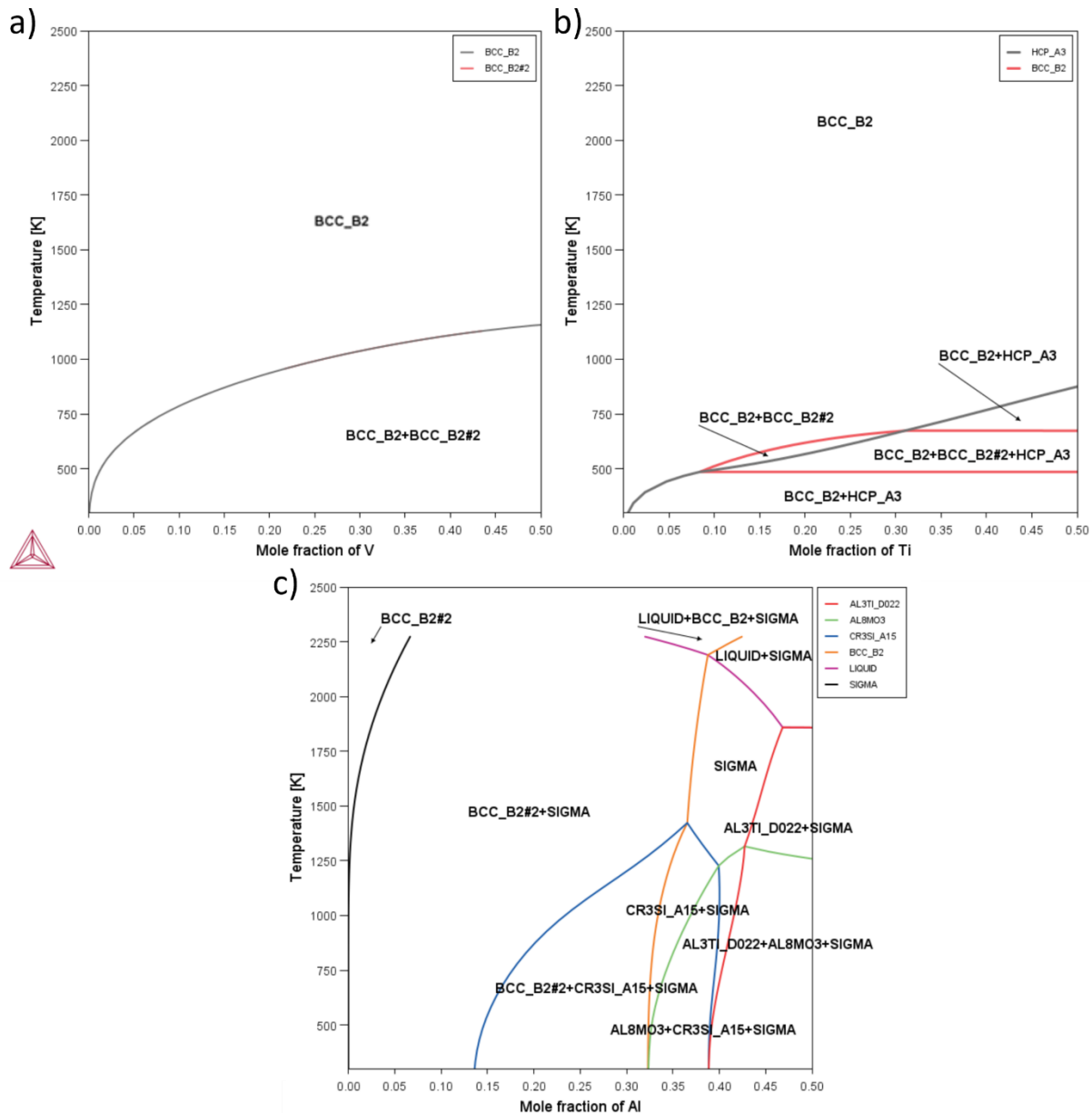


Figure 17: Pseudo binary phase diagrams for the systems (a) MoNbTaWV_x, (b) MoNbTaWTi_x, and (c) MoNbTaWAl_x.

As expected, the MoNbTaWAl system (Figure 17c) presents the formation of several intermetallic phases with the increase of the Al content. The main intermetallic observed is the sigma phase, commonly known to increase hardness and brittleness [61]. With the addition of 10 at% of Al, the sigma phase is formed, with a volume percentage of approximately 30%, being the remaining structure a solid solution with a BCC structure. With the addition of this amount of Al there will likely be an increase in hardness and brittleness of the alloy and, simultaneously, no significant reduction of the density. Thus, despite the interest in reducing the density, the predicted microstructural characteristics diminish the interest in Al alloying, as there would be a marked decrease in the alloy's ductility.

Concerning the MoNbTaWCr and MoNbTaWZr systems, which can be seen in Figure 18a and 18b, respectively, both present the formation of several intermetallic components. However, it is possible to highlight the formation of the Laves phase, which has been speculated to be a phase capable of considerably improving the mechanical strength of HEAs at high temperatures [3].

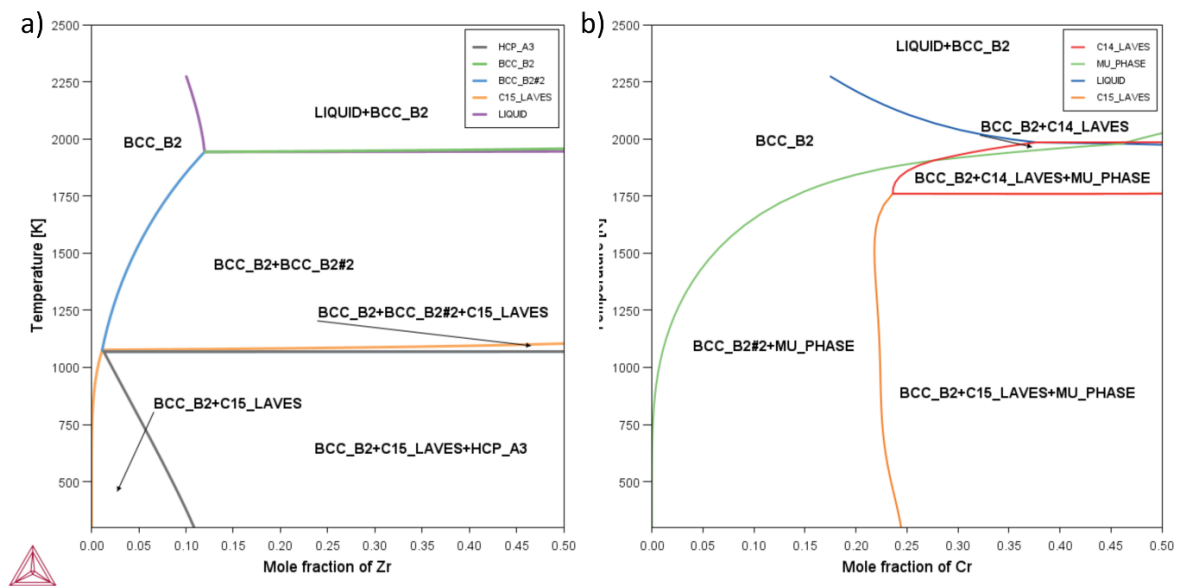


Figure 18: Pseudo binary phase diagrams for the systems (a) MoNbTaWZr_x and (b) MoNbTaWCr_x.

The construction of the equilibrium diagram is relevant for the structural property's prediction in several processing routes, such as casting, and for a general understanding of the alloying effect. However, since the alloys manufacturing will be realised by DED, the final structures will not present equilibrium characteristics. Therefore, non-equilibrium simulations were realised, by means of the *Scheil* with Solute Trapping model, to predict the influence of the rapid cooling rate on the microstructural characteristics.

Due to the fast-cooling rate, the MoNbTaWV (Figure 19a) and MoNbTaWTi (Figure 19b) present only the formation of a BCC_{B2} structure, showing, therefore, the intended structure for high-temperature structural applications. This type of result could be related to the stabilisation of a high-temperature structure, such as a single BCC_{B2} structure

observed on the equilibrium diagram, or due to the slow diffusion rate in HEAs explained by the high-entropy effect or sluggish diffusion effect, respectively.

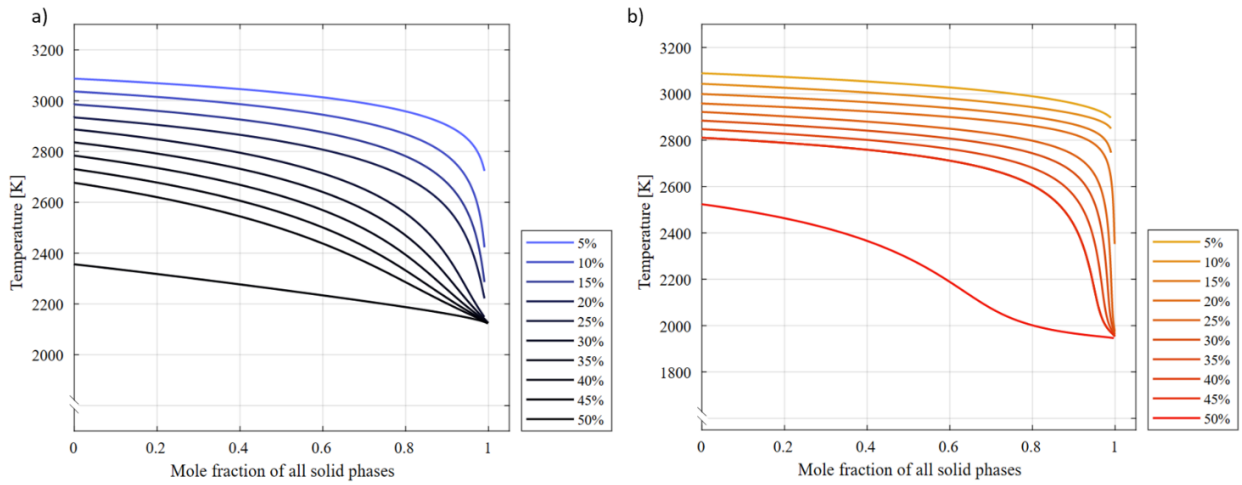


Figure 19: Scheil with Solute Trapping simulation of the phase transformation from $L \rightarrow BCC_B2$ for the (a) MoNbTaWV and (b) MoNbTaWTi systems.

From the *Scheil* curves, it is shown that the melting range, the difference between *liquidus* and *solidus* temperatures, is extensive large for V and for Ti addition higher than 15 at% to the base system. With the increase of the melting range, unwanted phenomena, such as microsegregation, solidification cracking, and overall heterogeneous properties, will be more likely to be observed when solidified under rapid cooling rates experienced by DED.

Since the systems with Al, Cr and Zr additions present several phases during solidification, the graphical representation of the Scheil curves grouped by each system was not performed since it presents high complexity making it imperceptible. In the MoNbTaWAl system, Figure 20, it is possible to observe that the brittle sigma phase is still present and could even exceed the amount of BCC_B2 solid solution at higher additions of this alloying element.

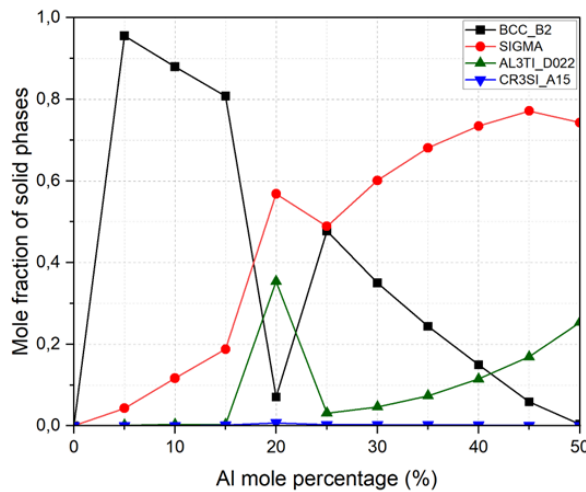


Figure 20: Mole fraction of non-equilibrium phases with the increase of Al.

However, the decrease in the amount of sigma phase compared to equilibrium cooling situations makes adding this element more promising. This variation of the phase relation could be justified by the high cooling rate, which does not allow for a complete redistribution of alloying elements, blocking certain phasic transformations.

Finally, in the MoNbTaWZr and MoNbTaWCr systems, Figure 21a and Figure 21b, respectively, it is possible to observe significant differences in the equilibrium diagrams. With the Zr additions, it is observed the formation of two BCC_B2 structures and almost the elimination of the Laves phase. On the other hand, the MoNbTaWCr system presents a single solid solution structure with the increasing formation of the Laves phase, following the increase in the Cr content.

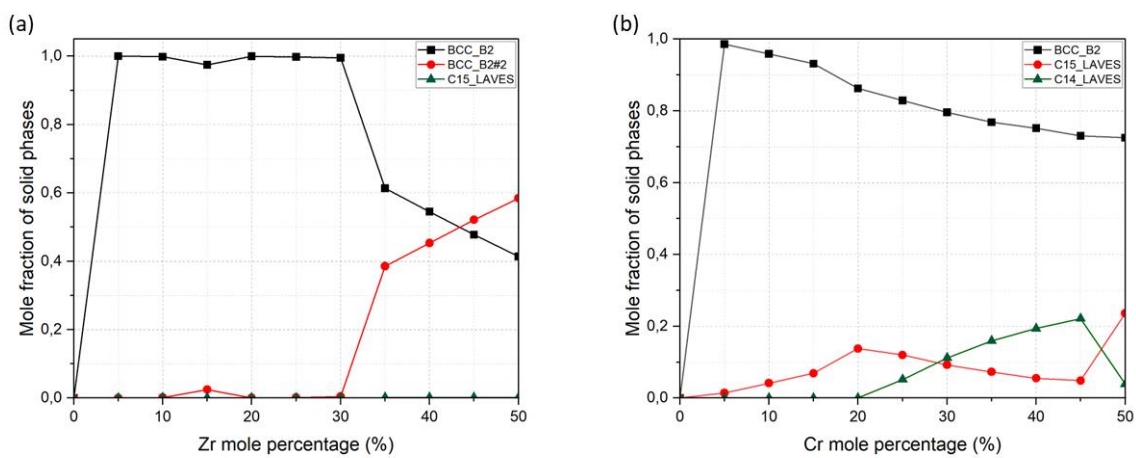


Figure 21: Mole fraction of non-equilibrium phases variation with the increase of the alloying element: (a) Zr and (b) Cr.

The simulations presented in this chapter allowed for a better understanding of the mechanisms of formation, thermodynamic stability of formed phases and their kinetics, as well as will serve as a key tool for the microstructural analysis of the alloys produced in the framework of the LiRAs project, where this master's thesis is included. Based on the simulations performed, V, Ti and Al were selected as elements of major interest for the proposed objective. The first two for presenting the intended structure and, the last one for presenting an interesting density reduction for aeronautics applications.

Since the literature existent retracts some studies on the V influence on the MoNbTaW system, this element was chosen as the starting point of the *in-situ* alloying tests due to the existence of reference points both in terms of structure and properties, allowing the assessment of the DED process influence on these characteristics mentioned above.

4.2 Powder Characterisation

The characterisation of the powders in a powder metallurgy process is crucial, as it will determine various characteristics of the samples/parts produced, as it may also help to understand an unexpected result [64-65]. Therefore, in this particle study, the characterisation of the PSD, morphology, alloy structure, and chemical composition of the powders under study is indispensable to confirm if this material presents the essential characteristics to be processed by DED.

The PSD of each powder was obtained by laser diffraction, as shown in Figure 22. The base-system powders present a distribution similar to a bimodal distribution, although this observation is almost insignificant due to the small height of the second peak. Regarding the V powders, it is observed a positive asymmetry.

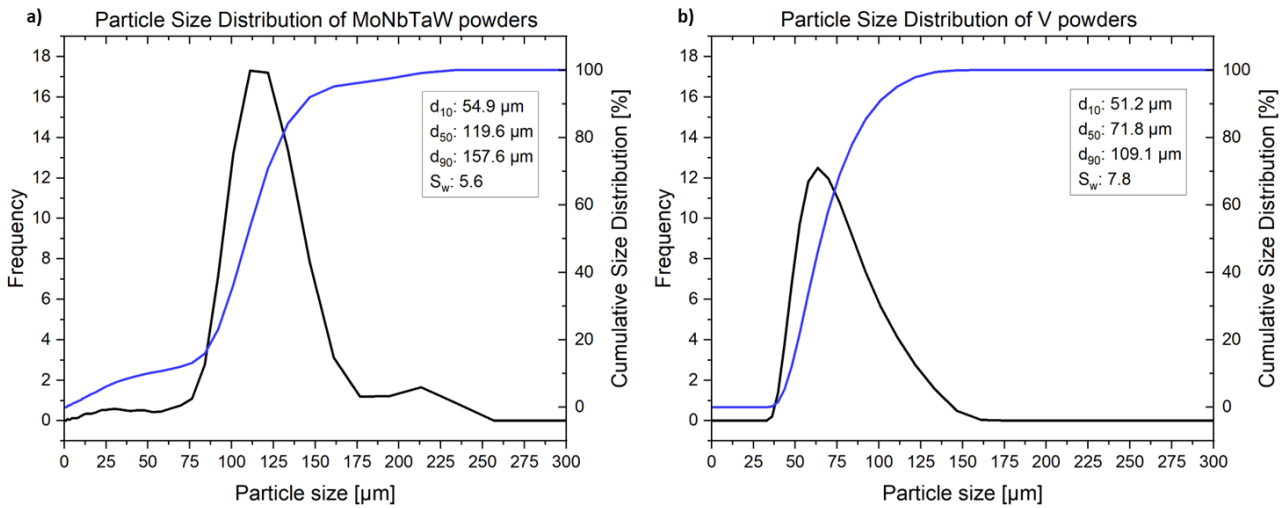


Figure 22: PSD curves for the (a) MoNbTaW powder; and (b) V powder.

Considering the d_{10} , d_{50} , d_{90} parameters, it is possible to evaluate the average particle size (d_{50}) and the distribution width, by the of the cumulative distribution slope (S_w) which is similar to the variation coefficient of the distribution. This parameter can be obtained by the following equation:

$$S_w = \frac{2.56}{\log(d_{90}/d_{10})} \quad (14)$$

In terms of the d_{50} , it is observed that the MoNbTaW powders present a bigger average size comparing to the V, being this 119.6 μm and 71.8 μm, respectively. On the other hand, although both powders present similar d_{10} values, the remaining values differ, leading to different S_w values.

Through the analysis of the S_w value, it is possible to state that the V powders present a narrower distribution than the MoNbTaW ones. It is essential to consider that for DED, it is relevant a narrow PSD to ensure that all powders present identical sizes to ensure that the laser interacts with all powders in a similar way.

From powder SEM/EDS analysis (Figure 23), it is possible to verify that MoNbTaW (Figure 23a) do not present a shape factor of 1; however, certain sphericity of the particles can be noted. A clear spherical form is observed in the V powders (Figure 23b).

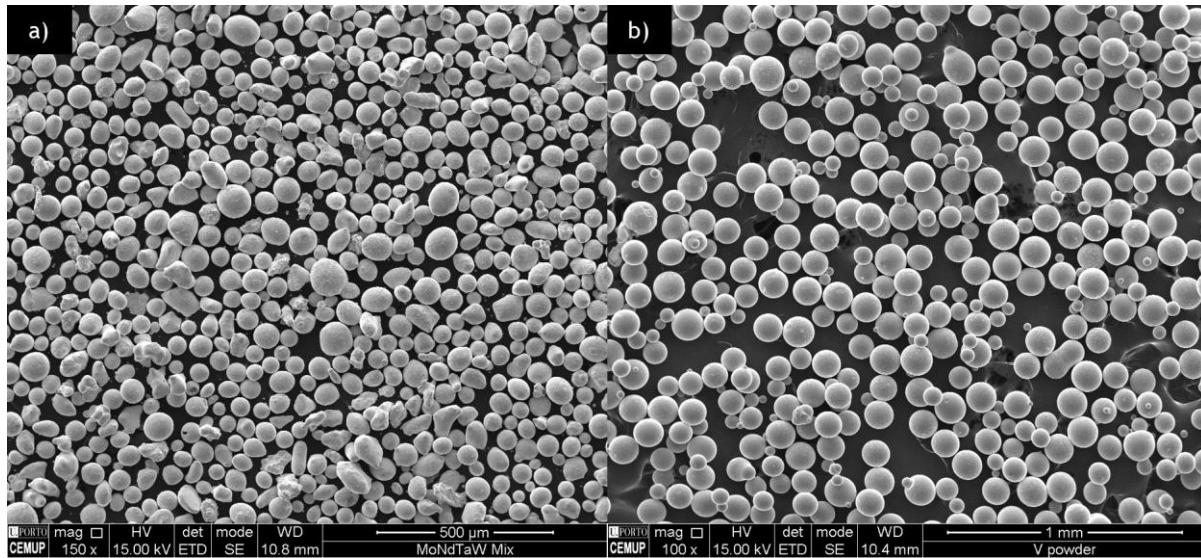


Figure 23: SEM images of the pre-alloyed (a) MoNbTaW and (b) V powders.

In terms of the powder's chemical composition, obtained by EDS analysis (Table 3), it is possible to detect the occurrence of oxidation in the base system powders which could be a result from the powders manufacturing or handling, while the presence of some carbon contaminations, which could be due to the carbon tape used during the analysis. Although there is no exact 1:1:1:1 ratio between the elements of the system, the ratio is extremely close. Thus, the base system will be referred to as MoNbTaW.

Table 3: EDS Global analysis for both powders.

at%	Mo	Nb	Ta	W	V	O	C
MoNbTaW powders	14.3	22.7	23.0	27.8	-	12.2	-
V powders	-	-	-	-	97.9	-	2.1

The phase structural characterisation was also realised on both powder batches by XRD analysis. Figure 24 shows the X-ray diffractograms for each powder. Both powders present the peaks at the same/similar 2θ , which indicates that the same structure is presented. The respective peaks observed can be associated with a BCC structure, which aligns with the performed simulations. Besides the slight peak intensity difference, it is possible to state that both powders present a preferential orientation of crystallites for the atomic plane (110).

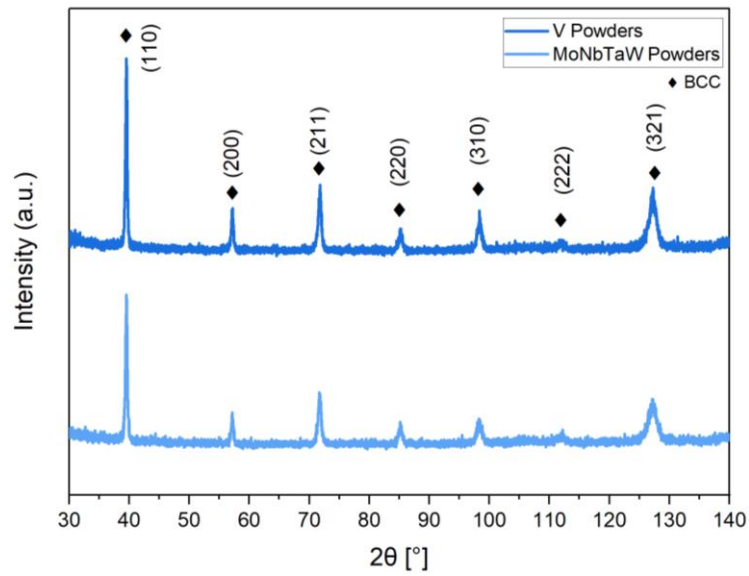


Figure 24: X-ray diffractograms for the MoNbTaW and V powders.

With this analysis finished, it is possible to affirm that the provided powders present the essential characteristics for DED processing and enable the production of quality samples/parts.

4.3 MoNbTaW RHEAs produced by Direct Energy Deposition

This chapter will assess the process window optimisation by an RMS. Afterwards, a block will be deposited with the optimal process conditions for the microstructural and mechanical characterisation of the MoNbTaW system.

4.3.1 Process Parameters Optimisation

In this sub-chapter is presented the optimisation, through RSM, of the MoNbTaW base system deposited by DED, based on the parameters window mentioned in sub-chapter 3.3. From this set of parameters, it was possible to obtain 27 single tracks, where the cross-sections are shown in Figure 25.

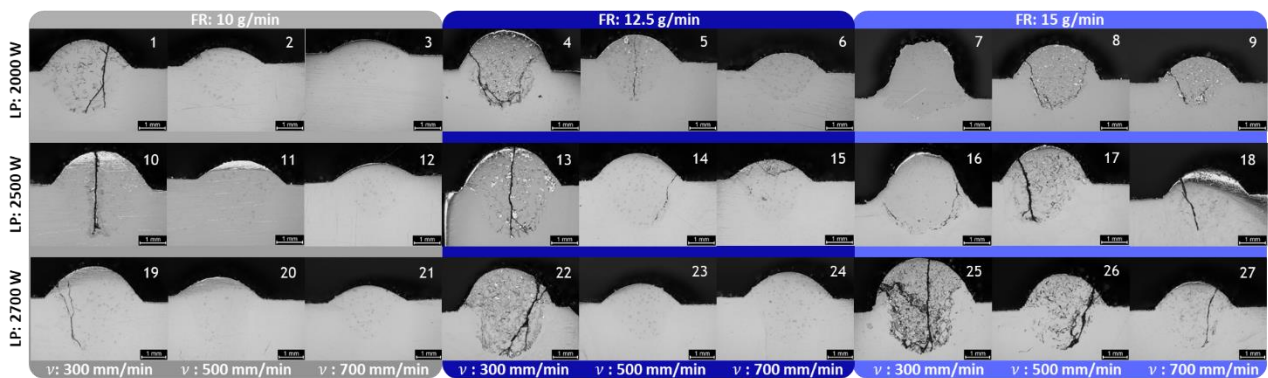


Figure 25: Single tracks obtained from the first DOE of optimisation.

Based on a first visual inspection, a large HAZ was observed on the substrate surface; however, the tracks presented a metallic appearance, indicating no extensive oxidation during the deposition process. Regarding superficial defects, all samples presented cracks, possibly due to the thermal shock between the melted alloy and the substrate since the substrate was at RT.

From the cross sections analyses it is observed the presence of two crack types, which were identified as delamination and solidification cracking. Delamination (e.g., Track 4) corresponds to the separation between the substrate and the track deposited due to the materials' different CTE, leading to residual stresses forming. This defect is associated with high cooling rates and thermal gradients [66].

Solidification cracking (e.g., Track 10) is verified in the partially melted zone of the track, wherein low melting point compounds, such as eutectics, are segregated and solidify last. This phenomenon leads to the development of internal stresses become sufficiently high to rip open the solidifying track and a crack appears. Solidification crack is usually associated with exaggerated energy applied; however, it can also be caused by thermal shock during the deposition [66].

Once all the typical characteristics used as efficiency and quality indicators of tracks in DED (such as height, dilution, wettability angle and width) were calculated and measured, Response Surface Regressions and Contour Plots were achieved through the *Minitab* software. The multiple interactions between the several parameters of this type of process make essential the application of an optimisation algorithm to define the optimal conditions of processing. The values from each characteristic assessed and measured of the 27 single tracks are shown in Table 4.

The application of these tools allows the selection of process conditions that lead to the desired response, always sustained, and verified with experimental results. A Response Surface Design (RSD) consists of various advanced DOE techniques that can assist in better understanding and optimising your response. RSD methodology is frequently used to refine models after essential factors have been determined using screening designs or factorial designs, especially if curvature in the response surface is suspected, which is the case since it is not expected a linear variation of the process outputs [67]. The Response Surface Model (RSM) was chosen from several RSD methodologies.

This methodology generates objective functions by considering the laser power (LP), relative surface speed (v), and feed rate (FR) as inputs, allowing to build objective functions regarding height, width, and dilution, respectively, based on the experimental data, which will allow the tracks characteristics prediction. During the regression process, parameters or parameter combinations that had no or almost no influence on the model were eliminated to improve its correlation with the experimental data. Thus, it was possible to obtain the regressions presented in Equations 15, 16 and 17, with a determination coefficient (R-squared) of 96.98%, 97.50% and 89.55%, respectively.

$$\begin{aligned} Dilution(LP, v, FR) = & 1.248 - 0.000414LP + 0.000971v - 0.0606FR - 0.000001v^2 \\ & - 0.00418FR^2 + 0.000044LP \times FR + 0.000034v \times FR \end{aligned} \quad (15)$$

$$\begin{aligned} Height(LP, v, FR) = & -2.00 + 0.00314LP - 0.00606v + 0.091FR - 0.000001LP^2 + 0.000005v^2 \\ & + 0.00946FR^2 - 0.000053LP \times FR - 0.000167v \times FR \end{aligned} \quad (16)$$

$$\begin{aligned} Withd(LP, v, FR) = & -5.50 + 0.00783LP - 0.00371v + 0.1162FR - 0.000002LP^2 \\ & + 0.000004v^2 - 0.000167v \times FR \end{aligned} \quad (17)$$

Using these equations, it is possible to construct several surface plots regarding the previously mentioned outputs, allowing a more in-depth analysis of these three process inputs' influence on the final characteristics of the DED tracks. From the *Minitab* software general analysis, it was also possible to obtain a Pareto chart of standardized effects of each variable into a certain output. Figure 26 shows the Pareto charts of standardized effects in the response for dilution (Figure 26a), height (Figure 26b), and width (Figure 26c).

Table 4: Process parameters, geometrical characteristics, and empirical parameters utilised as inputs for the MiniTab analysis.

Track	Laser Power [W]	Relative Scanning Speed [mm/min]	Feed Rate [g/min]	Power Density [W/cm ²]	kg/kWh	Height [mm]	Width [mm]	Depth [mm]	Θ [°] Right	Θ [°] Left	As [mm ²]	Ad [mm ²]	Dilution [%]
1	2000	300	10.0	577.43	0.30	1.15	3.50	1.61	47.45	52.60	2.63	3.73	58.7%
2	2000	500	10.0	577.43	0.30	0.66	3.23	1.60	37.18	37.35	1.30	2.57	66.4%
3	2000	700	10.0	577.43	0.30	0.56	3.04	1.12	32.98	33.03	1.11	1.93	63.4%
4	2000	300	12.5	577.43	0.38	1.53	3.51	1.48	60.69	63.03	3.75	3.06	45.0%
5	2000	500	12.5	577.43	0.38	1.00	3.29	1.48	46.24	48.90	2.14	2.67	55.5%
6	2000	700	12.5	577.43	0.38	0.74	3.05	1.08	39.58	41.58	1.49	1.94	56.6%
7	2000	300	15.0	577.43	0.45	2.14	4.00	0.75	36.59	37.36	5.12	1.38	21.3%
8	2000	500	15.0	577.43	0.45	1.31	3.29	1.18	65.76	56.68	3.11	1.99	38.9%
9	2000	700	15.0	577.43	0.45	0.99	3.05	0.96	50.24	53.47	2.11	1.37	39.4%
10	2500	300	10.0	721.79	0.24	1.38	3.86	1.88	41.97	50.90	3.49	4.51	56.4%
11	2500	500	10.0	721.79	0.24	0.82	3.40	2.03	37.51	38.10	1.81	3.44	65.5%
12	2500	700	10.0	721.79	0.24	0.62	3.22	1.56	33.09	37.44	1.25	3.01	70.7%
13	2500	300	12.5	721.79	0.30	1.57	3.88	1.83	53.61	45.52	4.00	4.43	52.6%
14	2500	500	12.5	721.79	0.30	1.05	3.45	1.81	43.64	45.54	2.34	3.77	61.7%
15	2500	700	12.5	721.79	0.30	0.77	3.24	1.47	39.29	37.23	1.67	2.85	63.0%
16	2500	300	15.0	721.79	0.36	2.01	4.27	1.14	42.76	35.95	5.03	2.78	35.6%
17	2500	500	15.0	721.79	0.36	1.40	3.53	1.53	54.32	55.67	3.25	3.14	49.1%
18	2500	700	15.0	721.79	0.36	1.08	3.28	1.32	54.19	52.80	2.34	2.42	50.9%
19	2700	300	10.0	779.53	0.22	1.26	3.75	1.87	46.92	49.44	3.17	4.85	60.5%
20	2700	500	10.0	779.53	0.22	0.79	3.39	1.84	38.56	31.06	1.61	3.86	70.5%
21	2700	700	10.0	779.53	0.22	0.64	3.06	1.38	31.75	34.95	1.15	2.56	69.1%
22	2700	300	12.5	779.53	0.28	1.54	3.76	1.89	72.33	48.00	3.99	4.64	53.7%
23	2700	500	12.5	779.53	0.28	0.78	3.06	1.35	42.90	39.42	1.65	2.55	60.8%
24	2700	700	12.5	779.53	0.28	0.99	3.43	1.75	45.38	47.24	2.25	3.67	62.0%
25	2700	300	15.0	779.53	0.33	1.89	3.97	1.79	62.64	67.54	5.29	4.42	45.5%
26	2700	500	15.0	779.53	0.33	1.32	3.38	1.56	54.85	56.15	2.99	3.37	53.0%
27	2700	700	15.0	779.53	0.33	1.01	3.13	1.55	50.32	50.21	2.11	3.14	59.8%

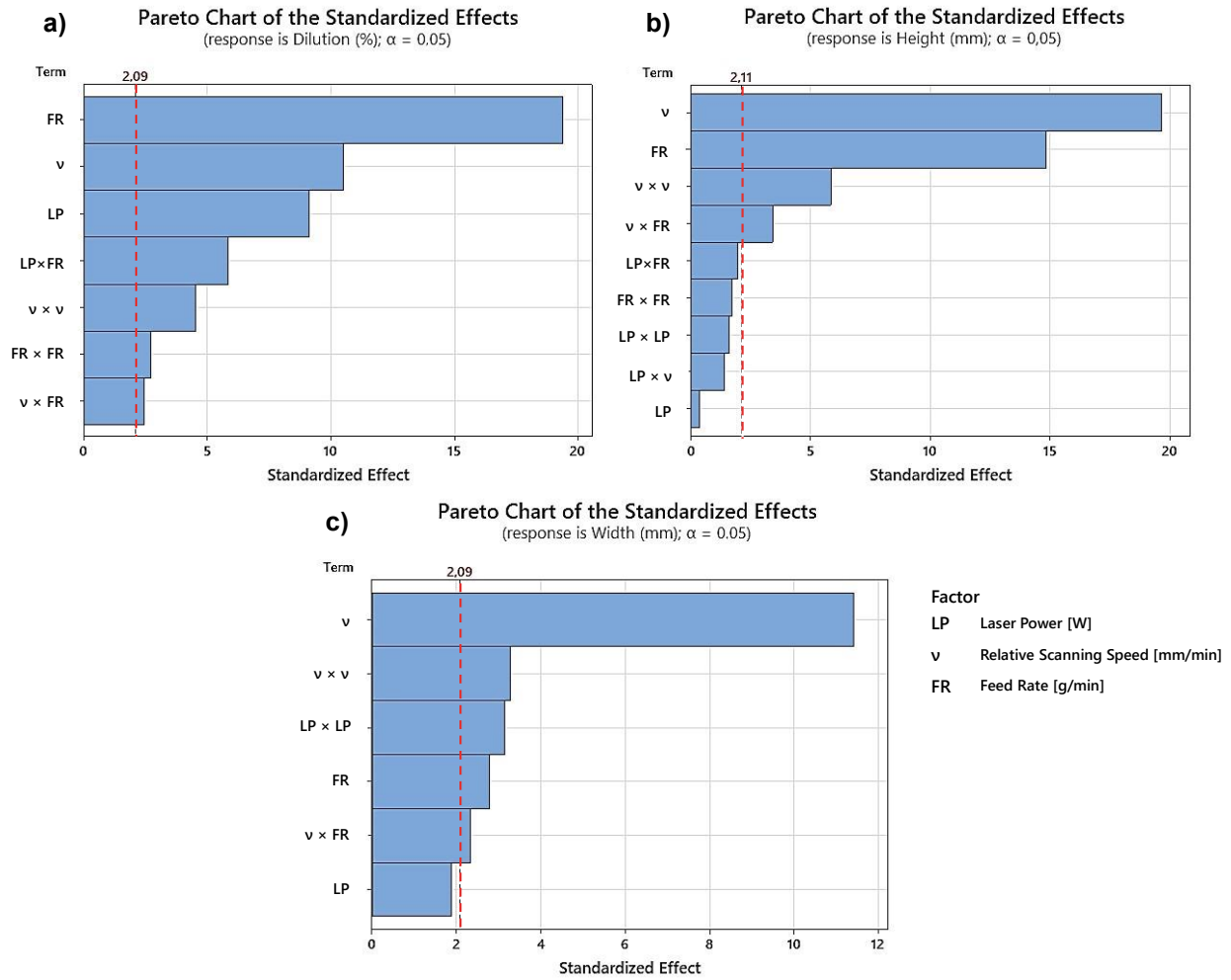


Figure 26: Pareto chart of the standardized effects response for (a) dilution; (b) height; and (c) width.

From these charts, it is possible to verify which factor will present a standardised effect with a 95% confidence level (factors with a standardised effect beyond the red dotted line for each response). Still, even though some relations present effects inferior to the line previously mentioned, they will be considered in the prediction since information is added to the model, improving the adjustment of the function to the experimental data.

Based on these analyses, it is concluded that the relative surface speed is the variable that most affect the dilution ratio, and the feed rate is the variable that most affects the height and width of the track since they correspond to the more considerable standardised effect of each output under study.

After defining the variables that hold a more significant effect on the single tracks' geometric characteristics, the construction of surface plots was realised to understand their evolution on the outputs.

Through the surface plots regarding the dilution (Figure 27), it is observed that an increase in the laser power and a decrease in the feed rate will lead to an increase in the dilution percentage, regardless of the relative surface speed. This variation will decrease the amount of powder per unit of energy delivered, thus leaving more free energy for interaction with the substrate.

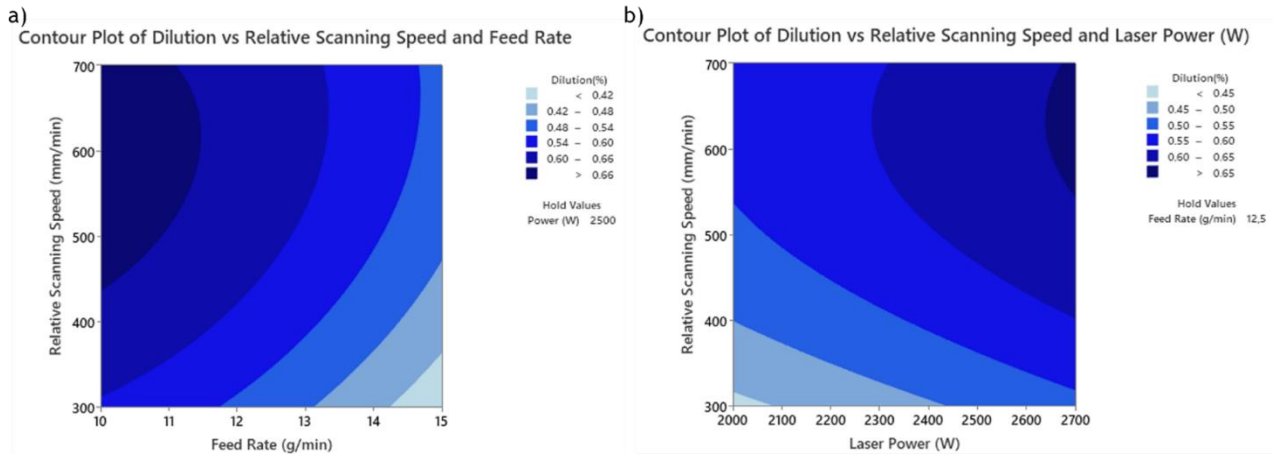


Figure 27: Contour Plots of Dilution Vs (a) Relative Scanning Speed and Feed Rate; (b) Relative Scanning Speed and Laser Power.

In terms of height, Figure 28 shows that the feed rate is the variable that most control this characteristic of the track; however, it is possible to increase positively its effect with the decrease of the relative surface speed.

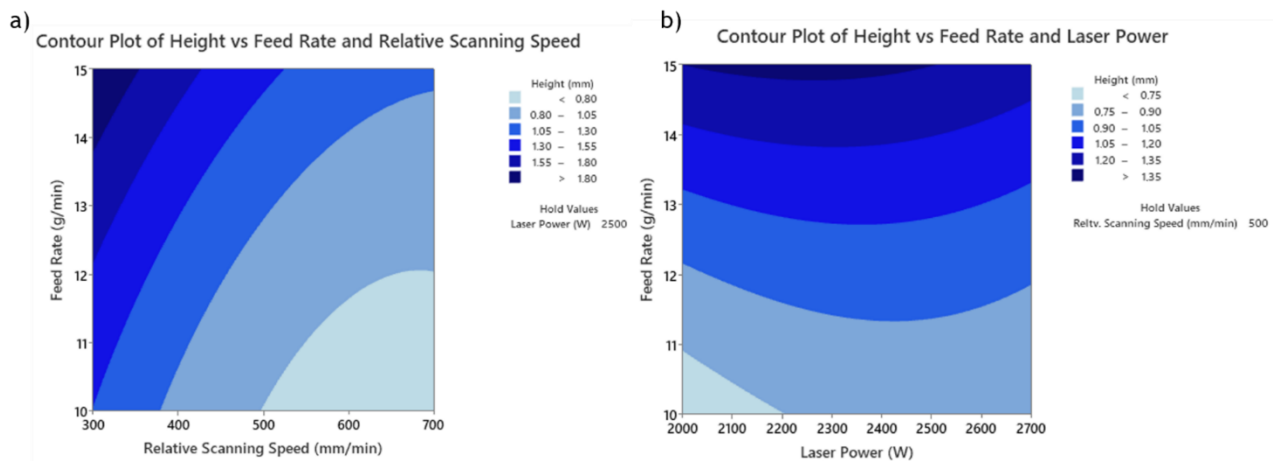


Figure 28: Contour Plots of Height Vs (a) Relative Scanning Speed and Feed Rate; (b) Feed Rate and Laser Power.

At last, the width of the track does not present a regular correlation with the laser power and feed rate. Yet is observed (Figure 29) that an increase of the relative surface speed will decrease the overall width of the tracks, assuming the remaining variables constant.

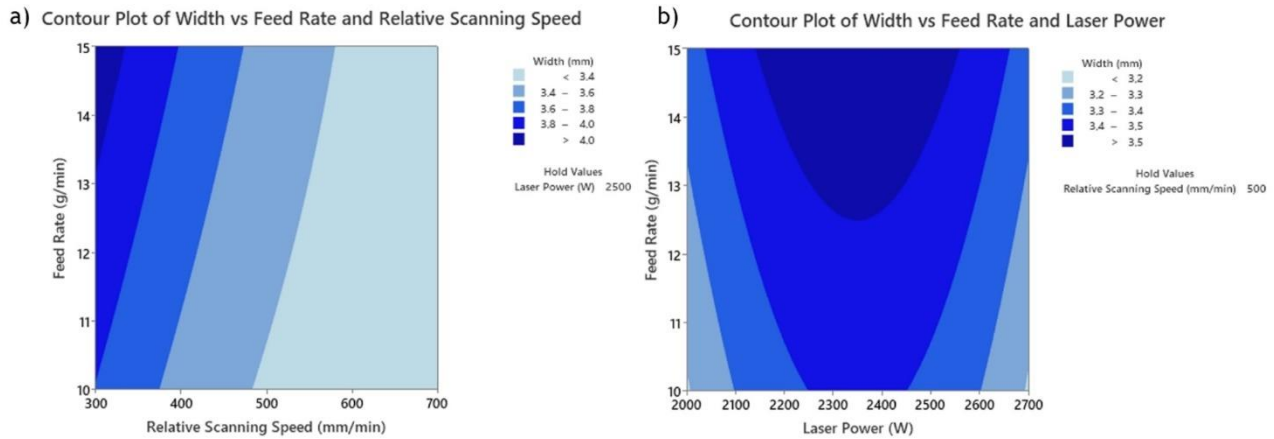


Figure 29: Contour Plots of Width Vs (a) Relative Scanning Speed and Feed Rate; (b) Feed Rate and Laser Power.

Finally, the RSM methodology was used to determine the process conditions of laser power, relative surface speed and feed rate that: (1) minimize the depth and dilution of the track since the dilution zone corresponds to the interaction of the deposited material and the substrate, which would correspond to “wasted” material; and (2) that maximizes the height while ensuring a good wettability, to guarantee an efficient process while ensuring the possibility to build cohesive structures. It is also important to mention that energy efficiency was considered through the power and feed rate ratio.

Afterwards, using the Response Optimizer feature of the *Minitab* software, the optimal solutions were obtained (Table 5) in descending order of desirability.

Table 5: Optimal Solutions for the intended optimisation.

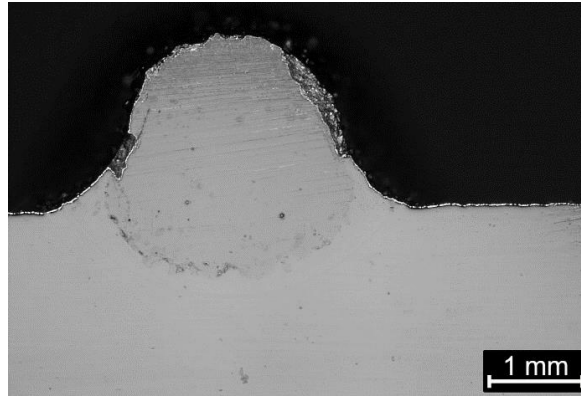
Solution	Laser Power [W]	Relative Surface Speed [mm/min]	Feed Rate [g/min]	Height [mm]	Width [mm]	Dilution [%]	Kg/kWh	Power Density [W/cm ²]
1	2067	300	15.0	2.08	4.01	26.13	0.44	596.69
2	2088	300	15.0	2.08	4.04	26.59	0.43	602.16
3	2042	300	15.0	2.07	3.99	25.56	0.44	589.65

Based on the Response Optimizer, the single-track 7 (LP: 2000 W; v : 300 mm/min; FR: 15 g/min) has the most similar process parameter. However, the track presented an irregular morphology, as observed in Figure 25. With the information gathered from the previous optimisation and the surface plots obtained, a second DOE was realised to confirm/improve the presented results. The parameters studied in this second DOE can be observed in Table 6.

Table 6: Inputs and Outputs from the second DOE.

	1	2	3	4	5	6
Inputs	Laser Power [W]	2000	2000	1800	1800	1800
	Relative Surface Speed [mm/min]	300	200	300	300	200
	Feed Rate [g/min]	15.0	15.0	15.0	12.5	15.0
Outputs	Power Density [W/cm ²]	577.43	577.43	577.43	519.69	519.69
	kg/kWh	0.45	0.45	0.50	0.42	0.50
	Height [mm]	2.14	2.89	2.17	1.79	2.63
	Width [mm]	4.00	3.40	3.47	3.53	2.82
	Depth [mm]	0.75	0.88	0.54	0.68	0.73
	Dilution [%]	21%	22 %	21 %	29 %	20 %
	Cross-section Fissures	No	No	No	No	Yes

Based on the presented outputs, it is possible to conclude that the fourth set of parameters (Figure 30) produced the best solution since the remaining tracks presented a considerable number of unfused powders, but also, due to small dilution percentage and quality of the track.

Figure 30: Single track 4 of the second DOE (LP: 1800 W; v : 300 mm/min; FR: 12.5 g/min).

Regarding the empirical parameters used for the energy efficiency of the deposition (kg/kWh), it is seen that the optimal parameters selected also allow the highest efficiency observed from all the beforementioned set of parameters while ensuring the quality of the built part/sample.

With the optimal conditions, a sample with two layers of two single tracks each was built with a zigzag printing strategy, using an overlapping of 40%. This build was used for microstructural and mechanical characterisation of the based system, presented in chapter 4.3.2.

4.3.2 MoNbTaW part microstructural and mechanical characterisation

Initially, the MoNbTaW system was studied without alloying elements to obtain a starting point for the present study and to evaluate the processability of this alloy by DED. Figure 31a shows three distinctive regions in the built part: (A) a darker one, corresponding to the dilution area with unfused powder particles; (B) a dendritic zone composed of the base system and a second phase formed by the interaction between the MoNbTaW powder and the substrate, and (C) the SAE 316L substrate.

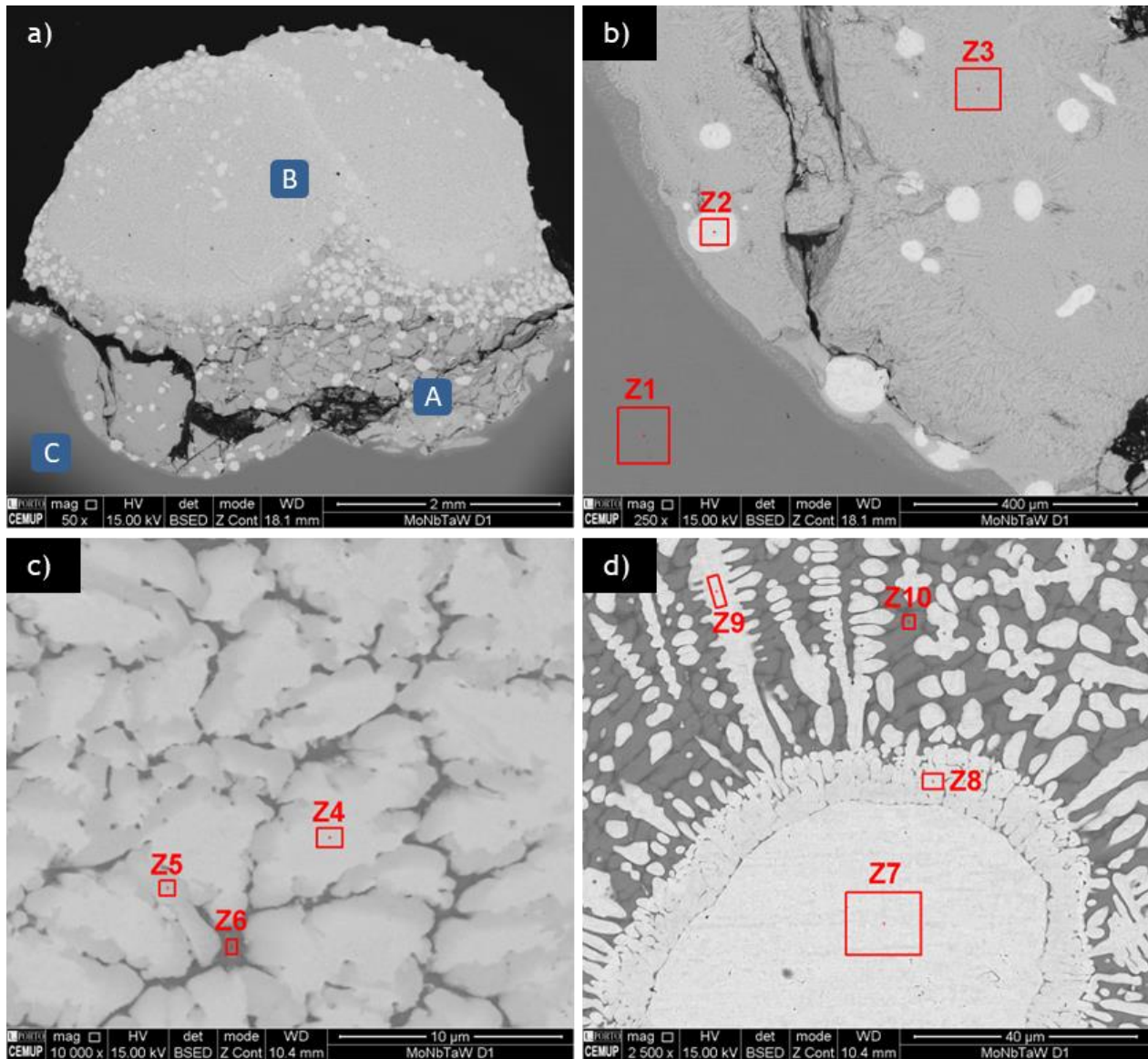


Figure 31: SEM images (a) Two layers MoNbTaW part; (b) Zone A: interface between the 316L substrate and the dilution region; (c) Region Z3 with a high magnification; (d) Zone B: built area.

Regarding the macro defects, it is possible to visualise several cracks in region A. This could be related to the presence of several unmelted powders, or the delamination phenomena related to the different CTE of the materials.

The microstructure of region A is presented in Figure 31b and 31c. SEM images show the interfacial zone between the SAE 316L substrate and the dilution zone, mainly composed

by unmelt MoNbTaW powders and several cracks. When taking a closer look at the dilution zone, it is possible to observe that zone 3 (Z3) is not homogeneous; this is composed of three different compounds with different interactions with the RHEA system, as it is shown by the EDS analysis presented in Table 7.

Table 7: Chemical Composition (at%) of the zones presented in Figure 31b and 31c.

Zone	C	Si	Mo	Cr	Fe	Ni	Ta	W	Nb
1	2.0	0.8	1.2	18.3	68.3	9.3	-	-	-
2	1.5	-	23.4	-	-	-	31.7	21.4	22.0
4	4.0	-	7.3	12.0	43.0	5.2	13.1	8.5	6.9
5	4.3	-	10.0	11.6	44.4	6.4	8.3	7.4	7.6
6	4.8	-	4.5	16.1	55.9	14.6	0.9	1.3	1.9

Region B (Figure 31d) itself did not present the intended single-phase structure, whereas instead, a biphasic structure composed of dendrites of MoNbTaW in a ferrous matrix. Through the EDS analysis, presented in Table 8, it is possible to observe that the matrix displays a similar composition to the SAE 316L SS; however, with a higher amount of interaction with the deposited alloy. Z7 and Z8 correspond to the unmelt powder or partially fused, presenting a similar composition to the MoNbTaW powder.

Table 8: Chemical Composition (at%) of the zones presented in Figure 31d.

Zone	C	Mo	Cr	Fe	Ta	W	Nb
7	3.7	20.8	-	-	32.5	26.7	16.4
8	6.3	22.6	2.5	4.0	26.4	27.1	11.0
9	4.8	22.2	2.9	5.0	24.1	30.6	10.5
10	3.4	8.6	10.2	40.9	19.2	2.9	14.8

According to the literature [16], the alloy should present a single-phase structure. However, it is possible to observe the presence of the other structure similar to substrates. The presence of a high amount of an SAE 316L-like phase on the built part can be justified by two phenomena: the Marangoni effect or the vaporisation of certain elements [68-69].

Since the MoNbTaW presents a T_m higher than double the substrate's T_m , the energy input to melt the material will produce a greater-than-normal amount of liquid substrate. Since there is a significant amount of molten substrate, the Marangoni currents lead to the incorporation of the substrate in the MoNbTaW part, forming this biphasic structure. The other possible justification can be the volatilisation of certain elements (such as Fe) since their boiling temperature is lower than the T_m of the deposited alloy.

The EBSD results, shown in Figure 32, confirmed the BCC structure described in the simulations for the MoNbTaW base system (Figure 32b) and also that the other phase observed was formed due to the interaction with the substrate since it presents an FCC structure (Figure 32c), which is the exact structure of the austenitic stainless steel used.

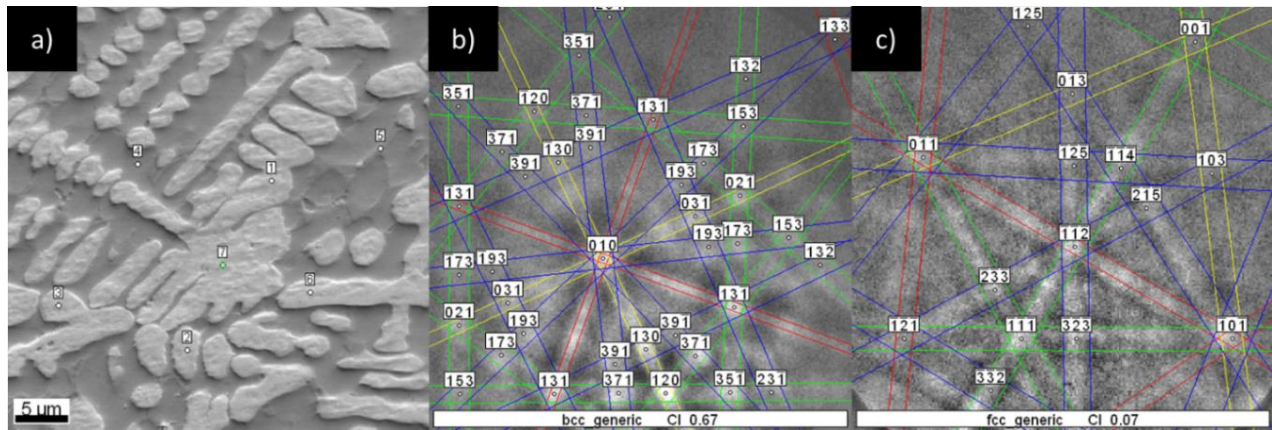


Figure 32: SEM image of the built block - zone 2 (a), and indexed EBSD patterns corresponding to MoNbTaW (b) and to the phase formed due to the substrate interaction (c).

As an attempt to eliminate the substrate interaction, a structure composed of seven layers of the base-system, each layer composed of two single-tracks, was built. Figure 33 shows the microstructural characteristics of several layers of the beforementioned block: the second layer (Figure 33a), the interface between the second and third layers (Figure 33b), and the third layer (Figure 33c).

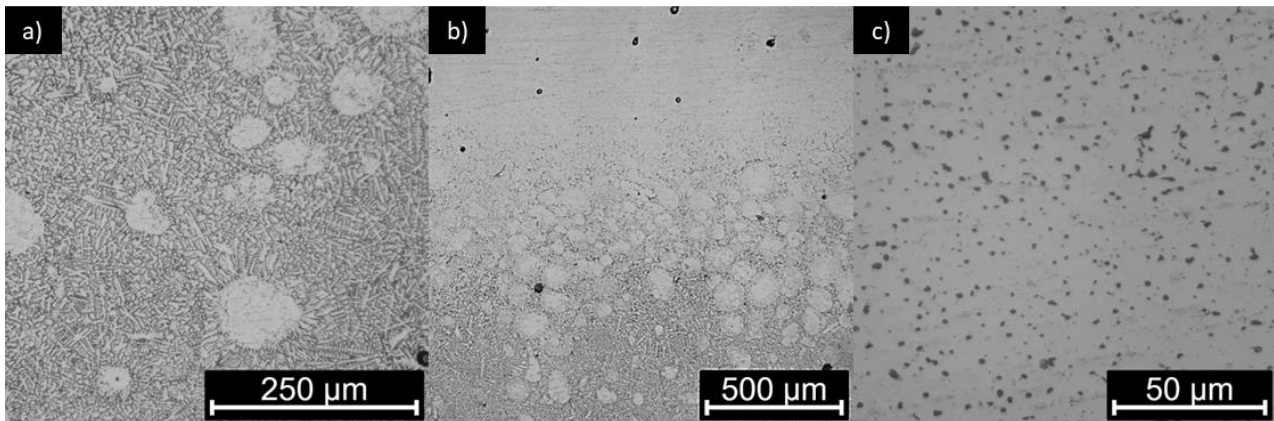


Figure 33: OM images related to the (a) second layer; (b) interface between the second and third layers; (c) third layer.

Regarding the first layer, it is verified that the microstructure is identical to the one observed in the two layers block, where a biphasic structure is present with several MoNbTaW powders partially unmelted. In terms of the third layer, a transition from a biphasic to a MoNbTaW single-phase structure is observed, thus eliminating the substrate's effect.

To further characterized the as-deposited structure of the MoNbTaW system, SEM/EDS analysis was conducted on the third layer, as shown in Figure 34. The microstructure of this zone of the built is composed by two distinctive phases, as observed in the OM analysis (Figure 33c). The unknown particles consist of oxides or contaminations, as confirmed by the EDS analysis in Table 9. The formation of these particles could be related to the inexistence of an inert atmosphere during depositions, despite the high flow rate of the shielding gas. Regarding the matrix, it is possible to observe some composition fluctuations

due to a contrast difference; however, Z2 and Z3 do not present considerable differences in their composition.

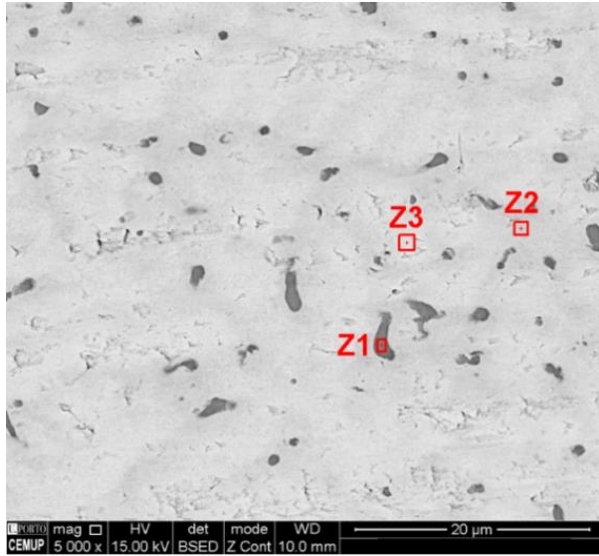


Figure 34: SEM image of the MoNbTaW built third layer.

Table 9: Chemical Composition (at%) of the zones presented in Figure 34.

Region	O	Mo	Nb	Ta	W	Ti
Z1	48.1	-	23.5	27.5	-	1.0
Z2	-	25.3	22.4	32.3	20.1	-
Z3	-	22.2	16.1	34.5	27.2	-

From the same built, it was also possible to evaluate the microhardness evolution of the MoNbTaW built (Figure 35) according to the layer of the built. Initially, it is observed hardness around 850 HV0.1 due to the biphasic structure. However, when single-phase structure is achieved, the hardness decreases to values around 500 HV0.1, stabilising around this value. From this assessment, it can be seen that the first layers are subject to heat dissipation from the last layers deposited; there is no significant hardness variation, thus stabilising at 503 ± 13 HV0.1 (blue stripe shown in Figure 35).

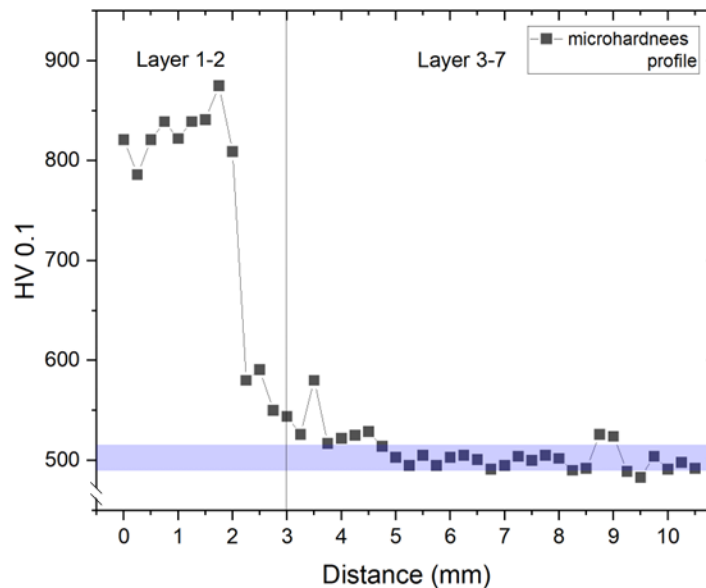


Figure 35: Hardness evolution with the built height.

4.4 *In-situ* alloying for high-throughput of RCCA/RHEAs

Following the optimisation of the base-system deposition, the production of the compositionally graded parts by *in-situ* alloying of V was conducted. For this purpose, the parameters were set as: 1800 W laser power; 300 mm/min relative surface speed; and 12.5 g/min global feed rate, for all the compositions studied. This chapter presents the graded parts' production, characterisation, and optimisation.

4.4.1 MoNbTaW_x compositionally graded parts production and characterisation

To guarantee the overall integrity and a gradual variation in the composition of the intended produced structures, the attempted compositions were split into four samples, each with the compositions presented in Table 10. Regarding the carrier gas flow rate, it was kept a flow of 4 L/min for the MoNbTaW and 2 L/min for the V powders due to the lower density of this metal compared to the base alloy and to obtain a higher sensitivity of the V addition.

Table 10: Feeding conditions for each powder for the compositionally graded parts.

Layers	Powder feed rate in g/min							
	MoNbTaW	V	MoNbTaW	V	MoNbTaW	V	MoNbTaW	V
1-4	12.50	0.00	12.50	0.00	12.50	0.00	12.5	0.00
5-7	12.25	0.25	12.00	0.50	11.75	0.75	10.75	1.75
8-10	12.00	0.50	11.50	1.00	11.13	1.37	10.00	2.5
11-13	11.75	0.75	10.75	1.75	10.38	2.12	9.13	3.37
Parts	0/5/10/15 at% V		0/10/20/30 at% V		0/15/25/35 at% V		0/30/40/50 at% V	
Sample	a.1		b.1		c.1		d.1	

Each gradient structure presented approximately 20 mm wide and 19 mm high. As shown in Table 10, each sample presented three distinctive V additions. As observed in chapter 4.3.2, it was considered that for the depositions with *in-situ* alloying with V, four layers of the base alloy would be necessary to deposit before the alloying, thus ensuring that the substrate dilution was eliminated and that the alloying elements were added to a "substrate" equivalent to original alloy (powder) composition.

When characterising the first set of compositionally graded parts, it was observed that, due to the low feed rate of the alloying element, the presence of this alloying element was only observed in specimen d.1, being this the one with intended additions of 30, 40, and 50 at% of V.

Figure 36a depicts the as-built structure obtained. After the specimen preparation, it is possible to observe the presence of several porosities (Figure 36b). Their formation can be explained due to the use of a considerably high flow rate of the shielding gas, which was selected as an attempt to eliminate oxidation problems since the parts were not built under an inert atmosphere. Since the characterisation of the first four layers (equivalent to the base system) was already described in the sub-chapter 4.3.2, a more in-depth analysis was conducted from the fourth layer forward.

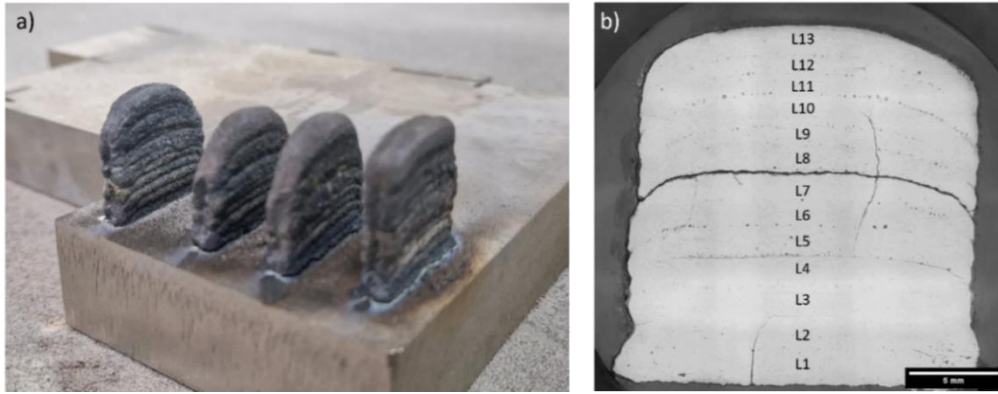


Figure 36: (a) Four graded samples produced by DED; (b) OM image of specimen d.1 cross-section.

Regarding the microstructural evidence (Figure 37), it is possible to observe that the as-built structure consists of a single phase with some compositional fluctuations in the interdendritic regions. This structure could result from the high overall melting range verified for the MoNbTaWV system, leading to a heterogeneous structure. Table 11 presents the EDS analysis for each region identified in Figure 37a and 37c.

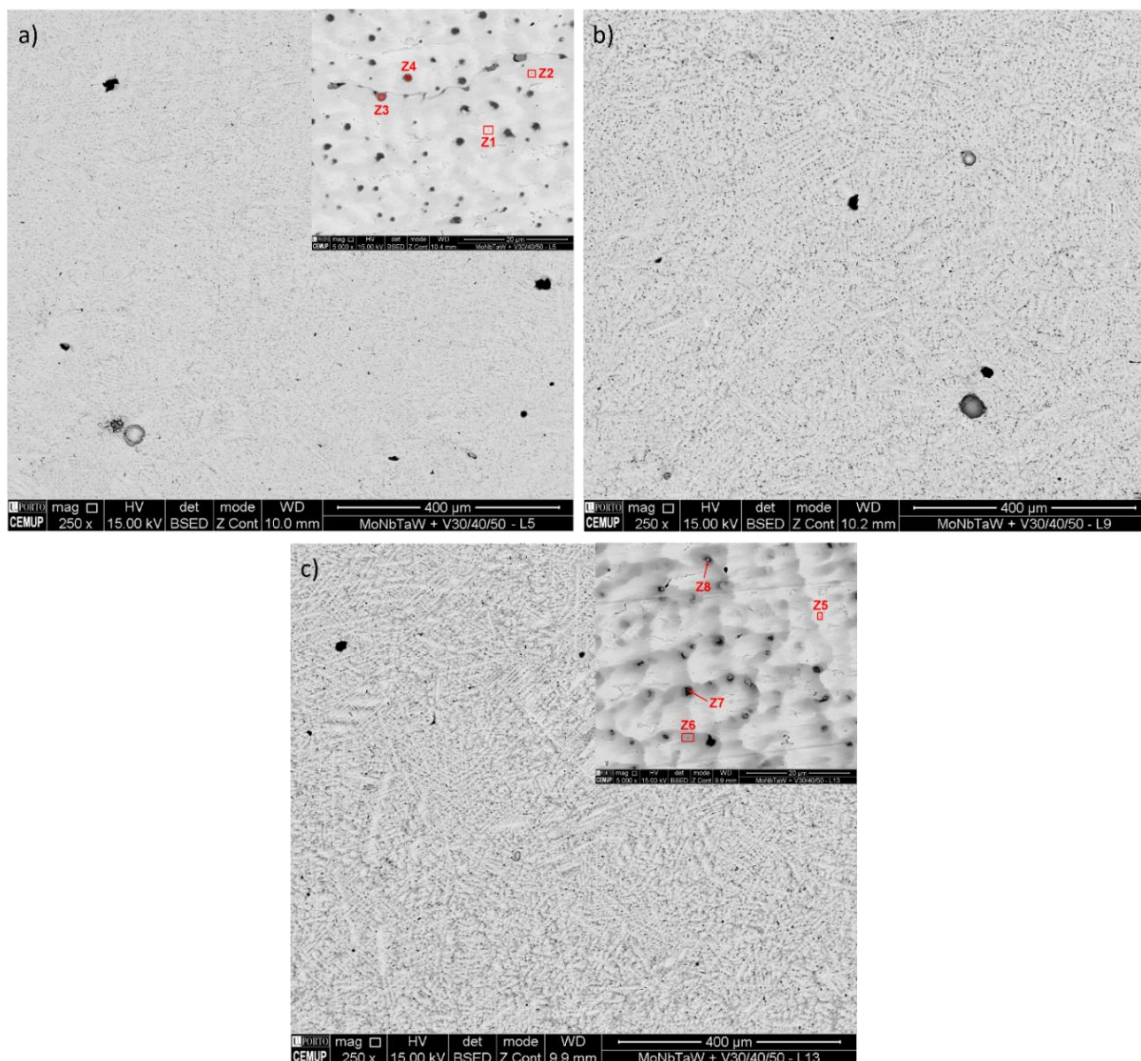


Figure 37: SEM images of the major microstructures of the as-built alloys in specimen d.1: (a) Layer 5; (b) Layer 9; (c) Layer 13.

Table 11: Chemical Composition (at%), obtained by EDS analysis, of the regions presented in Figure 37

Region	O	Ta	W	Nb	Mo	V	Ti	Hf
Z1	-	31.4	23.8	16.1	21.1	7.6	-	-
Z2	-	28.5	14.2	22.2	21.4	13.7	-	-
Z3	44.4	31.7	-	5.6	-	18.4	-	-
Z4	39.1	16.8	-	16.0	-	28.2	-	-
Z5	9.2	25.6	21.8	12.1	17.6	13.7	-	-
Z6	13.9	16.8	5.0	19.2	11.2	33.9	-	-
Z7	35.7	8.3	-	9.2	-	45.4	1.4	-
Z8	39.4	11.8	8.8	-	-	31.1	1.3	7.5

All the different alloys studied present a matrix composed of two distinctive zones (Z1-Z2 in Figure 37a and Z5-Z6 in Figure 37b), mostly varying in the V content. This type of structure could indicate that the conditions lead to a structure similar to the one described by the pseudo-binary diagram (Figure 17a, point 4.1.2) or could result from the high melting range, which leads to a heterogeneous structure. Regarding the darker particles presented in every layer, according to the EDS analysis, it is possible to identify them as oxides or contaminations (Z3, Z4, Z7 and Z8) due to the high amount of oxygen and some foreign elements.

From a more intense EDS analysis, it was possible to verify, through EDS elemental distribution maps, as the one presented in Figure 38, that besides the slit V fluctuations, the macrostructure is homogeneous in terms of Mo, Nb, Ta, and W. Regarding the O, it is possible to verify its presence all-over the analysed zone, despite being in low quantities. It is also observed the presence of a larger oxide in the eleventh layer.

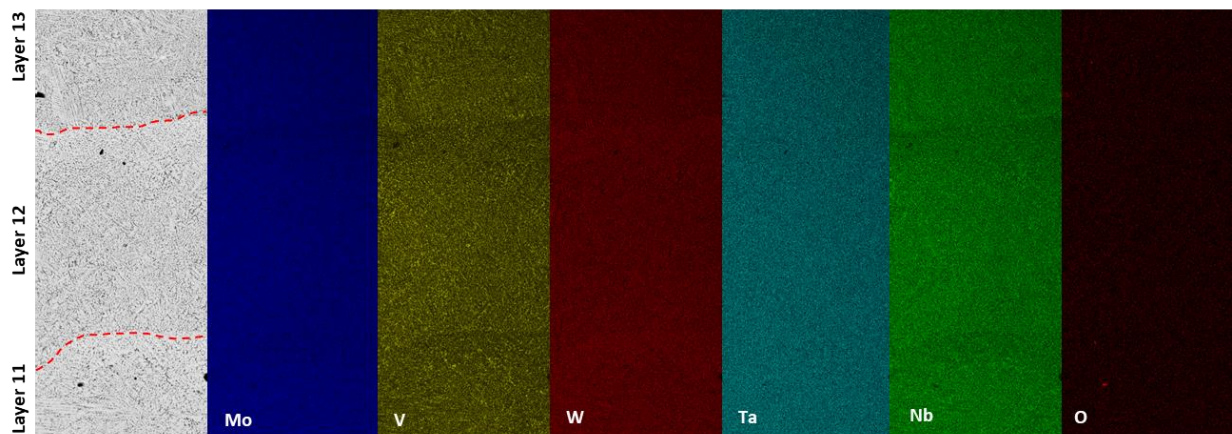


Figure 38: SEM images and EDS elemental distribution map of the three top layers of sample d.1.

Finally, through an EDS analysis of a larger area on each layer, it was possible to observe an average V at% of $11.3 \pm 1.2\%$, $16.8 \pm 0.5\%$, and $21.4 \pm 2\%$ for the layers 5-7, 8-10, and 11-13, respectively. As mentioned, the alloying strategy did not produce the intended V content, resulting in a smaller yield of around 41%. Therefore, despite the results' relevance, optimisation of the *in-situ* alloying is needed.

To understand the V heterogeneity of the solid solution observed in Figure 37, the *Scheil* with Solute Trapping model simulations, described in chapter 4.1.2, were studied with a

greater focus on the elemental distribution in each of the phases present during solidification, namely, the liquid phase and the BCC_B2 phase. Based on the average elemental composition of layers 11-13, the elemental redistribution during the non-equilibrium solidification is provided in Figure 39a for the liquid phase and the BCC_B2 in Figure 39b.

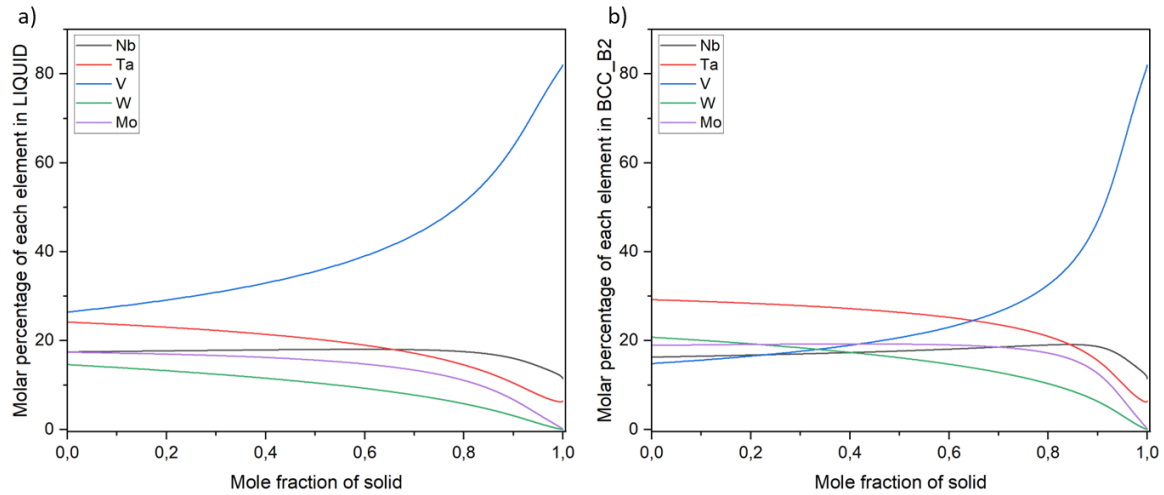


Figure 39: Elemental redistribution obtained from the Scheil-Gulliver calculations for an alloy with the average elemental composition as layers 11-13: (a) composition in the liquid phase; (b) composition in the BCC_B2 phase.

Even though the database used for these calculations does not present the possibility of considering the influence of O on the microstructure, it is verifiable in this simulation that V tends to be kept in the liquid phase throughout most of solidification (Figure 39a). This effect could be justified by the lower melting temperature of the elements compared with the remaining elements of the system. The analysis of Figure 39b, shows that due to the increasing V content in the liquid phase, the final BCC_B2 phase form will present a higher amount of V.

Yet, for a clearer analysis of the heterogeneity during solidification, the partition coefficient (k) can be considered. This coefficient serves as an indicator of how a particular element tends to distribute itself during the solidification process and is calculated as the ratio of the nominal concentration (c_i^*) to the solidus concentration (c_i^S). When the partition coefficient exceeds 1, a specific element is more concentrated in the interdendritic region. Conversely, a partition coefficient below 1 suggests an increased concentration of that element in the dendritic region. When the partition coefficient approaches 1, it indicates a uniform element distribution throughout the microstructure [70-71].

Considering the composition adjustment, due to the impossibility of considering the O in this simulation, it is possible to obtain a c_i^* of 26.4 at% and a c_i^S of 14.4 at% for V. Thus, it is observed that k is greater than 1, which indicates the tendency for a heterogeneous solidification and the tendency of the concentration of this element for interdendritic zones. Through this analysis, it is possible to justify the heterogeneity of the solidification and that some of the zones of higher V content observed in Figure 37 and Table 11 may even correspond to segregations of this element.

4.4.2 MoNbTaW_x compositionally graded parts optimisation

As an attempt to obtain the intended alloy compositions, the feeding rates of the V powders were increased, considering the previously calculated yield, to culminate the lack of this element. Table 12 shows the deposition parameters optimized.

Table 12: Optimized feeding conditions for each powder for the compositionally graded parts.

Layers	Powder feed rate in g/min							
	MoNbTaW	V	MoNbTaW	V	MoNbTaW	V	MoNbTaW	V
1-4	12.50	0.00	12.50	0.00	12.50	0.00	12.50	0.00
5-7	12.25	0.63	12.00	1.25	11.75	1.88	10.75	4.38
8-10	12.00	1.25	11.50	2.50	11.13	3.44	10.00	6.25
11-13	11.75	1.88	10.75	4.38	10.38	5.31	9.13	8.44
Parts	0/5/10/15 at% V		0/10/20/30 at% V		0/15/25/35 at% V		0/30/40/50 at% V	
Sample	a.2		b.2		c.2		d.2	

Initially, to assess if the parameters alteration resulted in an increase of the V content, global EDS was realised in each line for all the specimens. The V content in each group of layers with the same composition for all the specimens is shown in Table 13.

Table 13: Efficiency of the V feeding optimisation.

Intended V content [at%]	Observed V content [at%]	Alloying Yield [%]	FR(V) [g/min]
5	0.0	0.0	0.63
10	0.0	0.0	1.25
15	0.0	0.0	1.88
20	0.0	0.0	2.50
25	0.0	0.0	3.44
30	13.6 ± 0.5	56.8 ± 1.7	4.38
35	16.4 ± 3.8	38.8 ± 10.9	5.31
40	39.1 ± 13.5	97.8 ± 33.8	6.25
50	62.1 ± 1.9	124.2 ± 3.8	8.44

In general, it is possible to conclude that the V feed rate increase was not to produce alloys with the intended composition. For feed rates lower than 4 g/min, no V was possible to detect, which could be related to the following speculations: the V powders do not enter in contact with the laser, thus preventing them from being integrated into the melt and the part produced; or the equipment used does not have the precision to handle smaller powder quantities as required. These results highlight the importance of integrating monitorization systems, such as sensors that can detect the amount of a given powder being administered in real-time, as well as an off-axis camera that can provide a better understanding of, for example, the powder focus diameter, powder density distribution, powder focus position (working distance), and detection of wear damages.

Focusing on the group of layers that presented V in their compositions, Figure 40a and 40b depict the microstructures observed in layers 11-13 of specimens b.2 and c.2, respectively. It is shown that the microstructures are similar to the ones observed in chapter 4.4.1, where a dendritic structure is observed with some heterogeneities on the interdendritic zone and oxides present all over the structure.

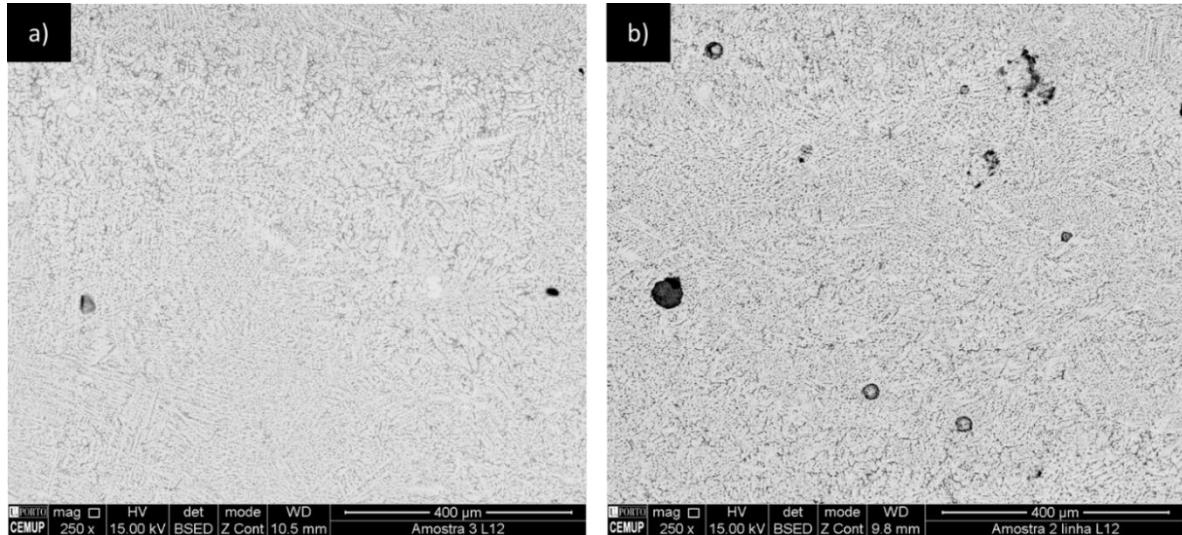


Figure 40: SEM images of the as-built specimens' microstructures for the top layers of specimen (a) b.2; and (b) c.2.

However, the alloys with an intended V content of 40 and 50 at% (layers 8-10 and 11-13 of sample d.2, respectively) presented a different structure, as seen in Figure 41a and 41b. From the EDS analysis (Table 14) it is possible to observe that the interdendritic region (darker phase) presents a higher concentration in V, approximately 41 at%. This could indicate that the V alloying to the base system was not complete, despite the fact that some V was present in the lighter phase. This biphasic structure can be explained by the low power input for the amount of material provided, leading to unfused MoNbTaW powders and an incomplete alloying of the base system.

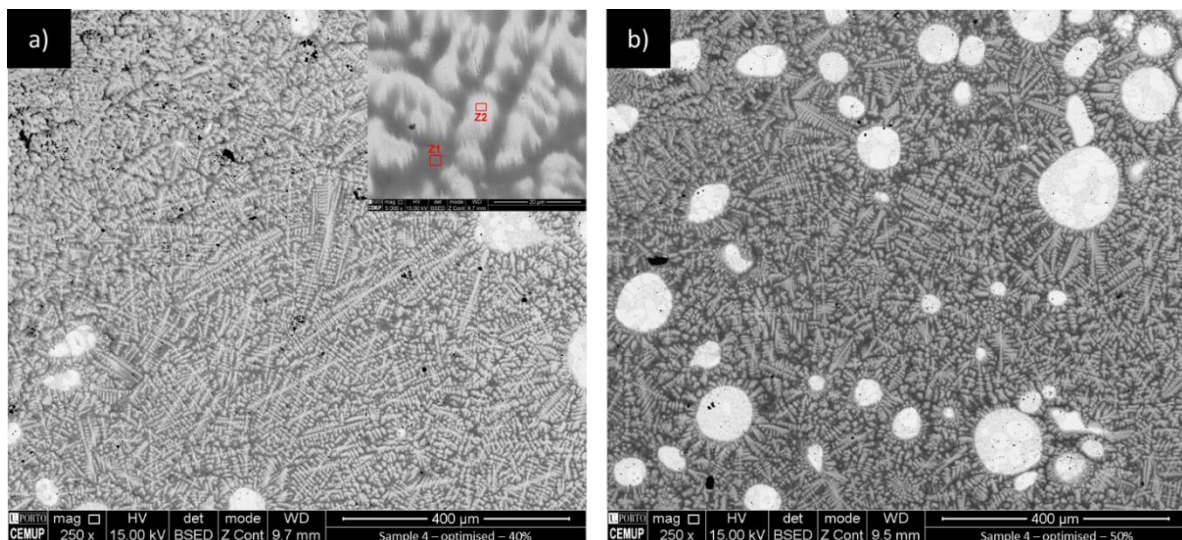


Figure 41: SEM images of the as-built specimens' microstructures for the (a) layer 8-10; and (b) layer 11-13 of specimen d.2.

Table 14: Chemical Composition (at%), obtained by EDS analysis, of the regions presented in Figure 41a.

Region	Mo	Nb	Ta	W	V	O
Z1	10.8	14.4	13.1	4.0	41.1	16.6
Z2	15.8	10.6	22.8	21.7	18.8	10.5

As an attempt to obtain a homogenous structure and a correct *in-situ* alloying two strategies were executed: homogenisation heat treatment and the optimisation of the process conditions, particularly the laser power. The first approach was conducted in a crucible laboratory furnace since it would enable the temperature measurement directly onto the sample using a thermocouple. The sample beforementioned was submitted to a 20-hour heat treatment at 1000 ± 10 °C, and afterwards, the metallographic preparation was realised for a microstructural characterisation, resorting to the procedure described in chapter 3.4.

Figure 42 shows the microstructures of the ninth layer before and after, respectively, the heat treatment. Despite the lack of contrast in the structure, it is possible to distinguish two different zones in each figure: (A) unfused MoNbTaW powders; (B) biphasic structure due to the incomplete structure homogenisation. The inadequacy of this treatment for the structure's homogenisation can be attributed to the low diffusion rate of the HEAs caused by the distorted structure provoked by the different atoms' sizes that constitute it.

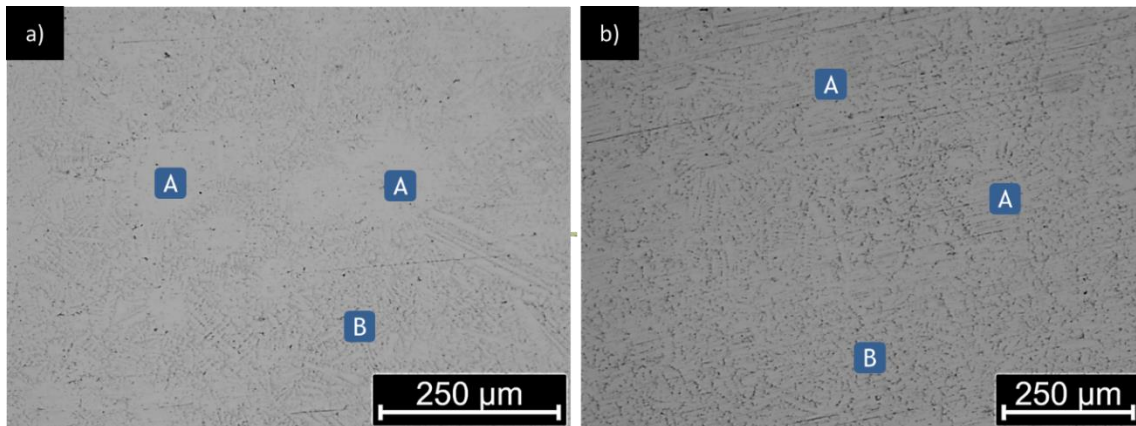


Figure 42: OM images of specimen c.2 ninth layer (a) before and (b) after the homogenisation heat treatment, each with the regions A and B identified as unfused powder and biphasic structure, respectively.

Although the strategy was ineffective for the homogenisation, the heat treatment served as a preliminary approach to verify the alloy's thermal stability and oxidation resistance at high temperatures since there was no significant variation of the structure and the oxidation superficial layer present in every specimen after its build.

Regarding the second approach of increasing the laser power, the parameters alteration was conducted based on the optimal parameter described in chapter 4.3.1. The optimal processing window was established using an LP of 1800 W; v of 300 mm/min; and a FR of 12.5 g/min, leading to an energy efficiency of 0.42 kg/kWh. However, with the increase of the V feeding rate, the amount of kg/kWh increased. This alteration led an insufficient energy delivery for the melting and deposition of the intended alloys.

In this way, the energy efficiency was calculated for each of the deposited alloys, as shown in Table 15. Through these calculations, it is possible to affirm that unfused powders can be observed only for kg/kWh higher than 0.52.

Table 15: Influence of the laser power and feed rate on the deposition energy efficiency.

Theoretical V content (at%)	5%	10%	15%	20%	25%	30%	35%	40%	50%
Laser Power [W]	1800	1800	1800	1800	1800	1800	1800	1800	1800
Total feed rate [g/min]	12.9	13.3	13.6	14.0	14.6	15.1	15.7	16.3	17.6
Unfused powder	No	No	No	No	No	No	No	Yes	Yes
Kg/kWh	0.43	0.44	0.45	0.47	0.49	0.50	0.52	0.54	0.59

Based on the evidence shown in Table 15, the laser power intensity adjustment was considered relevant to decrease the energy efficiency value for the value inferior to 0.52 kg/kWh, ensuring the complete fusion of both powders.

The increase of the laser power for 2000 and 2100 W for the alloys with 40 and 50 at%, respectively, is proposed as an attempt to verify if the as-built microstructure is indeed biphasic or if that structure is a result of an incomplete *in-situ* alloying. The alteration of this parameter would result in energy efficiency of 0.49 and 0.50 kg/kWh for each alloy, respectively. This hypothesis was not checked, although it is considered for future work perspectives.

4.4.3 Structural characterisations of the produced samples

Finished the evaluation of the alloying with V effect on the microstructure, a structural characterisation was conducted to correlate the results presented with the previous CALPHAD simulations realised, to confirm the structure obtained, and try to confirm if it is present other phases/structures unidentified. For this purpose, three specimens were selected to conduct XRD analysis on, these being: the MoNbTaW block (with no additions of V); and both specimens d.1 and d.2, since these specimens present in each three different compositions, therefore accelerating the analysis process. Specimens d.1 and d.2 presented 0/11/17/22 and 0/16/39/62 at% of V, respectively.

Figure 43 shows the global diffractograms for each specimen analysed. Firstly, a preferential orientation of the crystallites for the atomic plane (110) is observed due to the higher peak intensity for all diffractograms. It can also be noted that, from the MoNbTaW to the remaining specimens, there is a visible decrease in intensity and an increase in the width of the peaks, which could be associated with grain growth [72].

Regarding the base system and specimen d.1, it is observed that all the peaks present in the X-ray pattern can be indexed and are congruent with a single BCC phase shown in the powders XRD analysis. In addition, no other phase is observed [16,72]. This result suggests that these elements can still form the same BCC structures despite the different lattice parameters of the five elements, as observed in the CALPHAD non-equilibrium simulations and also by the powders' as-received structure (Figure 24, in chapter 4.2).

However, for the specimen d.2 the same is not observed. Despite the peaks presenting the maximum intensity at similar 2θ , a peak area increase is observed. To obtain a better understanding of specimen d.2, targeted XRD analysis was performed.

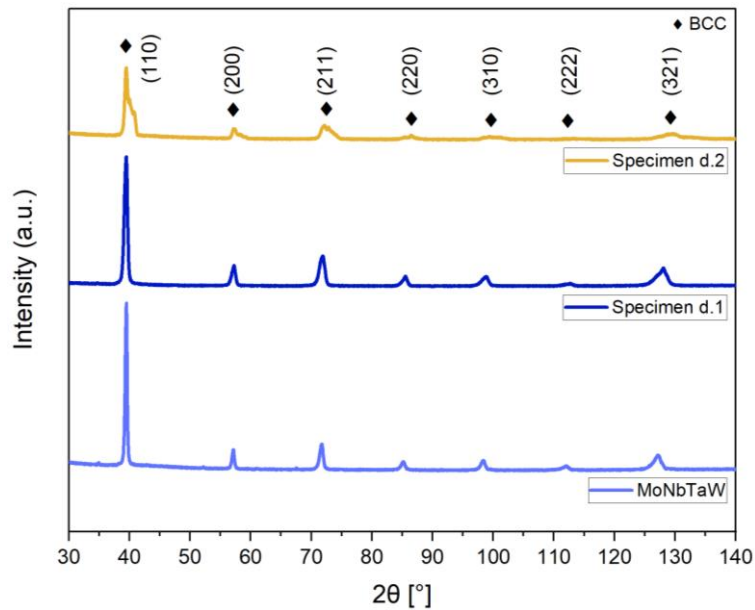


Figure 43: X-ray diffractograms for the MoNbTaW system and specimens d.1 (0/11/17/22 at% V) and d.2 (0/16/39/62 at% V).

For the targeted analysis of specimen d.2, two zones were selected: a region that comprehended from the first to the seventh layer; and another that comprehended the remaining layers. Figure 44 presented a schematic representation of the targeted regions alongside the respective microstructures and diffractograms.

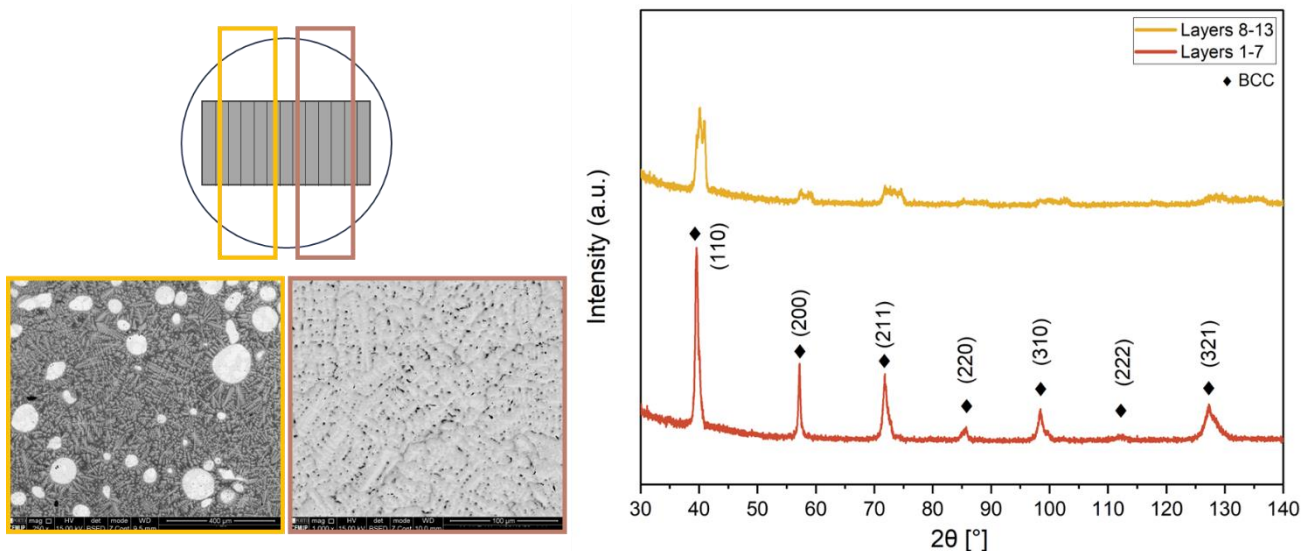


Figure 44: Schematic representation of the targeted X-ray analysis for specimen d.2, alongside the respective microstructures and diffractograms.

As it is possible to observe, the diffractogram for layers 1-8 is identical to the ones presented in Figure 43 for the MoNbTaW and specimen 4.1, which could indicate that this region presents a BCC structure, like the ones observed before. In terms of the region with a higher amount of V, it is observed that its diffractogram presents characteristics of amorphous structures since the peaks could be more defined and present a considerable higher width when compared to the ones described above. These alterations in the peak geometry could also be related to the highly heterogeneous structure in the upper layers of this specimen, which was composed of unmelted MoNbTaW powders and a biphasic structure since the peaks for all the elements present in the system in study are extremely close to each other's.

4.4.4 Alloying effect on the hardness

Since the microstructure is practically identical for the three levels of V addition, it is more relevant to correlate the alloying influence on the mechanical properties studied. For all the compositionally graded samples, an EDS analysis was performed for each layer as an attempt to quantify the V content to correlate the alloying effect on the alloy hardness. Figure 45 summarizes the hardness measurements on all the samples produced and are plotted against the V content.

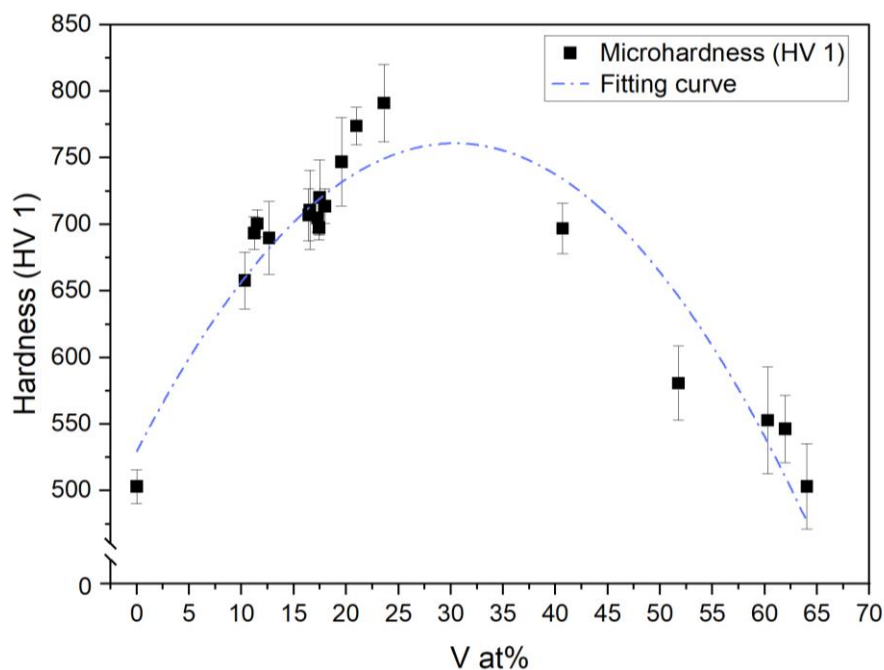


Figure 45: Hardness as a function of V content from all the compositionally graded samples produced.

From the acquired data, it is possible to observe that the relationship between the hardness and V content can be approximated to a polynomial function of second order, where the maximum hardness is achieved for a V content of about 24 at%. Until the peak of the fitting curve, the constant hardness increase can result from a solid solution strengthening. This is a result of the smaller V atomic radius when compared with the remaining elements of the system under study [73].

When the V content is higher, it is possible to observe that this element promotes a softening effect, decreasing the hardness to values similar or even smaller than the initial base system. This could be justified by the fact that V is more ductile than the remaining elements, and due to the cocktail effect observed in HEAs, this property of V will become more noticeable for higher amounts of the beforementioned element. Nevertheless, this theory should be tested on samples without unmelted powders to confirm if this decrease could be related by any means to the structure obtained.

05 CONCLUSIONS

5.1 Conclusions

In this dissertation, a methodology for designing innovative alloys within the MoNbTaW system was employed, where computational and experimental approaches were combined to achieve a high-throughput screening process. For this purpose, first principles calculations and CALPHAD simulations were realised to select possible elements that would lead to a single-phase structure or that could provide an attractive alteration of physical properties, such as the decrease of density. Afterwards, DED was utilised for *in-situ* alloying the base system with the intended element, thus producing compositionally graded build parts/samples based on the MoNbTaWX system. From the results presented, it is possible to draw the following conclusions:

- 1) CALPHAD simulations represent a robust and relevant tool for alloy design without resorting to extensive experimentation. In Scheil simulations, it was possible to consider the production route effect on the final structure, observing that: the addition of V and Ti to the MoNbTaW system allows the formation of a solid-phase structure; the addition of Cr and Zr leads to the formation of a solid solution with the presence of Laves phase; and Al lead to the formation of several intermetallics, mainly sigma phase. It predicted a high melting range for the MoNbTaWV and MoNbTaWTi, which could difficult the processability of these alloys. Since the additions of V and Ti would lead to the intended single-phase structure, they were selected for the production and characterisation step;
- 2) The powders used presented a mainly spherical shape and a d_{50} of 119.6 μm and 71.8 μm for the MoNbTaW and V powders, respectively. Therefore, present the basic characteristics for a DED processing;
- 3) Due to the lack of literature related to the production of RHEAs based on the MoNbTaW system through DED published, the RSM has been demonstrated as a highly efficient process for the optimisation of processes, allowing the best possible trade-off to be obtained between dilution, height, and width of single tracks, as well as always considering the energy efficiency of the process. For the set-up available, the optimal parameters were set as 1800 W laser power; 300 mm/min relative surface speed; and 12.5 g/min, with shielding and carrier gas set as 35 L/min and 4 L/min, respectively;
- 4) In terms of the microstructure and structural characteristics of the produced alloys, it was possible to conclude that for all the alloys with V content inferior to 40 at%, a single-phase structure was observed, identified as BCC through XRD analysis. It also verified the presence of some oxides, owing to the deposition. The deposition parameters must be adjusted for V contents higher than 40 at% to eliminate the unmelted powders observed;

- 5) In terms of hardness, it was possible to verify that a 25 at% V increase promotes the strengthening from approximately 550 HV1 to 770 HV1, representing an increase higher than 40%; however, due to the more ductile behaviour of V, an overall hardness decrease will be observed.

Based on the presented results, it is possible to state that the qualification of DED for the high-throughput screening of RHEAs was accomplished, and it was possible to increase the practical knowledge of RCCA/RHEAs. Yet, further characterisation of the produced alloys must be conducted to evaluate their suitability for high-temperature applications.

5.2 Future work perspectives

Although this dissertation demonstrates the capability of screening RCCAs/RHEAs by means of in-situ alloying through DED, there are still questions to consider for further research and some testing to carry out. Based on preliminary studies, it is suggested to: apply the deposition parameters alteration based on the kg/kWh, proposed in the sub-chapter 4.4.1; and also, to adjust the feed conditions for the V powders, considering the equipment's sensitivity, to produce alloys with different V contents, allowing further to comprehend the effect of this alloy on the base system.

In addition, other tasks related to the Liras project will be developed. The tasks in question are:

- 1) Characterisation of the produced RHEAs at high-temperatures through nanoindentations, obtaining a better understanding of the RHEAs capabilities to surpass Ni-base alloys for high-temperature applications. This characterisation will be carried out at IMDEA Materials Institute, located in Madrid;
- 2) High energy synchrotron X-ray diffraction analysis will also be carried out on the beforementioned specimens to evaluate the presence of possible structures that were not identified during the XRD analysis. These analyses will be possible due to a collaboration with a research group focused on HEAs characterisation, located at the Universidade NOVA of Lisbon;
- 3) Alloying the MoNbTaW system with Ti, using the same strategy as depicted in this dissertation, adjusting the feeding conditions. In addition, the V addition will be repeated to verify the presented results. These depositions will be carried out at Fraunhofer IWS, located in Dresden, due to the possibility of realising the samples' production in a totally inert atmosphere.

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APPENDIX A

Prediction of alloying elements' effects on the structural properties of NbMoTaWX (X = Al, Ti, V, Cr, Zr, and Y) using the CALPHAD method

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Keywords: CALPHAD; MoNbTaWX; RCCAs; RHEAs; Simulation.

Refractory complex concentrated alloys (RCCA), as well as refractory high-entropy alloys (RHEAs), have the potential to surpass state-of-art Ni-based superalloys, due to the possibility of combining high-temperature stability with the higher melting temperature. Consequently, these alloys can actively contribute to a more efficient energy conversion process and reduction of CO₂ emissions. To obtain high thermal stability, several metallurgical criteria should be considered, one of the most important being attempting a single-phase solid solution structure, which assures increased high-temperature phase stability and strength while decreasing the probability of oxidation problems. Several RHEAs have been reported to exhibit interesting and unique characteristics, with the NbMoTaW system being one of the most explored since it can achieve yield strength greater than 500 MPa at 1200 °C [1]. Yet, these alloys present a brittle behaviour at room temperature, narrowing their applications. In this matter, alloying is presented as the best strategy to enhance ductility. There are, however, several obstacles related to the design and development of these alloys, including the identification and selection of the elements that can lead to the intended modification of the mechanical properties. The attraction, but also the challenge, of HEA/CCAs lies in its enormous range of combinations in terms of type, number, and ratio of the chosen elements, which directly affect the final properties and performance of the alloy. Direct Energy Deposition (DED) permits the in-situ alloying of compositions and has been presented as a resource-efficient high-throughput screening technique to accelerate alloy development, which can be even more efficient if supported by CALPHAD simulations [2]. The CALPHAD method allows the prediction of critical thermodynamic and microstructural characteristics of interest for the application in question. In this contribution, the CALPHAD method for property calculation, microstructural features prediction, and high-throughput composition screening in the context of developing new RHEA/RCCAs based on the NbMoTaWX (X= Al, Ti, V, Cr, Zr, Y) system, is presented. For each of the possible alloying elements several thermodynamic properties have been calculated, and phase diagrams in equilibrium and non-equilibrium conditions obtained. Based on these results, the influence of the composition at the microstructural and, consequently, the mechanical level will be evaluated, and the most promising compositions selected to be, later on, manufactured by DED and the properties validated. This study summarizes the first phase of LiRAs project (FCT exploratory project) on high-throughput screening and development of RHEA/RCCAs alloys.

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APPENDIX B

Alloying effect on the mechanical and microstructural properties of RHEAs based on the system MoNbTaWV

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Abstract

In recent years, High Entropy Refractory Alloys (RHEAs) have been presented as possible alternatives to the state-of-art Ni-based superalloys, due to an outstanding combination of properties under high-temperature service conditions. The MoNbTaW system has been particularly explored due to its considerable high yield strength at temperatures around 1200 °C. Yet, these alloys present a brittle behaviour at room temperature, narrowing their applications. To improve the MoNbTaW properties, in-situ alloying with additions of Vanadium (V) by Direct Energy Deposition (DED) assisted by thermodynamical simulations (CALPHAD) has been explored to accelerate the screening of promising compositions. In this contribution, we present the room temperature microstructural and mechanical characterisation to evaluate the influence of V on the MoNbTaW system.

1. Introduction

Ni-based superalloys are commonly used materials for high-temperature applications, such as jet engines and propulsion systems. Although these alloys show great thermal-chemical-mechanical behaviour, melting point limits their maximum service temperatures to around 1000 °C. As an attempt to increase the service temperature, and resultant increase in system efficiency due to less fuel consumption and less CO₂ emissions, Refractory High Entropy Alloys (RHEAs) have been presented as an alternative to the state-of-art nickel-based superalloys, since their high-temperature properties can be combined with the high melting temperature of the refractory elements [1-2].

Literature defines RHEAs as alloys composed of refractory elements (e.g., Cr, Hf, Nb, Mo, Ta, V, W, Zr) that present a single-phase structure with a high configurational entropy. A broader group of alloys, similar to the aforementioned, but also interesting for this particular case, is the Refractory Complex Concentrated Alloys (RCCAs) which only differ in the type of structure presented, thereby being able to present more than one phase or even intermetallic compounds [3].

Most of the RHEAs/RCCAs present ultra-high strength but substantial brittleness. Adding elements in RHEAs can be a strategy to balance properties, namely strength and ductility [4]. Senkov et al. [5] demonstrated that the RHEAs MoNbTaW and MoNbTaWV exhibit an increase in their ability to deform without breaking (plastic strain) from 2% and 1.5%, respectively, to 10-15% at high temperatures. This increase in plastic strain is accompanied by a compressive strength of 421-506 MPa and 656-735 MPa, respectively, at temperatures as high as 1600 °C. The resistance to high temperatures of these RHEAs, like Ni-superalloys, can be attributed to the slow diffusion of elements, directly related to their high melting temperature. Generally, high-temperature softening occurs at 0.6 times the alloy's melting temperature (T_m), so this phenomenon is expected to be delayed with an increase in the alloy's T_m .

Despite the promising properties of these new materials, the correct and effective alloy design is diffculted by the number of variables to consider during this process, such as type, number, and content of each of the elements to obtain the structure and properties intended. Therefore, to accelerate the design of the RHEAs, two tools that have been proven effective for this purpose [6-7], were used, namely: (1) CALPHAD methodology, as a prediction tool, and (2) Direct Energy Deposition (DED), as a high-throughput tool for screening the most promising compositions.

Within the framework of this contribution, the room temperature microstructural and mechanical characterisation will be presented as a first step to assess the V influence on the MoNbTaW base system.

2. Materials and Methods

To fulfil the goal of accelerating the screening of RHEAs compositions, CALPHAD simulations were realized to select the most promising alloys to study. Parallel, the as-received powder feedstock materials were characterized, and DED depositions of the base system were carried out to obtain a reference point. Subsequently, in-situ alloying of MoNbTaW and Vanadium by DED was accomplished, and the volumes have been characterized.

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2.1. CALPHAD Simulations

Equilibrium and non-equilibrium simulations were performed by means of the Thermo-Calc Software, version 2023a, with TCHEA6 High Entropy Alloys database, concerning the alloy compositions MoNbTaWV_x, with *x* ranging from 0 to 50 at% with a 5 at% step.

2.2. Powder Characterization

MoNbTaW alloy powders (45-150 µm) were purchased from TANIOBIS (TANIOBIS GmbH, Goslar, Germany), and V powders (45-150 µm) from AEM (Advanced Engineering Materials Limited, Hunan, China). Both as-received powder batches were characterised through environmental scanning electron microscopy with energy dispersive spectroscopy (ESEM/EDS), using a FEI Quanta 400 FEG ESEM with an EDAX Genesis X4M EDS. The SEM powder images analysis was done using Image J (version 1.51, Wayne Ras-band, National Institutes of Health, Bethesda, MD, EUA), where the particle size distributions (PSD) was assessed by measuring 1000 particles for each powder batch.

2.3. RHEAs produced by Direct Energy Deposition

All the specimens were built on a SAE 316L stainless steel (SS) substrate, purchased from F. Ramada (Ramada Aços e Indústrias, SA, Aveiro, Portugal), using a Direct Energy Deposition (DED) setup mounted and fully operating at INEGI – Institute of Science and Innovation in Mechanical and Industrial Engineering. The setup used during the execution of the present work consisted of a Coherent Highlight FL3000 fibre laser (Coherent, Santa Clara, CA, USA), capable of delivering power of up to 3 kW and a laser spot size of 2.1 mm, and a KUKA 6 axis robot (KUKA, Augsburg, Germany), paired with a COAX12V6 nozzle (Fraunhofer IWS, Dresden, Germany). Two Fraunhofer IWS powder splitters and a Fraunhofer E-MAqS system were also mounted. Argon (purity ≥ 99.99%) was used as shielding and carrier gas.

For microstructural characterisation purposes, each built part was mounted using cold mounting epoxy resin and polished down to 0.06 µm colloidal silica. A detailed microstructure characterisation was carried out by ESEM/EDS, using the same equipment aforementioned. Crystallographic structure was assessed by Electron backscatter diffraction (EBSD). The mechanical characterisation was performed by Vickers hardness tests, according with the ISO 6507-1:2005 standard, where 10-15 indentations were made in each specimen/alloy produced with a 9.807N load, using a FALCON 400 micro/macro-Vickers hardness tester (INNOVATEST) at room temperature.

2.3.1. MoNbTaW parts production

For microstructural and mechanical comparison purposes, a base system (MoNbTaW) part, with two layers of two single tracks each, was built with a zigzag printing strategy, using an overlapping of 40%. The optimal parameters were set as: 1800 W laser power; 300 mm/min relative surface speed; and 12.5 g/min. Shielding and carrier gas, were set as 35 L/min, and 4 L/min, respectively.

2.3.2. Compositionally graded parts production

For the in-situ alloying of the base system with V, the parameters were set as: 1800 W laser power; 300 mm/min relative surface speed; and 12.5 g/min global feed rate. To manufacture structures with the desired concentration gradients, always guaranteeing their integrity and a gradual variation in composition, the attempted compositions were split into four specimens, each with the compositions presented in Table 1. Four layers of the base alloy were deposited, thus ensuring that the alloying elements were added to a "substrate" equivalent to original alloy (powder) composition.

Table 1: Feeding conditions for each powder for the compositionally graded parts

Layers	Powder feed rate in g/min							
	MoNbTaW	V	MoNbTaW	V	MoNbTaW	V	MoNbTaW	V
1-4	12.5	0	12.5	0	12.5	0	12.5	0
5-7	12.25	0.25	12	0.5	11.75	0.75	10.75	1.75
8-10	12	0.5	11.5	1	11.13	1.37	10	2.5
11-13	11.75	0.75	10.75	1.75	10.38	2.12	9.13	3.37
Parts	0/5/10/15 at% V		0/10/20/30 at% V		0/15/25/35 at% V		0/30/40/50 at% V	

3. Results and Discussion

3.1. CALPHAD Simulations

CALPHAD simulations have been presented as an effective tool for an efficient alloy design. In the present work, equilibrium, and non-equilibrium simulations for the MoNbTaW system with additions of V were performed through the Material-to-Material function and the *Scheil* with Solute Trapping model, respectively, for each type of simulation.

From the equilibrium simulations, presented in Figure 1a, it is possible to observe that the study system does not form a single-phase structure, forming instead a biphasic structure composed of two distinctive body-centred cubic (BCC) phases.

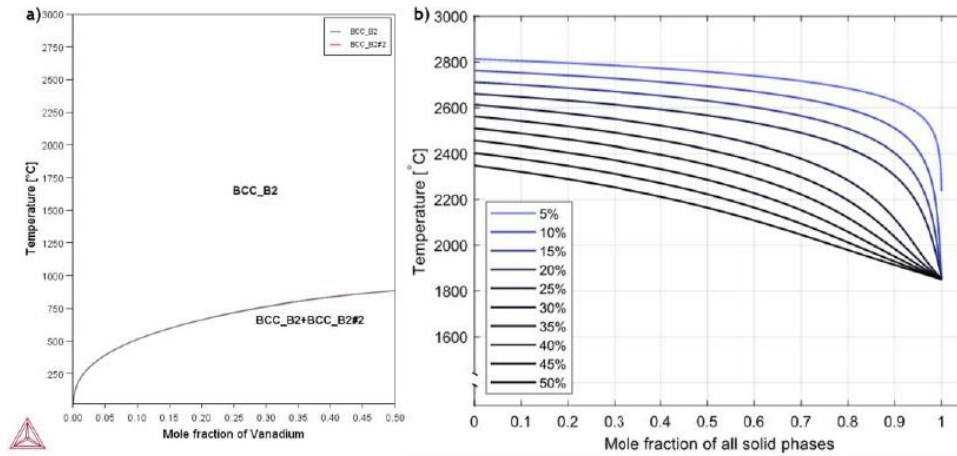


Figure 1: (a) Pseudo-binary phase diagram of MoNbTaWV_x and (b) Scheil with Solute Trapping simulation of the phase transformation from $L \rightarrow BCC_B2$.

DED is known for extremely high solidification rates, which is far from a solidification in equilibrium conditions. Therefore, a second type of simulation was conducted, the parameters were defined based on bibliographic research [8]. In Figure 1.(b), it is possible to observe that the alloys selected solidify into a BCC structure, being the only compound formed during the solidification step. Since V presents a lower melting temperature than the base system, it is also observed the continuous decrease of the alloy melting temperature with the increase of the V content.

3.2. Powder Characterization

From powder SEM/EDS analysis (Figure 2), it is possible to verify that MoNbTaW (Figure 2a) and V (Figure 2b) powders are mainly spherical; however, the MoNbTaW powders presents some irregular particles.

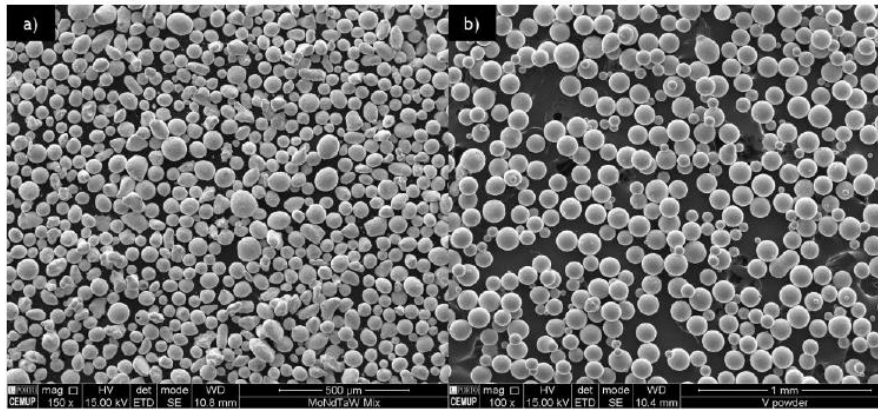


Figure 2: SEM images of the pre-alloyed (a) MoNbTaW powders and (b) V powders.

Regarding the global analysis through EDS, presented in Table 2, it is possible to verify the presence of some oxidation on the base system powders, being this due to their manipulation. Concerning the vanadium powders, the presence of some carbon contaminations, which could be due to the carbon tape used during the analysis.

Table 2: EDS Global analysis for both powders

at%	Mo	Nb	Ta	W	V	O	C
MoNbTaW powder	14.3	22.7	23.0	27.8	-	12.2	-
V powder	-	-	-	-	2.1	-	98.0

The MoNbTaW system has a D_{50} of 62 μm V powders has a D_{50} of 115 μm for the V powders, with a S_w (cumulative distribution slope) of 9 and 15, respectively. Both powders present an elevated S_w value indicating a narrow PSD, which is intended for DED process, since it is desirable for a similar general interaction of the powders with the laser.

3.3. MoNbTaW part microstructural characterization

Initially, the MoNbTaW system was studied without alloying element to obtain a starting point for the present study and to evaluate the capability to process this alloy by DED. Figure 3a shows two distinctive regions in the built part: (A) a darker one, corresponding to the dilution area with unfused powder particles; (B) a dendritic zone composed of the base system, and a second phase formed by the interaction between the MoNbTaW powder and the substrate, and (C) the 316L substrate.

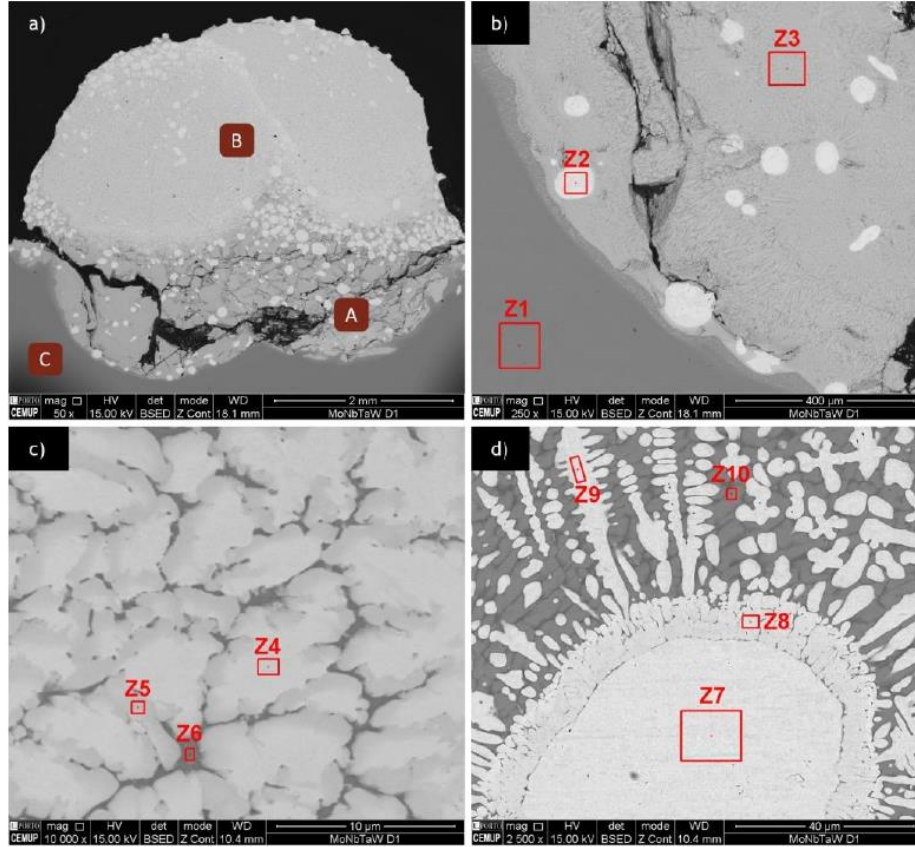


Figure 3: (a) Two layers MoNbTaW part; (b) Zone A: interface between the 316L SS substrate and the dilution region; (c) Region Z3 with a high magnification; (d) Zone B: built area.

The microstructure of region A is presented in Figure 3b and 3c. SEM images show the interfacial zone between the SAE 316L SS substrate and the dilution zone. This zone presents unmelt MoNbTaW powders and several cracks, mostly due to the different contraction coefficients of the materials, leading to the formation of residual stresses [9]. When taking a closer look at the dilution zone, it is possible to observe that zone 3 (Z3) is not homogeneous, this is composed by three different compounds with different interactions with the RHEA system, as it is shown by the EDS analysis presented in Table 3.

Table 3: Chemical Composition (at%), obtained by EDS analysis, of the regions presented in Figure 3.b and 3.c

Region	C	Si	Mo	Cr	Fe	Ni	W	Ta	Nb
Z1	2.0	0.8	1.2	18.3	68.3	9.3	-	-	-
Z2	1.5	-	23.4	-	-	-	31.7	21.4	22.0
Z4	4.0	-	7.3	12.0	43.0	5.2	13.1	8.5	6.9
Z5	4.3	-	10.0	11.6	44.4	6.4	8.3	7.4	7.6
Z6	4.8	-	4.5	16.1	56.0	14.6	0.9	1.3	1.9

Region B (Figure 3d) itself did not present the intended single-phase structure, but rather a biphasic structure composed of dendrites of MoNbTaW in a ferrous matrix. Through the EDS analysis, presented in Table 3, it is possible to observe that the matrix displays a similar composition to the SAE 316L SS, however, with a higher amount of interaction with the deposited alloy. Z7 and Z8 correspond to the unmelt powder or partially fused, presenting a similar composition to the MoNbTaW powder.

Table 4: Chemical Composition (at%), obtained by EDS analysis, of the regions presented in Figure 3.d

Region	C	Mo	Cr	Fe	Ta	W	Nb
Z7	3.7	20.8	-	-	32.5	26.7	16.4
Z8	6.3	22.7	2.5	4.1	26.4	27.1	11.0
Z9	4.8	22.2	2.9	5.0	24.1	30.6	10.5
Z10	3.4	8.6	10.2	40.9	19.2	2.9	14.8

The presence of high amount of a SAE 316L SS-like phase on the built part can be justified by two possible phenomena: the Marangoni effect or the vaporisation of certain elements. Since the MoNbTaW presents a melting temperature (T_m) higher than double of the substrate's T_m , the energy input to melt the material will produce a greater-than-normal amount of liquid substrate. Since there is a significant amount of molten substrate, the Marangoni currents lead to the incorporation of the substrate in the MoNbTaW part, therefore forming this biphasic structure. The other possible justification can be the volatilisation of certain elements, such as Fe since its boiling temperature is lower than the T_m of the deposited alloy.

The EBSD results shown in Figure 4, confirmed the BCC structure described in the simulations for the MoNbTaW base system (Figure 4b), and also that the other phase observed was formed due to the interaction with the substrate since it presents a face-centred cubic (FCC) structure (Figure 4c), which is the same structure of the austenitic stainless steel used.

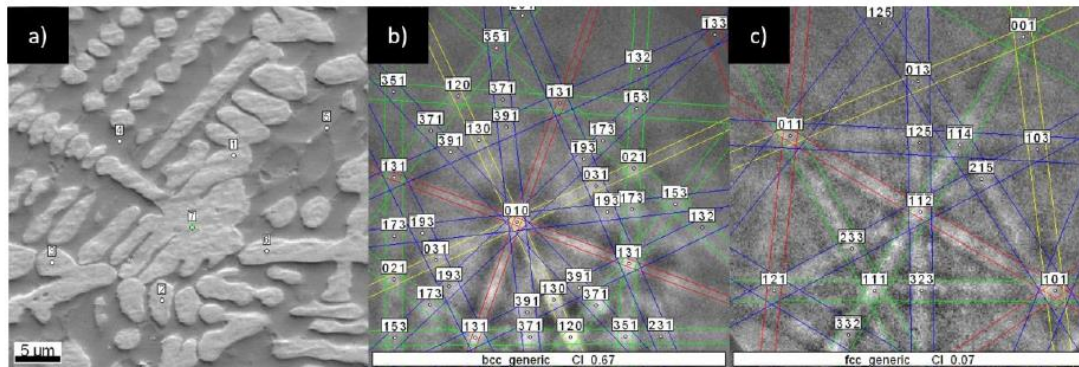


Figure 4: SEM image of the built block - zone B (a), and indexed EBSD patterns corresponding to MoNbTaW (b) and to the phase formed due to the substrate interaction (c).

3.4. Compositionally graded parts microstructural and mechanical characterization

Each gradient structure displayed approximately 20 mm wide and 19 mm high. As presented in Table 1, each specimen presented 3 distinctive V additions. Yet, due to the small feed rate of the alloying element, when compared to the feed rate of the base system powder, it was only possible to observe the presence of this alloying element in specimen 4, being this the one with intended additions of 30, 40, and 50 at% of V. Therefore, a more in-depth analysis was conducted in this specimen.

Figure 5 depicts the as-built structure obtained where; it is possible to observe the presence of several porosities. Their formation can be explained due to the use of a considerably high flow rate of the shielding gas, which was selected as an attempt to eliminate oxidation problems since the parts were not built under an inert atmosphere.

As it is possible to observe in Figure 5b and 5c, the deposition of the four initial layers allows the elimination of the substrate effect, being present a solid solution composed of MoNbTaW, and some smaller particles with similar composition to those present in Figure 3(d) in region Z10.

Regarding the alloyed layers, through EDS analysis, it was possible to observe an average vanadium at% of 11.3%, 16.8%, and 21.4% for the layers 5-7, 8-10, and 11-13, respectively. As mentioned, the alloying strategy did not result in the intended V content, resulting in a smaller yield around 41%.

In terms of the microstructural evidence, when comparing with the results generated by the CALPHAD simulations, it is possible to observe that the as-built structure is not a single-phase, as predicted, probably due to the lack of time for a complete homogenisation. The layers alloyed present almost the same composition, only differing in the V content in each phase. Table 5 presents the EDS analysis for each region described in Figure 5d and 5f.

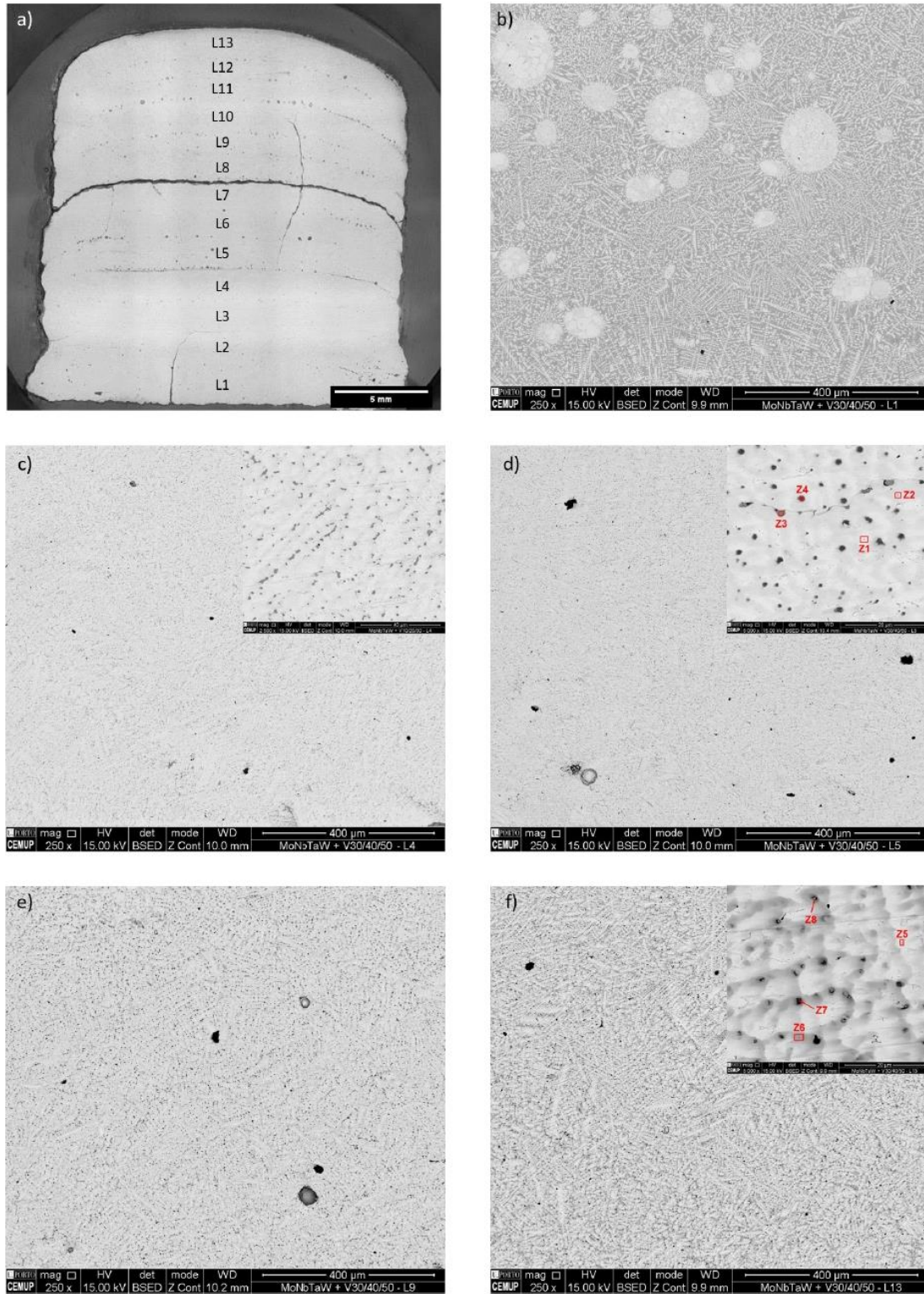


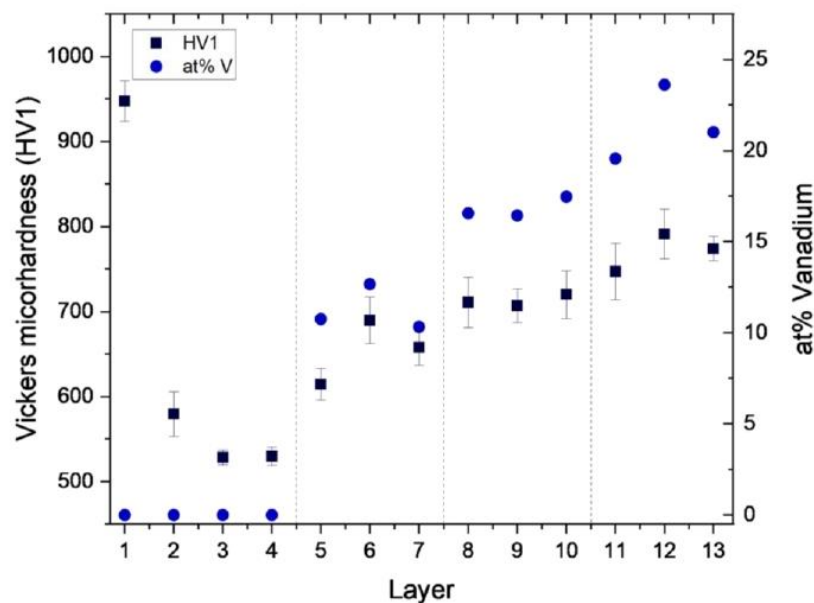
Figure 5: (a) Specimen 4 cross-section; SEM images of the major microstructures of the as built alloys in specimen 4: (b) Layer 1; (c) Layer 4; (d) Layer 5; (e) Layer 9; (f) Layer 13.

Table 5: Chemical Composition (at%), obtained by EDS analysis, of the regions presented in Figure 5

Region	O	Ta	W	Nb	Mo	V	Ti	Hf
Z1	-	31.4	23.8	16.1	21.1	7.6	-	-
Z2	-	28.5	14.2	22.2	21.4	13.7	-	-
Z3	44.4	31.7	-	5.6	-	18.4	-	-
Z4	39.1	16.8	-	16.0	-	28.2	-	-
Z5	9.2	25.6	21.8	12.1	17.6	13.7	-	-
Z6	13.9	16.8	5.0	19.2	11.2	33.9	-	-
Z7	35.7	8.3	-	9.2	-	45.4	1.4	-
Z8	39.4	11.8	8.8	-	-	31.3	1.3	7.5

All the different alloys studied present a matrix composed of two distinctive zones (Z1-Z2 in Figure 5d and Z5- Z6 in Figure 5f) mostly varying in the V content. This type of structure could indicate that the building process does not allow enough time for structure homogenization, or that the conditions lead to a structure similar to the one described by the pseudo-binary diagram (Figure 1a). Heat treating these samples could provide the required conditions to homogenise the structure, obtaining the intended single phase. This will be explored in future works. Regarding the darker particles presented in almost every layer, according to the EDS analysis, it is possible to identify them as oxides or contaminations (Z3, Z4, Z7 and Z8), due to the high amount of oxygen and foreign elements.

Since the microstructure is practically identical for the three levels of V addition, it is more relevant to correlate the alloying influence on the mechanical properties studied. In Figure 6 the obtained hardness values are plotted against the V content. In the first layer is possible to observe a microhardness of 924 ± 24 HV1; however, this layer composition is highly influenced by the substrate, being only possible to observe the effective hardness of the base material in the following layers (2-4), where it stabilises around the 550 HV1.

**Figure 6: Hardness evolution with the increase of V content**

When the V content starts to increase, it is observe an overall increase in hardness. This increase can result from solid solution strengthening, since V presents the smallest atomic radius of the system elements, thus being able to lattice strains [10]. Regarding the overall strengthening, it is seen that the alloying with nearly. 20 at% of V leads to an increase higher than 40% relative to the base MoNbTaW alloy.

4. Conclusions

DED allowed the *in-situ* alloying, thus being able to produce compositionally graded build parts based on the MoNbTaWV system. Therefore, it was possible to employ a microstructural and mechanical characterisation of different alloys with an effective V content ranging from 10 to 20 at%. From the results presented, it is possible to draw the following conclusions:

- 1) DED can be used for the *in-situ* high-throughput screening of RHEAs. However, adjustments must be made to obtain the intended alloying element content.
- 2) The microstructure of the produced alloys presented a biphasic structure, being closest to the equilibrium CALPHAD simulations than to the non-equilibrium ones. However, further tests must be run to confirm the obtained structure.
- 3) In terms of hardness, it was possible to verify that a 20 at% V increase promotes the strengthening from approximately 550 HV1 to 770 HV1, representing an increase higher than 40%.

Future Work

To further develop the work herein presented and to better correspond to the proposed goals of the funding project, the following activities will be carried out: optimisation of the powder feeding parameters to obtain the desired V additions; XRD analysis to confirm the phases/structures present in each alloy developed; and heat treatments to homogenize the alloys structures.

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APPENDIX C

High-throughput screening of RHEAs based on the system MoNbTaWX (X=Al, Ti, and/or V)

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Keywords: CALPHAD; Direct Energy Deposition; Mechanical and Microstructure characterization; MoNbTaWX; RCCAs; RHEAs.

Combustion processes in jet engines and propulsion systems for the aeronautic and aerospace sector would be more efficient, with lower fuel consumption and CO₂ emissions if the combustion could be conducted at a higher temperature. This is currently not possible mainly due to the material intrinsic constraints. In recent years, a whole new class of materials has been developed with the potential to surpass Ni-based state-of-art superalloys for high-temperature applications, these being the High Entropy Refractory Alloys (RHEAs). The NbMoTaW system has been considered particularly promising within this new class of material due to its yield strength greater than 500 MPa at 1200 °C [1]. Yet, these alloys present a brittle behaviour at room temperature, restricting their application.

Adding more elements to the composition is believed to be the key to improving room temperature ductility and, therefore, the processability of these alloys. The variety of possible combinations is often associated with extremely high development time and costs. To surpass the challenge related to the design and development of these alloys, such as the identification and selection of possible compositions that will lead to the intended thermal-chemical-mechanical behaviour, a High-Throughput Screening methodology, which combines Thermodynamical simulation (CALPHAD) with Direct Energy Deposition (DED), as well as advanced materials characterisation techniques, as started to gain the attention of the research community.

In this study, the combination of CALPHAD method and DED for composition screening in the context of developing new RHEAs/RCCAs based on the NbMoTaWX (X= Al, V, and/or Ti) system is presented. CALPHAD allows to select of the most promising compositions to be tested. DED allows the in-situ alloying of new compositions directly on the melt pool by mixing different powders, making it possible to gather further information on RHEAs and thus gain better insight into the interaction between process parameters, alloy composition, and structure, as well as application-relevant properties. Microstructural and mechanical characterization were conducted at room temperature to assess the influence of the alloying elements on the quaternary composition, aiming to increase its room temperature ductility while guaranteeing a structure that allows a high strength at high temperatures. Based on these results, it was possible to increase the practical knowledge of RCCAs/RHEAs, thus accelerating the potential application of these alloys in aerospace applications. This resumes a part of work developed in the LiRAs project (FCT exploratory project) on high-throughput screening and development of RHEA/RCCAs alloys.

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