



Influence of laser-based powder bed fusion processing parameters on the microstructure of a metastable HEA

Master's thesis in Master Programme Materials Engineering

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Cover: Transmission Kikuchi diffraction phase map of $Co_{45}Cr_{25}(FeNi)_{30}$ HEA, depicting the presence of thermally induced HCP martensite, taken along the plane parallel to the building direction.

Typeset in LATEX Printed by Chalmers Reproservice Gothenburg, Sweden 2022 Influence of laser-based powder bed fusion processing parameters on the microstructure of a metastable HEA

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Abstract

High entropy alloys (HEAs) constitute a novel class of alloys containing multiple principal elements in nearly equiatomic proportions. This compositional complexity increases the configurational entropy and hence stabilizes the formation of solid solutions. The unprecedented compositional complexity has reportedly enabled HEAs to perform better than conventional alloys in various situations. Manufacturing HEAs using additive manufacturing techniques such as laser based powder bed fusion (LB-PBF) helps in preventing the formation of detrimental phases, owing to high solidification rates compared to conventional casting. Rapid melting and solidification during the layer-by-layer printing could also result in martensitic transformations in some metastable HEAs. This work focuses on the development of non-equiatomic metastable HEAs based on the CoCrFeNi grade, aiming to engineer martensitic transformation via tuning the printing parameters. After evaluating the relative densities of the specimens from the parametric development using the design of experiments methodology, two specimens printed with a significant difference in laser power were selected for further analysis. Scanning electron microscopy analyses of as-printed specimens revealed the presence of banded features spanning across the microstructure. Subsequent analyses using transmission Kikuchi diffraction revealed that these bands correspond to the HCP phase, indicating the occurrence of the martensitic transformation during printing. Tensile testing of as-printed specimens with two different processing parameters exhibited a similar yield strength of 560 ± 10 MPa and an engineering strain of 34 %. This could be due to the similar transformation induced plasticity (TRIP) behavior of the two materials during loading.

Keywords: High entropy alloys, laser-based powder bed fusion, metastability, martensite, microstructural characterization.

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Vishnu Anilkumar, Gothenburg, May 2022

List of Acronyms

Below is the list of acronyms that have been used throughout this thesis listed in alphabetical order:

| AI | Artificial Intelligence |
|--------|--|
| AM | Additive Manufacturing |
| A_s | Austenite Start Temperature |
| A_f | Austenite Finish Temperature |
| BCC | Body Centered Cubic |
| BCT | Body Centered Tetragonal |
| CAD | computer aided design |
| DP | Dual-Phase |
| DIMT | Deformation Induced Martensitic Transformation |
| FCC | Face Centered Cubic |
| G | Thermal Gradient |
| HEA | High Entropy Alloy |
| iHEA | Interstitial High Entropy Alloy |
| KS-OR | Kurdjumov-Sachs Orientation Relationship |
| LB-PBF | Laser Based Powder Bed Fusion |
| ML | Machine Learning |
| MT | Martensitic Transformation |
| M_s | Martensite Start Temperature |
| M_f | Martensite Finish temperature |
| MAD | Metastability Alloy Design |
| NW-OR | Nishiyama-Wasserman Orientation Relationship |
| PBF | Powder Bed Fusion |
| QP | Quench and Partitioning |
| R | Solidification Rate |
| SFE | Stacking Fault Energy |
| SS | Stainless Steel |
| SHR | Strain Hardening Rate |
| SN-OR | Shoji-Nishiyama Orientation Relationship |
| TIMT | Thermally Induced Martensitic Transformation |
| TWIP | Twinning Induced Plasticity |
| TRIP | Transformation Induced Plasticity |

Contents

| Li | st of | Acronyms | viii |
|----|---|---|--|
| Li | st of | Figures | xiii |
| Li | st of | Tables | xv |
| 1 | Intr | oduction | 1 |
| 2 | The 2.1 2.2 2.3 | HEAs | $egin{array}{c} 3 \\ 4 \\ 4 \\ 7 \\ 9 \\ 10 \\ 11 \\ 11 \\ 13 \\ 14 \\ 14 \end{array}$ |
| 3 | Met 3.1 3.2 3.3 | Label StructureDesign of experimentsImage: StructureLB-PBF parametersImage: StructureImage: StructureMaterial characterizationImage: StructureImage: Structure3.3.1MetallographyImage: Structure3.3.2Electrochemical polishingImage: Structure3.3.3Optical microscopyImage: Structure3.3.4Scanning electron microscopyImage: Structure3.3.5Mechanical testingImage: Structure3.3.5.1Tensile testingImage: Structure | 17 17 18 18 19 19 21 23 23 |
| 4 | Res 4.1 4.2 4.3 | ults and discussionDesign of experimentsMicrostructural characterizationMechanical testing | 25 25 28 34 |

| | 4.3.1 | Tensile test | | | | | 34 |
|----------|------------|--------------|------|------|------|------|--------|
| 5 | Conclusion | ns | | | | | 37 |
| 6 | Future Sc | ope | | | | | 39 |
| Bi | bliography | | | | | | 41 |

List of Figures

| 2.1 | Visualization of (a) stacking sequence and (b) intrinsic stacking fault in {111} planes of FCC crystals | 5 |
|------------|---|----|
| 2.2 | Illustration of a perfect dislocation with Burger's vector b1 dissociat- ing into two partial dislocations b2 and b3 forming a faulted region | |
| | Adapted with permission from Ref^{15} | 5 |
| 2.3 | Visualization of a twin fault (left) and HCP martensite (right) formed depending on the nature of glide of Shockley partials on {111} atomic planes of an ECC grystal | 6 |
| 2.4 | Schematic representation of a typical LB-PBF machine, reprinted | 0 |
| | with permission from Ref^{91} | 11 |
| 2.5 | Illustration of (a) effect of G and R on solidification mechanism and (b) free energy change (Δ G) associated with heterogeneous nucleation in welding/LB-PBF and casting along with homogeneous nucleation. | 10 |
| 2.6 | Schematic of (a) LB-PBF processing parameters, reprinted with per- mission from Ref ⁴⁹ and (b) intensity (I) vs radial distance (R) depict- ing Gaussian distribution of laser power. Adapted with permission | 12 |
| | from Ref^{101} . | 13 |
| 3.1 3.2 | A photo of Zeiss Axioscope 7 optical microscope used for this study ¹⁰⁵ Schematic of interaction volume generated due to electron interaction with matter, showing the origin of secondary electrons, backscattered electrons, Auger electrons, characteristic, continuum and fluorescent | 19 |
| 3.3 | X-rays, and cathodoluminescence ⁹³ | 20 |
| | coupled device (CCD) camera for further processing. \ldots | 21 |
| 3.4 | Schematic representing the TKD geometry for specimen back tilted away from the detector and specimen mounted horizontally. Reprinted with permission from Ref ¹⁰⁶ | 22 |
| 4.1 | Contour map of relative density of samples with respect to hatch spacing and scan speed for both (a) 90 W 2 factor D-optimal DOE and (b) 110 W 2 factor D-optimal DOE | 25 |

| 4.2 | Schematic of (a) Relative density (%) v/s VED (J/mm ³), representing regions of full density for 90 W and 110 W samples, (b),(c),&(d) represents OM micrographs of specimens from 110W DOE with VED belonging to lack of fusion (I), high density (II), and key-hole (III) | |
|------|---|----|
| | regions respectively. | 26 |
| 4.3 | OM images of the 2F-D1 sample along the cross-section parallel to the building direction (BD) (a) depicting the presence of banded features at the center portion of the sample and (b) along the edges of the specimen | |
| 4.4 | SEM images of (a) banded features observed along the edges of the 2F-D1 sample and (b) that representing the solidification structure | 20 |
| 4.5 | (a) EBSD phase map of the 2F-D1 sample depicting the presence of HCP phase (b) SEM image with EDS map of the same region showing the chemical homogeneity of the elements across HCP and ECC phases and (c) pole figures and inverse pole figures of the HCP | 28 |
| 4.6 | and FCC grains showing the S-N orientation relationship EBSD phase map of the 2F-D1 sample (a) along with the calculated martensitic phase fraction and inverse pole figure map of 2F-D1 (b) | 29 |
| 4.7 | depicting the <100> crystallographic texture | 30 |
| 4.8 | in the as-printed state | 31 |
| 4.9 | substructures observed in the as-printed state | 32 |
| 4.10 | (a) EBSD phase map of the 2F-D1 sample along the plane parallel to the building direction and (b) band contrast (BC) map of the same | 32 |
| 4.11 | region | 33 |
| 4.12 | along the building direction showing the absence of banded features . TKD phase maps of as-printed the 3F-D2 samples showing the marten- | 33 |
| 119 | (c) to the building direction respectively | 34 |
| 4.13 | ples | 34 |

List of Tables

| 3.1 | The steps used for polishing and "Rotation" denotes the direction with which the sample holder and the polishing table are rotating | 18 |
|-----|---|----|
| 3.2 | Processing parameters used for electrochemical polishing using the | |
| | A3 electrolyte | 19 |
| 3.3 | Processing parameters used for twin-jet electrochemical polishing us- | |
| | ing the A3 electrolyte. | 23 |
| 4.1 | Processing parameters with the highest relative density from the 2 | |
| | factor D-optimal DOE | 27 |
| 4.2 | Processing parameters with highest relative density from the 3 factor | |
| | D-optimal DOE | 27 |

1 Introduction

Additive manufacturing (AM) also known as 3D printing, follows a bottom-up approach where the product is manufactured layer-by-layer, strictly following the 3 dimensional computed aided design (CAD). This is in contrast to the top-down strategy followed by traditional subtractive manufacturing techniques like computer numerical control (CNC) machining. The advantages of AM include the ability to produce intricate geometries, with high level of customization, coupled with reduced lead time to market. The AM processes depending on the principle of manufacturing, can be categorized as liquid state, solid state and powder based processes. This can be further sub-classified into seven categories among which powder bed fusion based processes are most widely studied. This is due to their ability to fabricate a wide range of metallic materials like titanium alloys, tool steels, stainless steels and various others to near net shape structures with minimal material waste.

Laser-based powder bed fusion (LB-PBF) belongs to the sub-category of powder bed fusion technique in which a laser beam of suitable power is employed to melt and consolidate selective regions of the powder bed. The interaction of laser beam with the powder bed leads to the formation of a small-sized meltpool followed by rapid solidification. To ensure proper consolidation, along with the melting of the newly deposited layer, remelting of powder bed over a few layers beneath this newly deposited layer is preferred. This leads to epitaxial grain growth, often than not leading to the formation of long columnar grains spanning across multiple meltpool boundaries. Apart from this, the thermal gradient (G) and growth rate (R) values in LB-PBF typically result in cellular solidification, enabling to manufacture materials with properties unlike from any traditional manufacturing route. The heat generated due to the layer-by-layer melting and solidification of powder bed in LB-PBF is transferred to the surrounding powder bed and solidified material. This leads to the in-situ heat treatment in LB-PBF offering the potential to bypass post heat treatment, if this is effectively executed with suitable-quality powder and optimized processing parameters, so as to prevent undesirable precipitation reactions.^{38,47,86-88,96}.

The aforementioned distinctive properties of LB-PBF render it to grow into an immensely researched field both from the academic and the industrial perspective. It is thus imperative to ensure the quality of parts produced using LB-PBF for industrialization of this technique. The quality of the final part is affected by multiple factors including the morphology and size distribution of powder feedstock, and the processing conditions in the build chamber⁸⁹⁻⁹⁰. Effective process parameter optimization and control of processing conditions such as processing atmosphere and quality of feedstock powder used are important to ensure consistency in printability and resulting quality of the final parts.

HEAs are a novel class of alloys consisting of multiple principal elements, some of which exhibit excellent mechanical properties. However, laborious manufacturing using conventional techniques makes it arduous to produce HEAs. In this context, LB-PBF helps address these aforementioned issues with its inherent rapid cooling and solidification along with freedom for optimizing part geometry and therefore assists fast advancements in this field^{45,60-63}. On the other hand, engineering materials in the metastable state could undergo athermal transformations under the influence of an applied load³⁴ which can increase the strain hardening response and thereby address the issue of strength-ductility trade off. LB-PBF of metastable materials such as transformation induced plasticity (TRIP) steels⁹⁴ and some Co-based alloys¹⁰⁰, has been found to trigger the formation of martensitic phase in the asprinted state.

The main objectives of this thesis work are:

1. To study the influence of processing parameters on resulting densification of the final parts.

2. To study how the processing conditions in LB-PBF govern the phase stability, resulting microstructure and mechanical properties of a metastable $Co_{45}Cr_{25}(FeNi)_{30}$ HEA.

2

Theory

The following sections consists of concepts of HEAs, stacking fault energy (SFE) and its influence on governing deformation mechanisms in face centered cubic (FCC) metals and alloys. A general overview on martensitic transformations (MTs) and LB-PBF is also elucidated.

2.1 HEAs

Conventional alloying strategy involves addition of small amounts of secondary elements to a base element for enhanced properties. This single principal element based alloy design limits the possible element combinations restricting the region of interest to corners of the phase diagram. In 2004, a new alloy design concept emerged, involving multiple principal elements (five or more) with equiatomic or near equiatomic proportions. This group of alloys were named high entropy alloys (HEAs), since the higher entropy of mixing was believed to cause the observed stabilization of the solid solution phase¹. Novel alloy design concept such as this provided material scientists a new way to probe the hyper-dimensional compositional space².

To attain a high configurational entropy, it was suggested to apply equiatomic alloying of elements, as the configurational entropy attains the maximum value at equiatomic proportions. The configurational entropy was calculated from the Boltzmann's equation:

$$\Delta S_{mix} = K ln W \tag{2.1}$$

where Δ S is the configurational entropy of mixing, K is the Boltzmann's constant and W is the number of states. The system attains a value of 1.61R (R is the universal gas constant) with the presence of 5 principal elements in equiatomic proportions. HEAs are in general defined as alloys having 5 or more elements with their compositions anywhere between 5 at% and 35 at%. Addition of any element less than 5 at% is considered as a minor element.

The vastness of possible elemental combinations for HEAs makes exploring for new solid solution forming compositions expensive and time-consuming. Addressing this issue through traditional computational methods coupled with experimental validation is extensively used, but the scopes are still rather limited due to difficulties in exploring the colossal region of interest and requirements for substantial investments. To this end, researchers have turned to machine learning (ML) which involves

the study of computer algorithms, evolving from deep learning of data to making predictions³. ML is considered to be a subset of artificial intelligence (AI) and has paved its way into the realm of materials science and engineering. It is gaining momentum quickly, with its role in assisting discovery of new materials with reduced costs⁴. ML has proved to be a useful tool in the discovery of certain bulk metallic glasses⁵ and high entropy ceramics⁶, thereby allowing researchers to explore the hyper dimensional compositional space for new solid solution forming HEAs.

2.1.1 Phase selection rules in HEAs

The phase selection rules for HEAs discussed here take into account chemical, topological and electronic parameters of the alloying elements in a convenient way to predict solid solubility and phase formation. A study on the tendency for the formation of solid solutions and the amorphous phase in HEAs using a two-parametric approach including atomic size polydispersity (δ) and enthalpy of mixing (ΔH_{mix}) was conducted. A higher negative $\Delta H_{mix} < -12$ KJ/mol of the system was found to favor the amorphous phase formation, while a value below $\delta < 0.065$ favors the formation of solid solutions and above that leads to the formation of the amorphous phase. The two-parametric approach reasonably depicts the phase selection between solid solutions and the amorphous phase, but the formation of intermetallics complicates the scenario⁷.

Another study was conducted to find the effect of valence electron concentration (VEC) on the phase selection between face centered cubic (FCC) and body centered cubic (BCC) solid solutions. A VEC value ≥ 8 was found to favor the FCC phase while ≤ 6.87 favors the BCC phase. A dual phase mixture was predicted for values in between⁸. However, exceptions do exist and are reported in the literature explaining the ambiguity of VEC based phase selection rules⁹. A single parameter approach was proposed for modifying the conventionally accepted concept of configurational entropy of mixing into a summation of this existing term and an entropy term closely associated with atomic packing size, and was found to produce a good fit model, although not perfect yet¹⁰. There is a need for better phase prediction models in HEAs to make the alloy design more efficient, the realization of which would help modern computing technologies like ML to accelerate novel discoveries in this field.

2.2 Stacking fault energy

Stacking fault energy (SFE) is an intrinsic material parameter, with its magnitude reliant on chemical composition¹¹ and temperature¹²⁻¹³. The concept of SFE is well understood and at times employed in the design of FCC metals and alloys for better mechanical properties¹⁴. Upon deformation of the FCC lattice, dislocation glide proceeds preferentially in closed packed planes and directions, namely {111} planes and <100> directions.



Figure 2.1: Visualization of (a) stacking sequence and (b) intrinsic stacking fault in {111} planes of FCC crystals.

The $\{111\}$ closed packed planes of FCC follow an ABCABCABC stacking sequence (where A, B, and C are the atomic planes of the material) as shown in Figure 2.1 (a). A stacking fault (SF) is a 2-dimensional defect causing disruptions to the ordered atomic arrangement, and forms when a perfect <110> type dislocation dissociates into two <211> type Shockley partial dislocations. This leads to an intrinsic stacking fault where an atomic layer is displaced from its position in the closed packed plane as seen in Figure 2.1 (b).



Figure 2.2: Illustration of a perfect dislocation with Burger's vector b1 dissociating into two partial dislocations b2 and b3 forming a faulted region. Adapted with permission from Ref^{15}



Figure 2.3: Visualization of a twin fault (left) and HCP martensite (right) formed depending on the nature of glide of Shockley partials on {111} atomic planes of an FCC crystal.

This splitting of perfect dislocation into glissile dislocation partials as illustrated in Figure 2.2 is energetically favorable and is expressed mathematically as follows: The burger's vector of a perfect dislocation in a FCC crystal is given by,

$$\overrightarrow{b_1} = \frac{a}{2}[01\overline{1}] \tag{2.2}$$

The dislocation splitting can be represented as,

$$\frac{a}{2}[01\overline{1}] \rightarrow \frac{a}{6}[\overline{1}2\overline{1}] + \frac{a}{6}[11\overline{2}] \tag{2.3}$$

Equation for energy of a dislocation is,

$$E_{dislocation} = Gb^2 \tag{2.4}$$

Thus, the energy of having a perfect dislocation and partial dislocations is given by:

$$E_{perfect} = G * \left(\frac{a}{2}[110]\right)^2 = \frac{Ga^2}{2}$$
(2.5)

$$E_{partial} = G * \left(\frac{a}{6}[112]\right)^2 = \frac{Ga^2}{3}$$
(2.6)

From equations (2.5) and (2.6), it can be inferred that energy for dislocation splitting $(E_{partial})$ is less than the energy associated with a perfect dislocation and hence this kind of dislocation splitting is favored. The faulted region so formed has an associated surface energy term (SFE) and a dislocation-interaction term with the former trying to minimize the separation and later causing a repulsive interaction force. Interactions such as these define the equilibrium separation distance between the partial dislocations. So, in principle, the probability of having wider stacking faults increases with decreasing SFE and vice-versa¹⁵.

This is one major reason why low SFE materials has a higher tendency to undergo athermal transformations like martensitic transformation (MT) and deformation twinning (DT) in addition to the dislocation glide. So, in principle depending on the magnitude of SFE and the nature of glide of Shockley partials, a twin or an ϵ martensite may be formed. The glide of partial dislocations on every consecutive {111} planes leads to a mechanical twin (Figure 2.3 (a)) and the same on every second {111} planes leads to a local HCP stacking sequence¹⁶ and is shown in Figure 2.3 (b). Dependence of SFE on the chemical composition leads to emergence of new concepts relating to alloy design. Metastability alloy design (MAD) is one such concept which focuses on altering SFE either throughout the bulk or at selective regions within the microstructure. More on this will be discussed in section 2.2.2.

The material science community has always been challenged with the ability to address the trade-off between strength and ductility. A high strain hardening rate (SHR) can increase the material's elongation to fracture as it increases the material's stress response to an applied strain and a sufficiently high magnitude of SHR means delayed necking. This SHR of engineering materials could be increased by additional deformation mechanisms such as DT and MT¹⁸⁻²⁰. Athermal transformations such as these are considered to increase the number density of interfaces (namely twin boundaries, phase boundaries) effectively reducing the dislocation mobility¹⁷. Magnitude of SFE plays a major role in affecting dislocation cross-slip. A process by which a dislocation moves from its slip plane to another adversely affecting the SHR of the material. In order for the dissociated dislocations to cross-slip, a constriction of the SF is required. This requirement for having a constriction of the SF ribbon becomes difficult at lower magnitudes of SFE, because of the enormity of the faulted region and requirement for a high value of additional stress, thus increasing the overall SHR¹⁵.

Utilization of SFE in prediction of deformation modes in FCC materials places it as a valid engineering parameter. The effect of SFE on microstructure and its implications on the mechanical response of the material will be discussed in the upcoming sections.

2.2.1 Martensitic transformation

Phase transformations in metals and alloys can be subdivided on the basis of the mechanism involved in realizing a phase or phases. Long range reconstructive mechanism is one such where phase formation is fulfilled through atomic diffusion over long distances (e.g., eutectoid transformation in steels). In contrast, the second type accomplishes the transition through a diffusionless displacive transformation (e.g., $MT)^{21}$. The nature of our discussion will be centered around MT and their features in general.

MTs falls into the category of diffusionless transformations where growth is controlled by the motion of glissile (capable of gliding) interfaces. Glissile interface migrates by dislocation glide and are athermal in nature, implying the interface migration is insensitive to changes in time²². This motion of glissile interface results in shearing the lattice of the parent structure into the product phase, and the interfacial atomic plane along which martensite nucleates is termed as the habit plane. Lack of long range atomic diffusion manifests in the form of no local change in chemical composition, however, accompanied by a change in the crystal structure^{14,23}. Thus MT is a phase transition involving the physical deformation of the parent lattice into the product phase. MT, like any other phase transition, necessitates the presence of driving force for the transformation. Owing to the nature of MT, it is not just a chemical driving force capable of causing the phase transition, but also a mechanical driving force such as an applied load (N)²⁴.

MT generated as a result of cooling alloys below M_s is termed as thermally induced martensitic transformation (TIMT). Its progress is a function of change in temperature below the martensite start temperature (M_s) till martensite finish temperature (M_f) , and the reverse transition on heating from austenite start temperature (A_s) to austenite finish temperature $(A_f)^{25}$. The volume fraction of thermally induced martensite depends on the extent of undercooling below M_s . This is expressed in the Koinstinen and Marburger equation²⁶.

$$1 - V_{\alpha} = exp\{\beta(M_s - T_Q)\}\tag{2.7}$$

Where V_{α} is the volume fraction of martensite, β is the material property, T_Q the temperature to which the specimen is cooled below M_s . Equation (2.7) clearly states that the amount of martensite is a function of undercooling temperature and not that of time, implying the athermal nature of transformation.

Transition of the parent austenite (herein thereafter referred to as γ) to martensite is also possible with an applied stress above M_s and below martensite deformation temperature (M_d) , leading to the deformation induced martensitic transformation (DIMT). It is important to note here the presence of M_d temperature, above which DIMTs are hindered owing to the increased stability of γ phase²⁴. Description of DIMTs requires an understanding about stability of the parent γ . Metastability in this context refers to the characteristic feature of a phase where a twinning induced plasticity (TWIP) or transformation induced plasticity (TRIP) takes place upon loading. Some of the terms found in literature that sometimes confuse the readers with metastable austenite are retained austenite and reversed austenite. Presence of retained austenite in the final microstructure is a result of rapid cooling, while reversed austenite refers to austenite found in the microstructure due to martensite reversal transformation, as a result of heating above A_s temperature. These austenites do exhibit the TRIP effect upon loading but cannot be considered directly equivalent to metastable austenite²⁷. In quench and partitioning (Q&P) steels, the γ phase is quenched to an intermediate temperature (quench point) between M_s and M_f favoring the formation of martensite which is subsequently subjected to heat treatment at or above the quench point. This leads to the enhanced atomic mobility of carbon atoms from the supersaturated solid solution of martensite, so that γ phase survives to room temperature. Such a microstructure consists of tempered martensite and retained γ and is found to exhibit a higher strength compared to conventional TRIP steels²⁹. The aforementioned processes showcase some ways of balancing strength and ductility in steels by utilizing the TWIP/TRIP effect of the metastable γ , formed as a result of thermal processing history. There exist ways of using SFE as a parameter for alloy design thereby achieving a thermodynamic state of bulk metastability, and more on this technique will be discussed in section 2.2.2.

The metastability of γ phase can be influenced by temperature as it affects the lattice parameter on which SFE has a strong influence¹⁴. It is well known that martensite preferentially nucleates along grain boundaries, twin boundaries, and autocatalytic sites produced during the transformation. To study whether TIMTs and DIMTs follow a similar trend in nucleation sequence an experimental study was conducted using a low-SFE steel. The characteristics of nucleation of DIMTs was revealed and compared to what was reported for TIMTs. A similar nucleation and transformation routes for both TIMTs and DIMTs was reported due to the alike behavior of both thermal and mechanical stability of γ phase²⁸. However, there exist a notable difference between TIMTs and DIMTs in terms of the specimen dimensions after the transformation. In DIMTs there is a macroscopic shape change associated with the transformation, while the specimens remain almost intact in terms of their initial dimensions in TIMTs²⁴.

A special crystallographic orientation relationship exists between the parent and product phase owing to the underlying mechanism of martensite formation. This is a reproducible orientation relationship and some of the commonly observed ones in FCC/BCC systems are Kurdjumov-Sachs orientation relationship (KS-OR) ($\{111\}_{\gamma}//\{011\}_{\alpha'}, <110>_{\gamma}//<111>_{\alpha'}$) and Nishiyama-Wasserman orientation relationship (NW-OR) ($\{111\}_{\gamma}//\{011\}_{\alpha'}, <112>_{\gamma}//<011>_{\alpha'}$)^{30,31,33}. Therefore, the martensite variants are all crystallographically equivalent with a special orientation relationship with its parent grain²⁴. In ϵ martensite forming alloys, the parent and product follow the Shoji-Nishiyama orientation relationship (S-N OR) ($\{111\}_{\gamma}//\{0001\}_{\varepsilon}, <110>_{\gamma}//<1210>_{\varepsilon}$)³²⁻³³. The SN-OR is similar to the ones reported in many FCC(γ)-BCT (α) martensite forming alloys (like in many steels) with maintaining parallelisms in closed packed planes and directions.

2.2.2 Metastability alloy design using HEAs

Thermodynamic metastability of phases may arise in many alloys depending on their processing and/or service history. The microstructure of a material consists not just features that are in thermodynamic equilibrium but also those that are not (e.g., dislocations, stacking faults etc.). Defects such as dislocations are essential for the material to plastically deform thereby improving the overall mechanical properties of the material.

The metastability alloy design (MAD) concept can be used to tailor spatially confined regions of metastability or bulk metastability via segregation engineering or compositional tuning. This is performed with an aim of triggering the athermal transformation mechanisms upon loading. Regions of spatially confined metastability is achieved by local change in chemical composition at lattice defects through equilibrium segregation of alloying elements in an orderly fashion. The aforementioned technique of introducing localized metastable regions that undergo athermal transformation upon sufficient driving force is called segregation engineering. This enrichment of lattice defects by solute atom can be attained through carefully designed heat treatments. In disparity to this, metastability engineering can be performed throughout the bulk of the material involving tuning of SFE values over a wide range. This can be attained by compositional adjustments where the flexibility in compositional tuning offered by HEAs emerge as a boon. To achieve thermodynamic metastability the inherent rules such as entropy maximization through equiatomic alloying of elements are overturned. This leads to a colossal amount of non-equiatomic compositions that can be explored for engineering metastability of phases ³⁴. To address strength-ductility trade-off in materials, MAD using HEAs has been widely studied. Several of these alloys displayed a high SHR due to the triggering of athermal transformation mechanisms. Some of these are discussed below.

A $Fe_{80-x}Mn_xCo_{10}Cr_{10}$ TRIP dual phase HEA was designed to study the effect of metastability on strength-ductility trade off. An apparent decrease in the Mn content from 45 at% to 30 at% leads to a conversion in the deformation mode from dislocation glide to TWIP (due to changes in the SFE values) and further down stabilizing a dual phase microstructure successfully forming a TRIP dual phase HEA. They reported an increased strength due to transganular and intergranular slip resistance and enhanced ductility owing to dislocation hardening of the stable phase and TRIP effect of the metastable phase³⁵. A similar study with SFE as a parameter for alloy design was conducted on novel-Co rich HEAs $(Co_x Cr_{25}(FeNi)_{75-x} (x=25-65))$ for attaining enhanced tensile properties. A shift in the deformation mode from DTs to MTs was observed with an increase in Co content along with a decrease in Fe and Ni content. They reported that, alloys with metastable FCC phase when Co content was 35 at% and 45 at%, were found to show a better combination of strength and ductility than other FCC based counterparts, while compositions with stabilized dual phase microstructure displayed a higher strength at the expense of ductility, producing an undesired outcome for the study 16 .

2.3 Laser-based powder bed fusion (LB-PBF)

The powder bed fusion (PBF) process falls into a highly studied realm of additive manufacturing methods in the field of aerospace, biomedical and transportation industries, with applications in consumer products fast growing³⁶⁻³⁷. The PBF process such as LB-PBF melts and consolidates the powder feedstock following a bottom-up approach exhibiting capabilities to achieve near net-shape structures³⁸⁻³⁹. Features such as this open up a window of possibilities to either design intricate geometries (aesthetic⁴⁰/ functional⁴¹⁻⁴³) or to develop novel materials/ tailored microstructure⁴⁴. This is difficult or even impossible to execute using conventional manufacturing techniques. This capacity to build geometrically intricate parts with superior surface finish, along with the processability of an ever- increasing spectrum of metallic materials, endows LB-PBF as a dominant additive manufacturing (AM) technique⁴⁵. In the following sections the principle of LB-PBF, processing parameters and their influence on the microstructural evolution, opportunities and obstacles in producing HEAs via AM are discussed briefly.

2.3.1 Principle of LB-PBF

The main components of LB-PBF machine are shown in Figure 2.4. The pre-stage of printing in LB-PBF takes place with a creation of a 3-D CAD model of the components to be printed. This 3-D model is then sliced into numerous 2-D layers and sent to LB-PBF machine for printing. After the pre-stage procedure, the machine starts printing by applying a predetermined thin layer of powder (in the order of a few micrometers) using the recoater onto the build plate. Eventually the powder bed is scanned selectively by the laser on areas which corresponds to the sliced 3-D CAD model. The build platform is then lowered to a magnitude to match the layer thickness value where the next layer of powder is recoated followed by selective melting of the newly deposited powder and the previously solidified layer. During the printing stage, the powder bed is shielded from oxygen by flushing the chamber with an inert gas such as argon. This is facilitated in order to prevent ignition and oxidation of the powder bed with optimized processing parameters in a controlled atmosphere could result in fully densified final parts.



Figure 2.4: Schematic representation of a typical LB-PBF machine, reprinted with permission from Ref⁹¹

2.3.2 Microstructures in LB-PBF materials

The repeated melting and solidification of the powder bed together with the cyclic heating lead to a complex and spatially varying microstructure. Meltpool boundaries, epitaxial grain growth, and highly textured columnar grains are common characteristics of LB-PBF microstructure. The solidification in metals and alloys is dictated by thermal gradient (G) and solidification rate (R) which influence the undercooling needed within the liquid state for the solid/liquid (S/L) interface to proceed. This is schematically depicted in Figure 2.5 (a). The process of solidification in LB-PBF is analogous to welding, with no activation barrier for nucleation and is illustrated in Figure 2.5 (b). This is because the newly deposited layer is melted along with the substrate, leading to formation of new grains from the pre-existing sites (surface or interface), and result in negligible or no energy barrier for nucleation. This scenario leads to growth of new grains from the pre-existing grains of the substrate and is known as epitaxial grain growth. As a consequence of this, a crystallographic texture is developed depending on the easy growth direction (<100> for cubic crystals and <1010> for hexagonal crystals) parallel to the temperature gradient⁴⁷⁻⁴⁸.



Figure 2.5: Illustration of (a) effect of G and R on solidification mechanism and (b) free energy change (ΔG) associated with heterogeneous nucleation in welding/LB-PBF and casting along with homogeneous nucleation. Adapted with permission from Ref^{48,92}

Epitaxial grain growth more often than not leads to the formation of long columnar grains spanning along multiple meltpool boundaries. This is undesired as it introduces anisotropy in the mechanical properties of as-printed parts. A high G and low R usually found along the meltpool boundaries favors columnar grain growth whilst a low G and high R at the center of the meltpool produces suffice undercooling for the formation of equiaxed grains⁴⁹. LB-PBF presents itself as a robust physical metallurgy route to develop or tailor novel microstructures that are hard to obtain by traditional manufacturing methods. A few cases where researchers produced unique microstructures and/or optimized materials properties are presented here. The unique solidification conditions under LB-PBF led to cellular solidification structures in an as-printed 316L SS. This unique AM microstructure is hard or rather impossible to attain using conventional fabrication methods and provides it with a high yield strength owing to the presence of dislocation cells acting as soft pinning sites⁵⁰. Printability of certain non-weldable alloys such as Al-7000 series alloys are poor due to solidification cracking. To address this, researchers have proposed an ex-situ addition of hydrogen stabilized Zr nanoparticles. These particles formed the Al_3Zr phase during printing which acted as inoculants resulting in grain refinement⁵¹.

2.3.3 Influence of processing parameters on microstructure

The main processing parameters in LB-PBF commonly optimized to ensure full densification of parts are laser power (W), hatch spacing (μ m), scan speed (mm/s) and layer thickness (μ m). A schematic of these parameters is given in Figure 2.6 (a). More on these parameters and their influence on the resulting microstructure is discussed in this section.



Figure 2.6: Schematic of (a) LB-PBF processing parameters, reprinted with permission from Ref⁴⁹ and (b) intensity (I) vs radial distance (R) depicting Gaussian distribution of laser power. Adapted with permission from Ref¹⁰¹.

Laser power dictates the amount of heat supplied to the powder bed for melting and is responsible for the meltpool formation. An optimal amount of laser power is desired as extreme or inadequate values leads to vaporization or partial melting of the powder bed. This leads to defect formation in the as-printed samples adversely affecting the final properties⁵². The effect of laser power on the resulting densification of final parts produced using LB-PBF has been investigated by various researchers. For example, an increase in the density of titanium alloys fabricated using LB-PBF was reported after a raise in the laser power input⁵³.

Hatch spacing is the distance from the centers between two adjacent laser scan vectors. The spatially varying distribution of laser power within the spot size due to the Gaussian distribution of laser power as shown in Figure 2.6 (b) leads to difference in the heat distribution within the meltpool. To compensate for this variation in heat distribution within the meltpool, a sufficient hatch overlap is desired⁵⁴. A very small hatch spacing however implies multiple overlap of the laser scanning vector leading to undesirable heating of the laser track, whilst an increased hatch spacing would mean unmelted or partially melted regions⁵². Experimental observations were made in validating the aforementioned statements in which hatch spacing was varied and a decrease in its value led to increased density in a titanium alloy fabricated via LB-PBF⁵⁵. Similar observations were also reported, where the researchers studied the effect of energy density on the resulting densification and mechanical properties of a stainless steel (SS). It was shown that an increase in hatch spacing led to a raise in porosity levels and diminishing tensile strength⁵⁶. Effect of hatch spacing on surface quality and densification of a LB-PBF fabricated 316L SS was studied. It was reported that an appropriate hatch spacing produced high density and average to low surface roughness⁵⁷. These experimental observations provide insights into the effect of hatch spacing in LB-PBF.

Scan speed is defined as the speed of the laser scanning vector in the powder bed, a parameter that influences the shape of the meltpool and solidification process. A high speed scanning vector implies shallower meltpool or in some cases even cause improper melting. Decreasing the scan speed was found to improve the density of as-printed SS samples⁵⁸. Quite similar results were obtained with a titanium alloy (Ti-6Al-4V) showing increased density values with a reduction in scan speed⁵⁵.

Layer thickness defines the thickness of the powder bed. A high value could mean faster production rates. A high value of thickness for the powder bed needs to be offset with a higher laser power or slower scanning speed so as to ensure suffice meltpool depth. These statements were validated by studies where an increase in layer thickness resulted in lower density values for a 18Ni-300 alloy⁵⁹.

2.3.4 LB-PBF of HEAs

Conventional manufacturing of HEAs (e.g., casting and spark plasma sintering) possesses many advantages as well certain drawbacks. These drawbacks mainly include elemental segregation^{60,61} and inability to produce parts with intricate geometries. In this context, LB-PBF turns out to be an important technology for synthesis of HEAs, owing to the high cooling rate that can suppress elemental segregation^{60,63} along with the ability to build intricate geometries⁴⁵. Nevertheless, there exist obstacles that are making this process undesirable. In the following section, promising results from LB-PBF of certain HEAs and a few obstacles that make users of this technology ponder are discussed briefly.

2.3.4.1 Opportunities and obstacles

The rapid melting and solidification conditions of LB-PBF result in unique microstructures, which were reported to improve the mechanical properties in some cases compared to their conventionally manufactured counterparts 62 . In a C-CoCrFeNi HEA fabricated using LB-PBF, researchers reported complete solubility of C atoms in the FCC single phase solid solution. The fabricated samples presented with high density and a tensile strength of 650 MPa with elongation to fracture of 13.5 %, underlining the printability of this iHEA (interstitial HEA) variant⁶⁴. A single phase FCC solid solution was stabilized in a LB-PBF processed CoCrFeMnC_{0.5} iHEA, in contrast to casting which resulted in a dual phase microstructure comprising of FCC and HCP phases⁶⁵. The high stress induced by rapid melting and solidification directly produced nanotwins in a Cantor alloy, absent in its conventionally fabricated variants⁶⁶. Precipitates were observed in LB-PBF synthesized HEAs^{60,68}. Sigma phase was observed in a LB-PBF processed Cantor alloy, while similar phase formations were not observed in as-cast or plastically strained variants below a true strain of $3.7\%^{66}$. Layers of Cu rich precipitates were found in the grain boundaries of a AlCrCuFeNi HEA⁶⁷. Similar observations were found in a LB-PBF printed Ni₆Cr₄WFe₉Ti HEA, where the formation of Ti rich precipitates along intergranular boundaries was noticeable⁶⁹. The presence of precipitates in the as-printed materials was partly attributed due to an increase in the grain boundary volume fraction due to fine grain size along with sub-grains and dislocations networks commonly observed within LB-PBF printed parts. The intrinsic heat treatment in LB-PBF during the printing stage accelerates their formation⁶⁶, which could be beneficial or detrimental to mechanical properties. Other challenges include the presence of unstable substructures (like dislocation networks formed as a result of high cooling rate) which might affect the high temperature properties 62 . The fact that they are massively alloyed with expensive metals in most cases⁷¹, coupled with added cost for powder manufacturing and printing using LB-PBF without exhibiting a wide bank of properties, also makes producing HEAs via AM hard to popularize.

2. Theory

Methods

3.1 Design of experiments

Design of experiments (DOE) is a statistical methodology performed to optimize variables in an experiment when the desired yield is influenced by multiple parameters⁷². It is particularly of use in processes such as LB-PBF where multiple parameters (such as laser power, hatch spacing, scan speed, etc.) influence the properties of the resulting component. DOE also helps in bringing down the time and investment required for optimization of experiments. Due to the absence of optimized processing parameters, for the material of choice used for this study, DOE was performed to optimize the processing parameters for attaining fully densified parts in the asprinted state. In the present study three different DOE models were developed using the JMP software (from SAS Institute, Cary, North Carolina, USA) following a Doptimal design procedure with relative density as a common yield. The processing parameters, namely scan speed and hatch spacing, were varied between 400 mm/s to 1200 mm/s, and 0.06 mm to 0.1 mm for the 90 W and 110 W 2-factor D-optimal designs. In addition to the 2-factor D-optimal DOE, the laser power, hatch spacing, and scan speed were varied over a broader range from 70 W to 170 W, 0.04 mm to 0.12 mm, and 400 mm/s to 1600 mm/s in the 3-factor D-optimal DOE, respectively. It is important to note here that layer thickness was fixed to a constant value of 20 μm in all the DOEs. A total of 16 runs for the 2-factor DOEs and 30 runs for the 3-factor DOE were performed to obtain statistical significance.

3.2 LB-PBF parameters

Prealloyed inert gas atomized powder (Höganäs AB) of chemical composition $Co_{45}Cr_{25}$ (FeNi)₃₀ was used as the feedstock for the LB-PBF process. The printing of this powder feedstock was implemented using an EOS M100 (EOS GmbH) machine equipped with a 200-W Yb fiber laser producing a spot size of 40 μ m. DOE was performed to optimize the processing parameters with relative density set as the desired yield. The so obtained parameters were used to print cubic samples with dimensions of 8 x 8 x 8 mm³. Printing was carried out on a circular build plate which is 100 mm in diameter and 95 mm in height in a build chamber purged with argon gas in order to keep oxygen levels below 1000 ppm. A bi-directional scanning of the laser beam with a 67° scan rotation between subsequent layers was adopted as a scan strategy for manufacturing the test specimens. The samples after printing were removed from the build table using EDM (ROBOFIL 310 from Charmilles

Technologies).

3.3 Material characterization

3.3.1 Metallography

The as-printed samples were mounted using a conductive poly-fast resin in a Citopress-20 hot mounter (Struers, Denmark) and were ground using emery papers followed by sequential polishing using grit sizes of 9 μ m, 3 μ m and 1 μ m, and finally OP-S in a TegraPol-31 (Struers, Denmark) polishing machine. This was performed in order to get a mirror-like surface finish with absolute minimum deformation. The samples were cleansed using running water and ethanol (96%) preceded by a 5 minute ultrasonication using Metason 200 HT (Struers, Denmark) after each step of polishing to remove partially melted powder particles present within the pores and polishing residues. The parameters used for grinding and polishing are given in Table 3.1.

Table 3.1: The steps used for polishing and "Rotation" denotes the direction with which the sample holder and the polishing table are rotating.

| Speed [rpm] | Time [min] | Force [N] | Rotation | Lubricant | Grit |
|-------------|------------|-----------|----------|-----------------------------------|----------|
| 150/150 | 12 | 15 | QQ | Dia Pro Largo $9\mu m$ | MD-Largo |
| 150/150 | 7 | 15 | QQ | DiaPro Dac $3\mu m$ | MD-Dac |
| 150/150 | 4 | 15 | QQ | Dia Pro Nap 1 $\mu {\rm m}$ | MD-Nap |
| 150/150 | 4 | 15 | U) | OP-S suspension | OP-Chem |

Etching was performed to reveal the microstructural features on selected samples using the V2A etchant (equal parts of H_2O and HCL with 5 % HNO₃) for 5 minutes or until a green colorization of etchant in contact with the metal surface was observed. For the etching procedures, a freshly polished sample surface was used so as to prevent the oxide layer formation.

3.3.2 Electrochemical polishing

Electrochemical polishing was also performed owing to the nature of the material to undergo DIMTs due to loads (N) used during mechanical polishing⁷³⁻⁷⁵. The formation of DIMTs under such circumstances affects the current study as it is difficult to distinguish TIMTs and DIMTs based on their morphology in low-SFE materials³³. To bypass this, electrochemical polishing was carried out using a LetroPol-5 (Struers Denmark) using the A3 electrolyte. The samples were ground to 1200 μ m grit size before polishing so as to facilitate a flat surface with good surface finish and to maintain appreciable conductivity during polishing. The parameters used for polishing are given in Table 3.2. In the end a mirror- like flat surface was obtained which is ideal for surface sensitive characterization techniques like electron backscatter diffraction, which was extensively used during this study.

| Table 3.2: | Processing | parameters | used f | for | electrochemical | polishing | using | the | A3 |
|--------------|------------|------------|--------|-----|-----------------|-----------|-------|-----|----|
| electrolyte. | | | | | | | | | |

| Material | Area (cm^2) | Temperature (°C) | Voltage (V) | Flow rate (m/s) | Time (s) |
|----------|---------------|------------------|-------------|-------------------|----------|
| HEA | 1 | 25 | 30 | 13 | 80 |

The samples after polishing were immediately cleaned in distilled water followed by ethanol (96%), dried and attached to the sample holder using conductive carbon cement for SEM analysis and characterization.

3.3.3 Optical microscopy

Optical microscopy (OM) employs light in the visible spectrum of wavelength (400 nm- 700 nm) to probe the sample surface. The reflected light from the surface of the specimen under investigation is processed using a set of lenses subsequently forming an image. A Zeiss Axioscope 7 microscope (Figure 3.1) was employed in the present study for acquiring stitched images of the samples along the build direction for porosity analysis. Fiji Image J^{76} software was used for analyzing porosity by adjusting the brightness, contrast, and threshold values to calculate the area fraction of the pores. In addition, OM was also used to image microstructural features of the etched samples.



Figure 3.1: A photo of Zeiss Axioscope 7 optical microscope used for this study¹⁰⁵

3.3.4 Scanning electron microscopy

The scanning electron microscope (SEM) in contrast to OM uses an electron beam as a source to probe the material of interest. The electrons are excited from the source either using a thermionic emission gun (TEG) or field-emission gun (FEG) and are accelerated through a potential difference. This beam of electrons is converged and focused using a set of condenser lens and an objective lens. In contrary to the physical lenses used in a typical OM, a magnetic field of sufficient strength is employed in the lenses owing to the charged nature of electrons. The sensitive nature of electrons also demands vacuum level to be high enough (almost 10^{-6} Torr in a FEG-SEM⁷⁷) to prevent the scattering.



Figure 3.2: Schematic of interaction volume generated due to electron interaction with matter, showing the origin of secondary electrons, backscattered electrons, Auger electrons, characteristic, continuum and fluorescent X-rays, and cathodoluminescence⁹³

The electron interaction with matter can be differentiated as scattering or diffraction depending on the treatment of electrons as particles or waves. The accelerated beam of electrons in contact with the sample (hundreds of micrometer in thickness) produces a tear drop shaped interaction volume. The depth of this penetration is influenced by the energy of the landing electrons and sample density. Interactions such as these results in both elastic (no or little energy lost) and inelastic (incident electron energy fully lost) scattering. Coherent (in-phase) or incoherent (out-ofphase) terminology is used to invoke the wave nature of the electrons, which, when coupled with elastic scattering, describes electron diffraction⁷⁸.

These scattering generates different signals such as secondary electrons (SEs), backscattered electrons (BSEs), characteristic and continuum X-rays, and depending on the conductivity of the sample heat is also induced. These signals carry different information regarding the sample and are captured and processed using specifically designed detectors inside the SEM chamber. A schematic of these interactions of electrons and various signals generated are depicted in Figure 3.2. In the present study microstructural characterization was conducted on the as-printed specimens using a LEO Gemini 1550 and LEO Gemini II 450 FEG-SEM. The SE and BSE modes in SEM were used for the imaging of etched and as-printed microstructure.

3.3.4.1 Electron backscatter diffraction

Electron backscatter diffraction (EBSD) is an important tool in the field of materials science as it helps understand phases of crystalline materials which can directly correlate to the microstructure and related properties. EBSD detector is attached to the SEM column and makes use of diffraction patterns arising from the sample owing to its crystalline nature to determine phases, orientation of grains and local texture⁷⁹.



Figure 3.3: Illustration of EBSD geometry depicting the electron interaction with the sample tilted to 70° leading to generation of electron diffraction patterns on phosphor screen, subsequently captured by charged-coupled device (CCD) camera for further processing.

A schematic of EBSD system is shown in Figure 3.3. Mechanical polishing or electrochemical polishing as discussed in sections 3.3.1 and 3.3.2 are commonly employed to achieve a scratch free mirror-like flat surface finish which is required for EBSD, a surface sensitive characterization technique. After the insertion of the sample into the SEM column the stage is tilted to 70° to fix the angle of diffraction and to increase the backscattering of electrons. Incident electrons interact with the sample causing scattering in all directions, and these scattered electrons undergo coherent backscattering by specific atomic planes that satisfy the Bragg's condition for diffraction. This gives rise to Kikuchi bands (a pair of bright and dark bands), and each pair corresponds to the plane responsible for the diffraction⁸⁰. The detector consists of a phosphor screen which converts the incident backscattered electrons into light which are then captured by the charged coupled device (CCD) forming electron backscatter patterns (EBSPs). These are then processed using software and indexed. Each pixel of data has an associated EBSP, and the data are collected and later used to produce various maps containing different information. However, the standard EBSD geometry is limited with its achievable spatial resolution owing to the shape of the interaction volume generated. In contrast to SEM, the interaction volume in EBSD due to its 70° tilt requirement is elongated along the beam direction resulting in a decrease in the spatial resolution. The origin of crystallographic pattern in an EBSD measurement is influenced by the cross section of scattering (probability of scattering), which depends on the atomic number (Z) and landing energy of primary electrons (kV). A decreased accelerating voltage was found to resolve narrow microstructural features in a TWIP steel but dedicated adjustments to working distance between the sample and the detector was optimized through trial and error method⁸¹. Since this optimized value is strictly limited to the material probed, requiring highly sensitive phosphor screen and involving sufficient time in conducting measurements, it is not always pragmatic to employ this technique. This limit in resolution of EBSD to an extent can be offset using transmission Kikuchi diffraction (TKD), which uses thin foil specimens (nearly 100 nm) to produce EBSPs with the help of transmitted electrons. The mounting of TKD specimens is either horizontal or back tilted away from the detector as shown in Figure 3.4. The EBSPs generated as such are mainly from the bottom few nm of the sample surface and a thin section would mean a very small interaction volume resulting in the noticeable increase in spatial resolution.



Figure 3.4: Schematic representing the TKD geometry for specimen back tilted away from the detector and specimen mounted horizontally. Reprinted with permission from Ref^{106}

In the present study, EBSD using standard geometry on bulk samples and TKD on thin foil specimens were conducted using symmetry detector (Oxford Instruments) fitted on to a LEO Gemini II 450 FEG-SEM. EBSD measurements were carried out at an accelerating voltage of 20 kV with varying step size and working distance for different samples. For the thin foil specimen preparation, cross sections parallel and horizontal to the building direction were machine cut from the bulk sample using an ISOMET 11-1180 low speed saw (Buehler LTD) to reduce the chances of DIMTs that might form during the study. The so obtained thin specimens ($\approx 600 \ \mu m$) were subsequently ground down to $\approx 100 \ \mu m$ using 500, 800 and 2000 SiC grit paper. These were then punched into circular shaped specimens and cleaned in a medium of isopropyl alcohol. Later, the specimens were thin down to create regions that are electron transparent using Struers TenuPol-5 twin-jet electrochemical polisher (Struers, Denmark) using an A3 solution. The parameters used for polishing are given in Table 3.4.

 Table 3.3: Processing parameters used for twin-jet electrochemical polishing using the A3 electrolyte.

| Material | Temperature (°C) | Voltage (V) | Flow rate (m/s) | Time (s) |
|----------|------------------|-------------|-----------------|-----------------|
| HEA | $\approx +2$ | 28 | 4 | $\approx 30-60$ |

The specimens were mounted onto the TKD holder and measurements were made using an accelerating voltage of 30 kV, working distance varying between 5 mm to 10 mm with a varying step size of (20 to 30 nm) and current of 5 nanoamps. AztecHKL software was used for data acquisition which was later processed using an open-source MTEX toolbox in MATLAB⁸².

3.3.5 Mechanical testing

3.3.5.1 Tensile testing

Tensile specimens of gauge length 12.5 mm, width 2.5 mm and thickness 1 mm were prepared using EDM from as-printed bulk samples of dimensions 55 mm x 10 mm x 10 mm. The tests were conducted using an Instron 5500R tensile tester at a constant cross head velocity with a simulated strain rate of 10^{-3} s⁻¹.

3. Methods

Results and discussion

4.1 Design of experiments

The as-built samples with processing parameters modeled using 2 factor D-optimal DOE were characterized for the relative density analysis. This was performed to get a predictive model to study the influence of parameters on the densification.



Figure 4.1: Contour map of relative density of samples with respect to hatch spacing and scan speed for both (a) 90 W 2 factor D-optimal DOE and (b) 110 W 2 factor D-optimal DOE

Fourteen processing parameters from both 90 W and 110 W DOEs resulted in samples with a high relative density (99.9%>) in the as-printed state. An overall increase in number of samples with high relative density was observed for samples printed with 110 W power as compared to their 90 W counterparts as shown in Figure 4.1 (a) & (b). This is attributed due to an increased energy input in the powder bed⁵³, but there still exist processing parameters which failed to attain high density, implying the influence of multiple parameters in realizing full density.

Volume energy density (VED) is a widely used parameter when studying the influence of processing parameters on densification in LB-PBF⁸³⁻⁸⁵. It was utilized to identify the processing window. The influence of VED on the densification of the alloy is shown in the Figure 4.2.



Figure 4.2: Schematic of (a) Relative density (%) v/s VED (J/mm³), representing regions of full density for 90 W and 110 W samples, (b),(c),&(d) represents OM micrographs of specimens from 110W DOE with VED belonging to lack of fusion (I), high density (II), and key-hole (III) regions respectively.

The VED plot in Figure 4.2 (a) is complemented with OM micrographs of 110 W samples, with VED belonging to the three distinct regions as shown in Figures 4.2 (b), (c) and (d). Samples falling into region I exhibit porosity mostly due to lack of sufficient energy input in the powder bed. Metallic powder particles, when partially melted due to lack of sufficient energy input, form lack of fusion defects. These may consist of partially sintered and/or unmelted powder particles¹⁰². A decrease in relative density values is also observable in region III (Figure 4.2 (a)), and the micrograph corresponding to one of the samples in this region is shown in Figure 4.2 (d). This decrease in the relative density is due to increased energy input in the powder bed leading to the formation of key-hole defects. Owing to the strong influence of meltpool in formation of the key-hole porosity, a decreased laser power or increased scan speed can potentially serve as a solution to avoid it¹⁰³. The presence of a processing window with relative densities greater than 99.9 % is observed in region II, where the samples are found to exhibit high relative density values as shown in Figure 4.2 (a) & (c). However, the presence of gas porosity can still be observed in region II, formation of which might be due to the defects in powder and improper size distribution leading to poor packing density in the powder bed¹⁰⁴. It is clear from Figure 4.1 (a) that an increase in the laser power from 90 W to 110 W resulted in a broader processing window with regard to the samples produced with high relative densities. This is attributed to an increased VED as a result of increase in power. The VED values pertaining to this region represent the optimal combination of the processing parameters which result in the observed densification in as-printed parts.

The existence of processing window for attaining near full density, validates the use of VED as a criterion for process optimization. Two processing parameters, which resulted in the highest density for 90W and 110W DOEs in sample 2F-D1 and 2F-D2, respectively, are shown in Table 4.1.

| Table 4.1: | Processing | parameters | with | the | highest | relative | density | from | the | 2 |
|---------------|------------|------------|------|-----|---------|----------|---------|------|-----|---|
| factor D-opti | imal DOE | | | | | | | | | |

| Sample name | 2F-D1 | 2F-D2 |
|---------------------|--------|-------|
| Laser power (W) | 90 | 110 |
| Hatch spacing (mm) | 0.07 | 0.07 |
| Scan speed (mm/s) | 1010 | 1010 |
| Density (%) | 99.988 | 99.99 |

It can be inferred from Table 4.1 that, the same set of hatch spacing and scan speed resulted in a higher relative density when accompanied by an increase in laser power. This was noticeable with multiple samples crossing the threshold of > 99.9 % for relative density when printed using a higher laser power (W). The current 2 factor DOE, however, has limitations such as lack of spread in processing parameters (e.g., laser power) thus limiting the possible parametric interactions. In order to further optimize the time and resources, and to further explore the potential of using high powers on densification and subsequent microstructural evolution, a more robust 3-factor D-optimal DOE was performed. VED was chosen as a factor of constraint in the 3 factor D-optimal DOE, in which laser power (W), hatch spacing (mm) and scan speed (mm/s) were varied over a wide range. However, only 2 samples, 3F-D1 and 3F-D2, with processing parameters as shown in Table 4.2 were able to cross the set threshold of > 99.9 % for densification.

 Table 4.2: Processing parameters with highest relative density from the 3 factor

 D-optimal DOE

| Sample name | 3F-D1 | 3F-D2 |
|--------------------|--------|-------|
| Laser power (W) | 115 | 170 |
| Hatch spacing (mm) | 0.04 | 0.084 |
| Scan speed (mm/s) | 1240 | 1180 |
| Density (%) | 99.977 | 99.97 |

For this study, mainly two samples 2F-D1 and 3F-D2 were studied intensively, where the laser power used for fabricating the latter was almost twice that for the former. This selection was made as the thermal history of these samples might vary a lot due to a substantial difference in power, thereby creating a good opportunity to study the effect of laser power on the as-printed microstructure.

4.2 Microstructural characterization

The microstructural characterization of the as-printed and heat treated samples performed using various characterization techniques such as OM, SEM, EBSD and TKD will be discussed in this section. The as-printed samples after etching revealed the meltpool boundaries as shown in Figure 4.3 (a) which is a common feature of LB-PBF microstructure formed as a result of laser interaction with the powder bed. Apart from these meltpool boundaries, presence of parallel banded features could also be seen in Figure 4.3 (a)&(b).



Figure 4.3: OM images of the 2F-D1 sample along the cross-section parallel to the building direction (BD) (a) depicting the presence of banded features at the center portion of the sample and (b) along the edges of the specimen



Figure 4.4: SEM images of (a) banded features observed along the edges of the 2F-D1 sample and (b) that representing the solidification structure between bands

These banded features appeared to be morphologically distinct and far less in number density compared to the martensites found in LB-PBF printed TRIP steels⁹⁴. Due to the in-homogeneity in etching, their presence were mostly seen along the edges of the cubic samples (Figure 4.3 (b)), with a very few getting revealed at the center as shown in Figure 4.3 (a). To the best of our knowledge, microstructural features with similar morphology and presence were not seen in the literature. The issue of in-homogeneous etching limited the area of study towards the edges of the cubic specimens. With further characterization of these features from the edges of the specimens in SEM, a visible difference in solidification structure between the bands and its surrounding was observed and is shown in Figure 4.4 (a) & (b). This difference in structure after etching possibly implies the presence of a different phase. One such banded feature (by random selection) was subjected to EBSD analysis for phase identification. The inter band regions similar to Figure 4.4 (b) were indexed as HCP phase and bands were indexed as FCC phase, as shown in the EBSD phase map in Figure 4.5 (a).



Figure 4.5: (a) EBSD phase map of the 2F-D1 sample depicting the presence of HCP phase (b) SEM image with EDS map of the same region showing the chemical homogeneity of the elements across HCP and FCC phases and (c) pole figures and inverse pole figures of the HCP and FCC grains showing the S-N orientation relationship.

As the alloy system used in the present study is reportedly known to undergo MT¹⁶, subsequent energy dispersive spectroscopy (EDS) analysis was conducted to check the compositional distribution. As martensitic transformations are diffusionless shear transformation and shall have the same composition as that of the parent FCC phase. The lack of compositional change found from the EDS map of the region indicates the formation of HCP phase as a result of MT, as shown in Figure 4.5 (b). To further confirm this observation, orientational relationship analysis between a selected FCC and HCP grain was performed. From the pole figure (PF) and inverse pole figure (IPF) shown in Figure 4.5 (c), it is clear that the FCC and HCP follow S-N OR $(\{111\}_{\gamma}//\{0001\}_{\varepsilon}, <110>_{\gamma}//<1210>_{\varepsilon})$ which is widely observed in alloy systems forming martensitic HCP phase³²⁻³³. This kind of blocky martensitic morphology is usually found in low-SFE materials during TIMTs or DIMTs, which is preferred when the growth of the martensitic phase is not obstructed by planar defects such as stacking faults, grain boundaries, etc. This growth mode leads to the blocky structured martensitic phase as the strains associated with the phase transition can be accommodated without the demand for nucleation of new crystallographic variants in low-SFE materials³³. Further, EBSD analysis was performed on a larger region in the same 2F-D1 sample. The results are portrayed using a phase map seen in Figure 4.6 (a), which shows the presence of randomly distributed multiple martensitic grains accounting to about 5.90 % in phase fraction.



Figure 4.6: EBSD phase map of the 2F-D1 sample (a) along with the calculated martensitic phase fraction and inverse pole figure map of 2F-D1 (b) depicting the <100> crystallographic texture

In addition to this, the presence of a <100> crystallographic texture along the build direction is evident (Figure 4.6 (b)) and is attributed to the epitaxial growth of grains across multiple layers⁴⁷⁻⁴⁸. The presence of martensitic phase found might be TIMTs formed as a result of the high cooling rates ($10^4 - 10^6$ K/s) innate to LB-PBF⁹⁵, although such a transformation is seldom reported in the AM literature. The presence of FCC (rather than HCP) bands might be due to the intrinsic heat treatment in LB-PBF⁹⁶, in which the martensite underwent a reversed austenite transformation. Reversed austenite transformations were previously reported in steels where such banded FCC structures were seen to coexist with martensite and was found to form during tempering⁹⁷. However, the absence of martensite in subsequent samples printed using the same set of processing parameters but prepared by electrochemical polishing questioned the mechanism behind their formation. In the literature the presence DIMTs were reported in low-SFE materials due to the loads applied during mechanical polishing and it was suggested to use electrochemical polishing as the best alternative for sample preparation⁷³⁻⁷⁵. This suggests that the martensite found here could be due to DIMT rather than TIMT, as initially conceived. Electrochemical polishing was performed on 2F-D1 and 3F-D2 specimens as these were printed using parameters selected for this study. The specimens were not etched as etching was found to be uneven, poorly revealing the banded features towards the center portion of the printed specimens. Further characterization of the electrochemically polished specimens using SEM-BSE mode produced images with enhanced contrast in comparison to the mechanically polished specimens. This enhanced BSE contrast observed with electrochemically polished specimens was helpful in observing the presence of banded features, as shown in Figure 4.7, spanning the entirety of the microstructure, which was not possible with mechanically polished specimens.



Figure 4.7: BSE images of the 3F-D2 (a-d) from the building direction, illustrating the presence of banded features and defect substructures observed in the as-printed state.

The banded features and dislocation networks found are similar to a deformed microstructure^{35,98}, which is in agreement to the fact that materials printed in LB-PBF are subjected to local plastic strain as a result of the residual thermal stresses owing to cyclic heating and cooling. This strain in the material in as-printed state can be up-to 1.7 $\%^{99}$. A similar result was obtained for the 2F-D1 sample, and the presence of substructures was also observable as seen in Figure 4.8 (d).



Figure 4.8: BSE images of the 2F-D1 (a-d) specimen obtained from the building direction, illustrating the presence of banded features and defect substructures observed in the as-printed state.

These banded features were also observable in the 3F-D1 sample in the as-printed state, exhibiting similar characteristics such as orientational change across grain boundaries and their presence accompanied with seemingly dislocation networks as shown in Figure 4.9 (a) and (b).



Figure 4.9: SEM-BSE images of the 3F-D1 sample obtained along the building direction, showing the presence of banded features

The subsequent EBSD analysis, as shown in Figure 4.10 (a), however, showed that the microstructure consisted entirely of FCC phase, and did not show the presence

of any HCP phase that was previously observed in mechanically polished samples in Figures 4.5 (a) and 4.6 (a).



Figure 4.10: (a) EBSD phase map of the 2F-D1 sample along the plane parallel to the building direction and (b) band contrast (BC) map of the same region.

This is complemented with a band contrast (BC) map of the same region indicating the presence of un-indexed banded features in Figure 4.10 (a). These observations deserve special attention though, as if the features are nano sized, there is a possibility of wrong indexing due to the limitations of spatial resolution in the standard EBSD geometry. The 2F-D1 and 3F-D2 samples were subsequently subjected to heat treatment analysis at 800°C for 24 hrs to study the thermal stability of the banded features. Observations made under SEM revealed the absence of the banded features and the comparison can be made between Figures 4.7 (a), (b) and Figures 4.11 (a) & (b).



Figure 4.11: SEM-BSE images of 800° C/24hrs heat treated 3F-D2 sample obtained along the building direction showing the absence of banded features

These observations suggested that the bands could possibly be nano-scale laminates of martensite, which are too fine to be captured by standard EBSD and will transform to austenite after annealing at high temperatures (800°C in this case). A similar microstructure with nano-scale laminates of martensite was observed in a Co-Cr alloy manufactured using LB-PBF, where the presence of epsilon-martensite was found in both powder and as-built specimens¹⁰⁰. To resolve these banded features, TKD was performed on the 3F-D2 sample on planes both parallel and perpendicular to the building direction. TKD phase maps confirm the presence of HCP phase in multiple grains, as shown in Figures 4.12 (a), (b), & (c). The rapid cooling in LB-PBF have led to the formation the observed martensitic HCP plates, which shall be categorized as TIMTs.



Figure 4.12: TKD phase maps of as-printed the 3F-D2 samples showing the martensitic HCP phase from planes both perpendicular (a) & (b) and parallel (c) to the building direction respectively

4.3 Mechanical testing

4.3.1 Tensile test



Figure 4.13: Engineering stress-strain curves for as-printed 2F-D1 and 3F-D2 samples

In order to understand the influence of different process parameters and microstructure on mechanical behavior of these materials, tensile tests were performed at room temperature and the results are shown in Figure 4.13. Both samples exhibited a similar yield strength of 560 ± 10 MPa and 34 % engineering strain. The observed yield strength is higher than what was reported for the same alloy fabricated using casting (300 MPa), which is accompanied with a significant decrease in the engineering strain from 75 % to 35 % ¹⁶. The observed rise in the yield strength could be due to the presence of dislocation cells formed as a result of in-situ thermal cycling in LB-PBF. The presence of dislocation cells was found to increase the yield strength in a 316L stainless steel manufactured using LB-PBF⁵⁰. It is also worth noting that the change in processing parameters seems to have no influence on the yield strength and engineering strain values, indicating the similarity in TRIP behavior of the two specimens during loading.

4. Results and discussion

Conclusions

The major conclusions that are drawn from the study are listed below:

- 1. Printability of $Co_{45}Cr_{25}(FeNi)_{30}$ metastable HEA was evaluated using the DOE methodology. Results indicated excellent printability with a broad range of parameters showing high relative densities.
- 2. Microstructural analysis of etched 2F-D1 and 3F-D2 specimens using OM and SEM revealed the presence of banded features.
- 3. EBSD analysis on the specimens prepared by mechanical polishing revealed the presence of FCC and HCP phases. Upon re-evaluation by electropolishing, it was concluded that the martensitic HCP phase was indeed formed due to the deformation induced by the mechanical polishing. The mechanical polishing induced martensite HCP phase has an S-N orientation relationship to the FCC phase.
- 4. Electropolishing can be used to eliminate the formation of martensites during the mechanical polishing process. SEM-BSE analysis of 2F-D1 and 3F-D2 samples revealed the presence of high density banded features spread uniformly throughout their microstructures.
- 5. TKD analysis on electron transparent samples extracted from directions parallel to and perpendicular to the building direction revealed that these bands correspond to the HCP phase. This observation confirms the occurrence of martensitic transformation during LB-PBF.
- 6. Tensile tests on the 2F-D1 and 3F-D2 specimens showed similar yield strength of 560 ± 10 MPa and 34 % engineering strain. The similarity in mechanical properties could be due to the similarity in the TRIP behavior during loading.

5. Conclusions

Future Scope

A few aspects that can be considered for future work from this present study are listed below:

- 1. The present study is limited in scope due to the use of only two printing parameters. In the future, a more detailed analysis on the influence of various printing parameters, could be explored to thoroughly understand how printing conditions and especially the cooling rates affect the resulting microstructure and in particular the martensitic phase fractions.
- 2. High resolution electron microscopic analysis is required to better understand the microstructure in detail.
- 3. In this study, only the as-printed samples using two different parameters were mechanically tested. In the future, both as-printed and heat treated specimens shall be mechanically tested to get a full picture of the influence of martensitic phase on the mechanical properties.

6. Future Scope

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