Additive manufacturing of austenitic alloys with high strength and high ductility by selective laser melting

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Additive Manufacturing of Austenitic Alloys with High Strength and High Ductility by Selective Laser Melting

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School of Mechanical and Aerospace Engineering

2019

Additive Manufacturing of Austenitic Alloys with High Strength and High Ductility by Selective Laser Melting

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Supervised by

Assoc Prof Tor Shu Beng

School of Mechanical and Aerospace Engineering

A thesis submitted to

the Nanyang Technological University

in partial fulfilment of the requirements for the degree of

Doctor of Philosophy

2019

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research, is free of plagiarised materials, and has not been submitted for a higher degree to any other University or Institution.

19th August 2019

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Sun Zhongji

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I have reviewed the content and presentation style of this thesis and declare it is free of plagiarism and of sufficient grammatical clarity to be examined. To the best of my knowledge, the research and writing are those of the candidate except as acknowledged in the Author Attribution Statement. I confirm that the investigations were conducted in accord with the ethics policies and integrity standards of Nanyang Technological University and that the research data are presented honestly and without prejudice.

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A/P Tor Shu Beng

Authorship Attribution Statement

This thesis contains material from 3 papers published in the following peer-reviewed journal(s) / from papers accepted at conferences in which I am listed as an author.

Chapter 4 is published as Sun, Z., Tan, X., Tor, S. B., & Yeong, W. Y. Selective laser melting of stainless steel 316L with low porosity and high build rates. *Materials & Design*, 104 (201), 197-204.

The contributions of the co-authors are as follows:

- Dr Tan Xipeng conceived the project and advised the research. He also helped with the transmission electron microscopy characterization and interpretation.
- I prepared the manuscript drafts. The manuscript was revised together with Dr Tan Xipeng, and A/P Tor Shu Beng.
- I performed optical and scanning electron microscopy observation, collected X-ray diffraction patterns, carried the microhardness testing and conducted data evaluation.
- All the co-authors contributed to the technical discussion.

Chapter 5 is published as Sun, Z., Tan, X., Tor, S.B., & Chua, C.K. "Simultaneously enhanced strength and ductility for 3D-printed stainless steel 316L by selective laser melting." *NPG Asia Materials* 10, no. 4 (2018): 127.

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- I performed SLM sample fabrication, optical and scanning electron microscopy observation, collected X-ray diffraction patterns, did electron backscatter study, carried the tensile testing, made Monte Carlo simulation and conducted data evaluation.
- All the co-authors contribute to the technical discussion.

Chapter 6 is published as Sun, Z., Tan, X., Descoins, M., Mangelinck, D., Tor S.B., and Lim, C.S. "Revealing hot tearing mechanism for an additively manufactured high-entropy alloy via selective laser melting." Scripta Materialia 168 (2019): 129-133.

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- Dr Tan Xipeng conceived the project and advised the research work.
- I prepared the manuscript drafts. The manuscript was revised together with Dr Tan, Xipeng, A/P Tor Shu Beng, and Dr Dominique Mangelinck.
- I performed SLM sample fabrication, optical and scanning electron microscopy observation, collected μ -CT results, did electron backscatter study, carried the tensile testing, made transmission electron microscopy observation and conducted data evaluation.
- Dr Tan Xipeng, Dr Marion Descoin and Dr Dominique Mangelinck helped with the atom probe data collection and analysis.
- All the co-authors contributed to the technical discussion.

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Abstract

Selective laser melting (SLM) is a popular powder bed fusion technique used for manufacturing of metal parts. Due to its high-energy laser heat source, SLM process creates a high thermal gradient and fast cooling rate. As a result, it tends to generate a fine microstructure with high dislocation densities and small grain size. Since it's a layer-by-layer manufacturing process, there is a potential for microstructural control within a single build. However, the microstructural control for SLM process has yet to be fully understood.

This study thus aims to further the understanding of microstructural control for SLM process. Specifically, it aims to achieve a desirable microstructure with improved the mechanical properties.

Firstly, stainless steel 316L (SS316L), a common austenitic steel for additive manufacturing, was fabricated by SLM using a 380 W power input. The final parts exhibited good relative density ($>99\%$), and it had a $\langle 001 \rangle$ crystallographic texture along the build direction which is consistent with previous findings. Secondly, by designing a specific scanning strategy, a $\langle 011 \rangle$ crystallographic texture was achieved for SLM-built SS316L. Aided by deformation twinning, the $\langle 011 \rangle$ textured parts obtained a better strength-ductility combination compared to previously built SS316L parts.

Moreover, with the aim of extending existing material library for SLM, a novel austenitic high-entropy alloy (HEA) CoCrFeNi was produced by SLM. Extensive hot cracking was observed for SLM-built CoCrFeNi. The huge grain size caused high residual stress levels were found to be the root cause of the cracking. Compositional modification was attempted by powder blending with aluminium additions. Hot cracks were greatly minimized with the chemical composition of $\text{Al}_{0.5}\text{CoCrFeNi}$. The results were further validated by samples built using pre-alloyed $\text{Al}_{0.5}\text{CoCrFeNi}$ powders.

The study contributes to the scientific knowledge with regards to the microstructural control for SLM process. Moreover, hot cracking issues pertaining to SLM process is also discussed thoroughly in the last section of this thesis.

List of Publications

Peer-reviewed Journal Papers

1. **Z. Sun**, X. Tan, S.B. Tor, and W.Y. Yeong. Selective laser melting of stainless steel 316L with low porosity and high build rates. Materials & Design 104 (2016): 197-204.
2. **Z. Sun**, X. Tan, S.B. Tor, and C.K. Chua. Simultaneously enhanced strength and ductility for 3D-printed stainless steel 316L. NPG Asia Materials. 10.4 (2018): 127.
3. X. Tan, P. Wang, Y. Kok, W.Q. Toh, **Z. Sun**, S.M. Nai, M. Descoins, D. Mangelinck, E. Liu, S.B. Tor. Carbide precipitation characteristics in additive manufacturing of Co-Cr-Mo alloy via selective electron beam melting. Scripta Materialia 143 (2018): 117-121.
4. C. Wang, X. Tan, Z. Du, S. Chandra, **Z. Sun**, C.W. Lim, C.H. Wong. Additive manufacturing of NiTi shape memory alloys using pre-mixed powders. Journal of
5. **Z. Sun**, X. Tan, M. Descoins, D. Mangelinck, S.B. Tor, C.S. Lim. Revealing hot tearing mechanism for an additively manufactured high-entropy alloy via selective laser melting. Scripta Materialia 168 (2019): 129-133.

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Conferences

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Z. Sun, X. Tan, S.B. Tor. Effects of chamber oxygen concentration on microstructure and mechanical properties of stainless steel 316L parts by selective laser melting. 3rd international conference on pro-am progress in additive manufacturing. 2018 May.

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List of Symbols

E	volume energy density
v	laser scanning speed
h	hatch distance (distance between 2 adjacent scan lines)
t	layer thickness
q	laser power input
A	surface absorptivity
r_B	beam radius
k	thermal conductivity
T_m	melting temperature
T_0	initial temperature
α_t	thermal diffusivity.
L_m	latent heat of fusion
ρ	density
C_p	specific heat capacity.
φ_{opt}	powder flowability
σ_y	yield strength
σ_0	materials constant for dislocation movement stress
k_y	materials specific constant
d	average grain diameter
G_s	shear modulus
b	Burgers vector

$\rho_{\perp}$	dislocation density
G	thermal gradient
R	solid-liquid interface solidification velocity
β	shrinkage factor
μ	dynamic viscosity
λ	characteristic microstructural length
$f_s(T)$	solid fraction
$\dot{\epsilon}(T)$	strain rate
$E(T)$	elongation
T_L	liquidus temperature
T_S	coherency temperature
Δp_{sh}	solidification shrinkage
Δp_{ϵ}	mechanical strain
Δp_{max}	depression pressure
γ	FCC austenite phase
α	BCC ferrite phase
N	total number of lattice sites
F	mobility factor
Q	activation energy for grain boundary motion
K_B	Boltzmann's constant
P	probability of spin flip
σ_{tw}	twinning stress

γ_{sf}	stacking fault energy
b_p	burgers factor for Shockley partial dislocation
m	Schmid factor

Chapter 1 Introduction

This chapter provides the background, research motivation and objectives. The thesis organization in the form of a brief outline of the contents is also presented at the end of the chapter.

1.1 Background

Metal and alloys have always been an important aspect of engineering materials. Despite the recent advances of composites, metal still has its unique advantage due to its high fracture toughness, relatively isotropic nature, high conductivity, and excellent properties at elevated temperatures [1-4]. Strength and ductility are two important mechanical properties of metal parts and there has been an everlasting search for strong and ductile metals and alloys [5-8]. Traditionally, metal parts are mainly formed through casting, molding, forming and machining [9]. As a result, the microstructure is consistent throughout the entire body. Microstructural controls for specific areas within the built part are rarely, if not impossible, to be obtained.

On the other hand, additive manufacturing (AM) offers an innovative route of processing the metallic materials. It is often defined as a process of joining materials to make objects from a 3D model, usually layer upon layer, as opposed to subtractive manufacturing technologies [10]. As a result, it has some unique advantages as compared to the conventional manufacturing methods. Firstly, due to the additive nature of production, there is a direct translation of design to component. Therefore, structures of complex shapes can now be produced more easily [11-13]. Moreover, because of the design freedom, topological optimization [14], customized products as well as industrial goods [15-18] are fabricated with greater proficiency. Examples of AM made complex-shaped parts, topologically optimized bracket, intriguing jewellery, metal implant and fuel nozzle are shown in Fig. 1.1.

Figure 1.1 Advantages of additive manufacturing to produce (a) structures of complex shapes [11-13], (b) parts designed by topological optimization [14], (c) intriguing jewellery designs [15, 16] & (d) metal implant and GE Leap engine fuel nozzle [17, 18].

Besides the benefits brought towards the design aspects, AM also reduces the waste through recycling its feedstock materials. Therefore, it helps to limit our environment footprint. Moreover, it has a huge impact on the supply chain for spare parts. Due to the versatility of AM technique, part-specific tooling and/or machines are significantly reduced. It could translate to a huge potential for economic gains. The transportation cost, inventory cost and part obsolescence cost are all going to drop [19]. Fig. 1.2 summarizes all potential advantages of AM.

Figure 1.2 Some potential advantages of metal additive manufacturing [20].

For metal AM, it can be broadly categorized into powder bed fusion (PBF) and directed energy deposition (DED) as illustrated in Fig.1.3 [21]. For PBF technique, it is further categorized according to the energy heat source (laser or electron beam) and the various machine manufactures. PBF typically creates parts with smoother surfaces due to the smaller powder size used [22, 23]. As for DED, they were originally known as laser cladding and were used for coating and repairing works [24, 25]. Recently, they have also proven to have the ability of fabricate parts in 3D [26]. Other than using powder as the feedstock, metal wires have also been employed in DED [27]. It is believed that despite the poor surface finishing, wire feedstock can improve the manufacturing speed to a great extent.

Figure 1.3 Summary of metal additive manufacturing processes [21].

For the purpose of microstructural control, AM technique's small energy source (sub-millimeter in size) and layer-wise material addition provide a huge advantage. It thus holds the possibility for property enhancement. Among all metal AM technologies, selective laser melting (SLM) is probably the most popular powder bed fusion method [28]. It has gained huge interest due to its refined geometry accuracy and controlled operation environment.

Face-centered cubic (FCC) austenitic alloys are known for their high ductility [29]. In contrast to body-centered cubic (BCC) or hexagonal close-packed (HCP) metals, FCC materials have more slip systems to facilitate the deformation process [30]. The introduction of other strengthening methods to improve the strength will make it an ideal candidate for high strength and high ductility material. Therefore, it is of scientific interest to additively manufacture a strong and ductile metallic part using austenitic alloys via SLM.

1.2 Research Motivation and Objectives

The overall aim of the current PhD thesis is to improve the mechanical properties of the parts fabricated via Selective Laser Melting process. As a result, its application across different sectors shall be extended. The motivation of this research is to examine the possibilities of microstructural control for SLM process, and to explore mechanical property enhancement, namely strength and ductility, through microstructural control. New materials of good strength-ductility combination will also be attempted to extend the existing alloy availability for SLM.

There are mainly two objectives of the current PhD work. The first objective is to study the influence of scanning parameters/strategies towards the microstructure and mechanical properties of SLM-built SS316L. The second objective is to design a new material with good strength and ductility specifically catered for SLM process.

1.3 Organization of thesis

- Chapter 1 introduces the research background, motivation and objectives of this study.
- Chapter 2 reviews the literature on metal additive manufacturing and selective laser melting process. Typical defects related to the SLM process are also highlighted. The strength-ductility dilemma pertaining to metals is explained. It then discusses the common crystallographic textures obtained by metal AM and the hot cracking issues encountered by certain materials. The materials used in the current PhD stainless steel 316L and high-entropy alloys are introduced. Lastly, it states the scope of this PhD work as well as a research roadmap to achieve the stated research objective.
- Chapter 3 describes the experimental procedures and equipment used in this study.
- Chapter 4 presents the applicability of the energy density formula for the SLM-built SS316L.
- Chapter 5 states the method for crystallographic texture control and simultaneous improvement for strength-ductility combination for SLM-built SS316L.
- Chapter 6 investigates and explains the hot cracking mechanism observed within high-entropy alloy CoCrFeNi manufactured by SLM.
- Chapter 7 demonstrates the superior tensile property obtained by SLM-built high-entropy alloy.
- Chapter 8 concludes the present PhD work.
- Chapter 9 lists the possible future works.

Chapter 2 Literature Review

2.1 Metal Additive Manufacturing

Metal additive manufacturing, popularly known as metal 3D printing, has drawn great research interests worldwide in recent years [31]. It has the advantage of fabricating intricate parts with complex shapes and having the ability to handle a wide range of materials. Compared to the conventional subtractive manufacturing methods, materials are more effectively utilized in metal AM [32-34]. Moreover, metal AM offers unique mechanical properties for the printed parts [31, 34]. Since its invention in the late 1990s, it has progressed rapidly, especially within the last decade [35, 36]. The research focus has also been moved from fabricating high-density parts using traditional materials to functional parts using novel materials [37-41]. High-density metal parts (>99%) fabricated with different materials and various AM routes are a common sight nowadays [42-44].

Figure 2.1 Schematics of Directed Energy Deposition (DED) and Powder Bed Fusion (PBF) technique [45].

Fig. 2.1 schematically demonstrates the differences between DED and PBF. For DED, powder is typically carried by a shield gas to ensure a consistent powder feed rate. The shield gas (often chosen as argon gas) acts as a protective layer to prevent oxidation during melting [46]. Moreover, due to the “gas-carrying powder” nature of DED, its powder size typically larger compare to PBF to facilitate a constant powder flow [47]. As a result, DED often builds up material at a faster pace but has a rougher surface. Powder recycling is rather difficult for DED especially for large-sized machines. In contrast, PBF technique mostly operates in a controlled environment, either filled up with inert gas or under vacuum conditions [48]. After each layer’s heating, the platform will lower by one layer’s thickness. The precursor powder is constantly being fed to the top surface of the working platform until the whole part is done.

2.2 Selective Laser Melting

Among all the metal AM methods, powder-bed fusion techniques such as selective laser melting (SLM) shows the greatest promise for direct industrial applications. This is mainly due to their high geometrical resolution and controlled operational environment. Products like jet engine fuel nozzles made by SLM has been commercially employed with great success [49].

Fig. 2.2 shows the schematics of a SLM machine. The laser unit is always placed at the top of the operation chamber. Various types of lasers have been used on different SLM machines. To date, the Nd:YAG and Yd:YAG lasers are more commonly observed by companies such as the Concept Laser GmbH, EOS and the SLM Solutions . Several companies like the Renishaw also prefers to employ pulsed laser instead. It is reported that pulsed laser does have an advantage for manufacturing materials with high thermal conductivity and/or high reflectivity [50]. The laser travelling is guided by two deflection mirrors according to the 3D computer-aided design (CAD) model. Due to the mechanical nature of these deflection mirrors, the laser’s scanning

speed for SLM is significantly lower compared to the electron beam's scanning speed which is controlled via magnetic fields for electron beam melting (EBM) [51]. Compared to the standard spherical lens, f-theta lenses can ensure a planar scan plane. In other words, the spot size is kept constant across the build platform. It greatly enhances a smaller spot size and the consistency of the laser fabrication process. The working platform will lower by exactly a layer's thickness after the scan and then the powder dispensing unit, either a recoater or swiper is used to spread new layers of powders onto the platform. The excessive powders are usually stored separately, in this case the powder recycling containers. This process will repeat itself until the whole part is fabricated.

Figure 2.2 Schematics of a SLM machine

There are many factors that could contribute to the overall part quality of a SLM print, such as the chamber oxygen concentration [52]. The commonly

accepted guideline for parameter selection of a SLM process is the volumetric energy density formula [53] whereas

$$E = \frac{q}{v \times h \times t} \quad \text{Eq. 2.1}$$

q is the laser power, v is the laser scanning speed, h is the hatch spacing (distance between two adjacent laser scan lines), t is the layer thickness and E is the volumetric energy density. Due to its simplicity, it is widely utilized among the SLM community. However, it is later found out that this formula alone is not able to ensure a consistent printing quality [43, 54]. Materials and machine related properties such as the absorptivity and laser beam diameter were not considered in this simplified formula. Thus, a normalized model for PBF techniques was proposed in hope of unifying the process parameter selection criteria.

The original dimensionless parameters for laser processing of materials was proposed by Ion et al. [55]:

$$q^* = \frac{Aq}{r_B \times k \times (T_m - T_0)} \quad \text{Eq. 2.2}$$

$$v^* = \frac{v \times r_B}{\alpha_t} \quad \text{Eq. 2.3}$$

Where q^* is the normalised beam power, A is the surface absorptivity, r_B is the beam radius, k is the thermal conductivity, T_m is the melting temperature, T_0 is the initial temperature v^* is the normalised velocity and α_t is the thermal diffusivity. The above equations are enough for laser welding purpose. However, for metal AM, two new terms are proposed [56]. They are normalised layer thickness t^* and normalised hatch spacing h^* :

$$t^* = \frac{2t}{r_B} \quad \text{Eq. 2.4}$$

$$h^* = \frac{h}{r_B} \quad \text{Eq. 2.5}$$

To simplify the analytic calculations, it is assumed that the latent heat of fusion L_m :

$$L_m = 0.5 \times \rho \times C_p \times (T_m - T_0) \quad \text{Eq. 2.6}$$

Therefore, the minimum amount of energy to melt per unit volume of material is expressed as:

$$H_{min} = 1.5 \times \rho \times C_p \times (T_m - T_0) \quad \text{Eq. 2.7}$$

Given:

$$\alpha_t = \frac{k}{\rho \times C_p} \quad \text{Eq. 2.8}$$

Whereas ρ is the material density and C_p is the material's specific heat capacity. Finally, by combining Eq. 2.2 to Eq. 2.8 and assuming the powder packing density is ~ 0.67 , it is derived that the minimum dimensionless heat input per unit volume required for melting is defined as:

$$E_{min}^* = \frac{q^*}{v^* \times l^*} = \frac{Aq}{2v \times t \times r_B \times \rho \times C_p \times (T_m - T_0)} \quad \text{Eq. 2.9}$$

Figure 2.3 Normalized processing diagram for layered additive manufacturing of a range of alloy systems [56].

Fig. 2.3 is an example of normalized processing diagram between the normalized hatch spacing and the normalized minimum energy input. For a variety of materials, when the normalized energy density E_{min}^* falls below a critical value, the void and porosity will appear. On the other hand, part swelling, and solidification cracking tend to occur. It is because when the energy input is lower compared to required value, insufficient melting will introduce porosity and lack-of-fusion cracks. If more than required energy is inserted, a bigger melt pool resulted in higher thermal stresses tends to cause deformation and potentially solidification cracks.

Besides the above-mentioned factors, powder feedstock is also considered to be a key factor for the overall part quality [57]. One of the key aspects of the precursor powder is its shape. Fig. 2.4 demonstrates different shapes of the powder feedstock. It is well recognized that spherical powders are preferred for metal AM due to its better packing density and flowability.

POWDER PARTICLE SHAPES

Figure 2.4 Powder particle shapes [58]

There are different methods of manufacturing metal powders. Table 2.1 summarizes the powder characteristics from various manufacturing processes [59]. Ranked with increasing production cost, water atomization is cheapest manufacturing route, followed by gas atomization, plasma atomization, plasma rotating electrode process and finally centrifugal atomization. Gas-atomization powders are more popular among the AM community due to its balance between quality and price.

Figure 2.5 SEM micrographs of typical particle morphologies made by (a) crashing and milling (b) gas atomization (c) plasma atomization and (d) plasma rotating electrode process. All powders displayed are Ti-6Al-4V [60].

Table 2.1 Summary of powder characteristics by different manufacturing processes [59].

Manufacturing process	Particle size, μm	Advantages	Disadvantages	Common uses
Water atomization	0–500	High throughput Range of particle sizes Only requires feedstock in ingot form	Post processing required to remove water Irregular particle morphology Satellites present Wide PSD	Non-reactive
Gas atomization (Inc. EIGA)	0–500	Wide range of alloys available Suitable for reactive alloys Only requires feedstock in ingot form High throughput Range of particle sizes Use of EIGA allows for reactive powders to be processed Spherical particles	Low yield of powder between 20–150 μm Satellites present Wide PSD Low yield of powder between 20–150 μm	Ni, Co, Fe, Ti (EIGA), Al
Plasma atomization	0–200	Extremely spherical particles	Requires feedstock to either be in wire form or powder form High cost	Ti (Ti64 most common)
Plasma rotating electrode process	0–100	High purity powders Highly spherical powder	Low productivity High cost	Ti Exotics
Centrifugal atomization	0–600	Wide range of particle sizes with very narrow PSD	Difficult to make extremely fine powder unless very high speed can be achieved	Solder pastes, Zinc of alkaline batteries, Ti and steel shot

Fig. 2.5 shows scanning electron microscopy (SEM) images of powders made by different methods [60]. Typically, powders made by crashing and milling are non-suitable for metal AM. Gas-atomization typically generates spherical powders but with the presence of many small satellites. Powders generated by the plasma atomization are much more spherical and with little satellite. Majority of the powder feedstock follows the gaussian distribution, which is in turn favors the powder flowability and packing density [61, 62]. Instead of using specific measurement instrument, a quick optical classification of powder flowability φ_{opt} can be made according to Fig. 2.6.

Figure 2.6 Optical classification of powder flowability φ_{opt} [63].

For powders with good flowability, when it's placed upon a flat surface, they tend to spread evenly without any sharp edge. However, as the powder shape or powder distribution changes, more edges will appear as powder flowability worsens. It is recommended that when powder flowability $\varphi_{opt} < 3$, it is no longer suitable for AM process. Other than the virgin powder's morphologies, it is reported as the recycle-time increases, the flowability and final built part's mechanical property increases [64, 65]. It is suggested to be due to the increase of satellite which assists the powder flow.

Another factor which influences the final built part is the scanning strategy employed during the SLM process [66]. Fig. 2.7 shows the two most popular scanning strategies, stripe scanning strategy and chessboard scanning strategy [67]. The definition of hatching distance is the same between these

two strategies. For stripe pattern, there is a choice between unidirectional and bidirectional scans patterns. It is reported that unidirectional scan patterns tend to create a stronger crystallographic texture within the built part [68]. As for the chessboard scanning strategy, the islands are usually scanned randomly to minimize the residual stress. For consecutive layers, there is always a shift to avoid warping.

Figure 2.7 Schematics of stripe and chessboard scanning patterns [67].

Other than the normal scanning patterns shown above, other scanning patterns have also been observed. Fractal scan strategies have been used and reported to be beneficial towards the hot cracking minimization of SLM built superalloys [69, 70]. It is relatively more difficult to design. Other strategies such as “round-corner design strategy” is also used to minimize cracks at the border [71], as shown in Fig. 2.8.

Figure 2.8 (a) Fractal scan strategy [70] and (b) other scan strategy [71].

2.3 Typical Defects in Selective Laser Melting Process

As mentioned above, there are many factors which can influence the final built part's quality in SLM. Inappropriate selections of process parameters, feedstock material and the scanning strategy can lead to defects. Some of the typical defects are shown in Fig. 2.9.

Figure 2.9 Typical defects in SLM process: (a) keyhole porosity [72], lack of fusion pores and gas induced porosity [73], and (c) delamination in additive manufacturing [74].

Keyhole is a term developed for the welding process. Usually, it involves high laser intensities which is crucial towards the deep penetration welding [75, 76]. As the high-intensity laser irradiates upon the base material, it goes through melting and subsequently vaporizes. The vapor flux generates a recoil pressure above the heated area [77]. Thermo-capillary force is also induced due to the high temperature gradient on the liquid/vapor interface [78]. Together they create a driving force for liquid ejection which in turn generates a vapor-filled cavity termed the “keyhole” [75].

Fig. 2.10 depicts a schematic of laser keyhole welding process. Compared to the usual melt pools from conduction melting, keyhole melt pools are much narrower and much deeper [79]. The keyhole normally inclines towards the laser traveling direction and leaves behind an elongated melt pool. It has been reported for materials with high conductivity and low absorptivity, keyhole mode can help to improve the welding efficiency [80]. It is because for the keyhole-shaped melt pool, the laser experiences multiple reflections which directly helps the energy absorption [81].

Figure 2.10 Schematic of laser keyhole welding process [75].

However, keyhole mode is not always desirable. Simulation has demonstrated the presence of keyhole induced porosities in Fig. 2.11. As the laser induced keyhole melt pool passes from left to right, underneath porosities are generated as the long and narrow keyhole collapses. Excessive keyhole is detrimental to the final built part's density. Therefore, keyhole

should be carefully employed for metal AM. It is recently discovered that keyhole actually exists in almost all laser processes including those conduction modes [79].

Figure 2.11 Keyhole yielded porosity for SLM-built SS316L revealed by simulation [82].

Lack-of-fusion (LOF) defect is a term catered specifically towards to the AM community. Fig. 2.12 describes and explains this phrase with greater clarity. Clearly, if the hatch spacing, distance between two adjacent laser tracks, is too big, there is a region of insufficient melting. It is illustrated by “LOF” in Fig. 2.12. Also, sometimes when the laser scan cannot penetrate through the powder bed layer, lack-of-fusion crack can also occur. Thus, this phenomenon mainly stems from insufficient bonding from adjacent layers and/or laser tracks. It is primarily due to inaccurate estimation of single-track size. Moreover, if the powder bed is not uniformly distributed and/or there is swelling for the solidified part, lack-of-fusion crack can also happen. Therefore, accurate assessment of the melt pool size, powder spreading, and

part deformation should all be carefully controlled to avoid lack-of-fusion defects.

Figure 2.12 Schematic of lack of fusion crack in SLM process [83].

As for gas induced spherical porosity, it is previously believed to be caused by the gas pores trapped within the precursor powders [84]. However, it is recently found that spherical pores mainly form at the last stage of solidification due to the reduction in gas solubility as temperature decreases, Fig. 2.13 [85]. Revealed by synchrotron X-ray, as the molten metal solidifies from left to right, porosities only start to appear at 384 ms. Immediately after melting, no porosity was observed at 334 ms. Carried by the Marangoni convection, the gas pores will circulate within the melt pool at 390 ms. Marangoni convection within the melt pool is a result of fluid density change due to temperature gradient. The cooler liquid melt on top will become heavier and drops into the melt pool. Circulations within the melt pool will occur consequently. Some of them will float to the top surface and escape to the atmosphere shown by the open pore at 406 ms. While the rest will remain in the solid and form porosities. To date, it remains challenging to avoid these type of porosities as they are related to gas solubility within the liquid. However, several studies did show laser re-melting can improve the relative density of the SLM-built parts [86].

Figure 2.13 Pores nucleate, coalesce and collapse, resulting in an open pore (pink dotted line) as well as trapped pores. Scale bars is 250 μm [85].

Lastly, since SLM is a layer-wise fabrication process, there is non-uniform heating and cooling which in turn generates high residual stress levels [87]. For brittle materials, it could lead to delamination, Fig. 2.9 (c). Sometimes, this delamination process can be useful for metal process though. For instance, for electron beam melting (EBM) process, Ti6Al4V is typically built on a stainless-steel substrate. Thus, it is very convenient for part removal after the whole process is finished.

Other than the macroscopic defects, AM products also have many microscopic defects, namely dislocations. Fig. 2.14 shows a typical TEM image of SLM-built SS316L compared to its wrought and heat-treated counterparts. SS316L samples built by SLM obviously contains more dislocations as compared to the wrought samples, Fig. 2.14 (a) to (d). These dislocations exist in the form cellular structures which are later found out to be caused by fast cooling and elemental segregation [88]. After the SLM-built samples go through heat treatment in Fig. 2.14 (e) to (h), dislocations disappear to form clean interiors.

These dislocations have a profound influence on the mechanical properties of the SLM-built parts, especially for the yield strength. Due to the presence of many dislocations, the yield strength is increased as a result. As compared to the samples made by casting, AM built samples typically have more dislocations. It is mainly due to the fast cooling rate, so that there is insufficient time for regular atomic packing [48].

Figure 2.14 Bright field TEM images of SS316L: (a)(b) wrought, (c)(d) SLM as-built, (e)(f) SLM-built sample heat treated at 650 °C for 30 mins and (g)(h) SLM-built sample heat treated at 1050 °C for 30 mins [89].

Moreover, the rapid cooling rates involved in SLM can also greatly suppress elemental segregation in comparison to conventional processing routes such as casting and forging. At the same time, it promotes the formation of martensitic phases and dislocations [90]. This tends to give the AM fabricated metal parts a higher yield and ultimate tensile strength but a decreased elongation [21]. It is clearly demonstrated in Fig. 2.15 for the comparison between various metal AM techniques and the wrought, annealed counterparts. Generally, samples made by AM process tend to have a higher yield strength and ultimate tensile strength. However, they suffer from a reduced ductility compared to the conventional manufacturing methods.

Figure 2.15 Summary of Ti-6Al-4V AM tensile properties. Abbreviations: DMD, direct metal deposition; DMLS, direct metal laser sintering; EBM, electron beam melting; HT, heat treatment; LENS, laser-engineered net shaping; UTS, ultimate tensile strength; YS, yield stress [21].

2.4 Strength-ductility Dilemma of Metals and Alloys

The reason for a decreased ductility of metal AM manufactured parts can be attributed to the strength-ductility dilemma of metal parts [91-93]. Strength and ductility are usually inversely proportional to each other. For metal AM fabricated samples, they tend to have a smaller grain size and a higher dislocation density. These will improve the yield strength as shown in Equation 2.10 and 2.11 [94, 95].

$$\sigma_y = \sigma_0 + \frac{k_y}{\sqrt{d}} \quad \text{Eq. 2.10}$$

$$\Delta\sigma_y = G_s b \sqrt{\rho_{\perp}} \quad \text{Eq. 2.11}$$

Equation 2.10 is the classical Hall-Petch relationship whereas, σ_y is the yield strength, σ_0 is a materials constant for the dislocation movement stress, k_y is a materials specific constant, and d is the average grain diameter. For Equation 2.11, G_s is the shear modulus, b is the Burgers vector and $\rho_{\perp}$ is the

dislocation density. Therefore, with a reduction in grain size and an increase in dislocation density, the yield strength will be improved. However, as the number of interfaces increases, the materials becomes more brittle which inevitably affects the AM built parts' toughness and industrial application [34].

Despite the long-standing strength-ductility dilemma, certain methods have proven to be successful to improve both properties simultaneously. Various strengthening methods such as dispersion strengthening, solid solution strengthening, and use of multiple heat treatment process did increase strength and ductility at the same time for certain materials [96-98]. Recently, coherent internal boundaries at nanoscale such as twinning, precipitation, phase interphase are proven to significantly improve the material's mechanical performance [99-103]. This owes to the excellent mechanical and thermal stabilities of these nanoscale interfaces.

Figure 2.16 Two-dimensional representation of (a) a typical grain boundary and (b) a defect-less coherent twin boundary. (c) Dislocation and twin boundary interactions. (d) to (f) Relationships of strength/hardness, elongation to failure and flow stress's rate sensitivity versus the characteristic microstructural sizes of grain size/twin length. [102].

Among all those previously mentioned techniques, twinning has proven to be one of the most effective measures for property enhancement [104-107]. For the commonly used strengthening methods in metals and alloys such as dispersion strengthening and grain boundary strengthening shown in Fig. 2.16 (a) and (b), despite an increase in strength brought by dislocation interactions with internal boundaries, ductility suffers as a result. In contrast, twin boundary offers some unique advantages compared to other interfaces. As illustrated in Fig. 2.16 (c), for twin boundary, atoms are mirror reflections of those on the other side of the interface. Due to the formation mechanisms, they can be classified as growth twins, annealing twins or deformation twins. They tend to be more stable both thermally and mechanically. As the characteristic microstructural length (either grain size or twin length) decreases, twinning behaves similarly to grain boundaries both for the strengthening capability and the influence on strain rate sensitivity, Fig. 2.16 (d) & (e). However, unlike grain boundary, the ductility increases as the characteristic microstructural length decreases for twinning, Fig. 2.16 (b). It gives twinning a huge advantage for property enhancement.

For instance, it is shown that by engineering a hierarchical twinning structure, the strength and ductility of an FeMnC TWIP (twinning-induced plasticity) steel can be enhanced together [108]. In order to achieve the gradient twinning structure, cylindrical specimens were torqued along the radial direction. As a result, the outer layer experiences more shear and thus more deformation twins were generated compared to the inner core. Fig. 2.17 (a) and (b) displays the relationship between torque applied and the tensile properties. Clearly, as more torque is applied the tensile stress and strain improved together. Also, the cylindrical specimen is illustrated in Fig. 2.17 (c). Fig. 2.17 (d) shows the schematics for increment of twin density from inner core to the periphery (from left to right).

Figure 2.17 Strengthening of FeMnC TWIP steel by pre-torsion treatment. (a) Engineering stress-strain curves for torsion experiments on samples at four different torsional angles. (b) Corresponding true stress-strain curves. (c) A cylindrical sample with a hard shell and soft core with distinct stress-strain behaviors. (d) A representative gradient microstructure composed of uniform grains with increasing twin density from the core to the surface of the cylindrical sample [108].

It is later found out that the gradient hierarchical nano-twinned structure facilitates the initiation of multiple twinning systems. Typically, for materials with low stacking fault energy, only one or occasionally two sets of deformation twinning system will be activated during deformation. However, for this case after torsion, three sets twinning systems were activated Fig. 2.18 (a). Moreover, due to this gradient twinning structure, multiple stacking faults and partial dislocations have been initiated among twinning interactions Fig. 2.18 (b) to (d).

Partial dislocations were also observed to either glide along and initiated from the twin boundary (Fig. 2.18 (e) & (f)) which is consistent with previous literature [102]. The twin boundary greatly increases the dislocation storage capacity by dissociating full dislocations into partial dislocations. It will then increase the work hardening capacity of the material. As a result, the strength and ductility of the material are simultaneously improved.

Despite the significant improvement for the mechanical properties, there are still several drawbacks of this method. Firstly, the property enhancement is only observed in a single direction, which is along the torsion axis. For structuring engineering materials, at least two dimensions should be considered. Also, for materials with high stacking fault energy such as aluminium alloys, this method is unlikely to be effective.

Figure 2.18 Hierarchical twin structures and interactions between dislocations and deformation twins. (a) Multiple activated twinning systems. (b) Interactions of primary and secondary twins. (c) & (d) Zoomed-in views of (b). (e) Interactions of partial dislocations and twin boundaries. (f) Enlarged image of (e) [108].

Besides the employment of twinning, heterogeneous microstructure and coherent nano precipitation have also been applied to increase the strength without losing ductility [99, 109, 110]. As shown in Fig. 2.19 (a), heterogenous microstructure was created by a combination of hot rolling, cold rolling and heat treatment for a medium Mn steel (10% Mn, 0.47% C, 2% Al and 0.7% V (wt.%) [110]. The final microstructure consists of a highly dislocated martensite α' grains separated by the soft γ austenite grains. There are huge amounts of dislocations created during the process and they significantly improved the material's yield strength by dislocation forest hardening. Moreover, these dense dislocations promote a high ductility through mobile dislocation gliding and the controlled release of martensitic phase transformation. Therefore, it was proposed that the extraordinarily huge

amounts of dislocations facilitate the improvement in ductility as the strength increases. It is against the conventional belief of dislocation theory though.

Figure 2.19 (a) EBSD phase image and orientation image showing the lamella microstructure of austenite (γ) embedded in tempered martensite (α') matrix. The austenite area fraction is 15%, and the martensite area fraction is 85%. (b) Tensile properties of our steel compared with those of other existing high strength metallic materials [110].

Fig. 2.19 (b) illustrates the comparison of tensile properties between the newly processed medium alloyed steel and other existing high strength metallic materials. The improvement of tensile properties is clearly demonstrated. The combination of the yield strength and the uniform elongation is superior compared to most of the existing research data.

Another method of improving the strength-ductility combination is to introduce coherent nano precipitations as shown in Fig. 2.20. Conventional, hard precipitates of different lattice spacing as the parent material is typically chosen to prevent dislocation gliding and thus increasing the strength of the material at the expense of ductility [111]. Interestingly, by introducing coherent precipitations, the tensile properties improve tremendously without suffering from ductility loss, Fig. 2.20 (a). It is later found out that the formation energy of coherent nano precipitation is much lower compared to other incoherent precipitates. Therefore, the precipitation density increases significantly, Fig. 2.20 (c). Unlike incoherent precipitates which strengthens the materials by blocking dislocation movement, the coherent precipitates create backstresses when the dislocation cuts through them. As a result, the strength and ductility improve concurrently.

Figure 2.20 (a) Improvement in strength and ductility for tensile test. (b) Coherent B2 precipitate within the parent grain. (c) Size, distribution and quantity of the nano precipitates, whereas the blue precipitate is Ni and Al based, yellow precipitate which includes C, B and P, lastly the blue precipitate which contains Mo [99].

Despite the previously mentioned interesting works, improving the strength and ductility simultaneously has been a challenging but intriguing scientific problem for many decades. Metal AM or SLM has the potential of achieving this goal due to its layer-wise fabrication manner. The possibility of microstructural manipulation by parameter selection has been demonstrated several times [66, 68, 112-118]. Thus, it is of great interest to use SLM to break the long-standing strength-ductility dilemma.

2.4 Common Crystallographic Textures and Grain Shapes of Metal AM

Before the beginning of this section, some simple crystallography basics need to be introduced. Majority of metal and alloys consist of regular atomic structures. Taking steel as an example, due to the processing route and compositional differences, it can exist in either body-centred cubic (BCC) or face-centred cubic (FCC) structures as shown in Fig. 2.21 (a). These atomic structures are the building blocks of the larger sample or part. The EBSD technique is used primarily to determine the orientation of these crystals. It is well known that material properties such as strength, ductility and electrical conductivity all depend on the crystallographic orientations.

On the other hand, crystallographic texture in AM is the relationship between overall atomic structure's growth direction and the build direction of the final part. For cubic atomic structure, three representative crystallographic textures are displayed in Fig. 2.21 (b). When the cubic atomic structure grows parallel to the build direction, it is a (0 0 1) crystallographic texture, and it is usually depicted as red in the orientation maps. If the atomic structure grows 45° away from the build direction, it is a (0 1 1) crystallographic texture which is typically colored as green. Finally, if the atomic growth direction is 45° away from the build direction and 45° out of the viewing plane, it is defined as the (1 1 1) crystallographic texture and blue is normally used for presentation.

Figure 2.21 (a) Schematics of body-centred cubic (BCC) and face-centred cubic (FCC) structures. (b) Atomic arrangement for different crystallographic textures observed in AM, namely (001), (011) and (111) textures.

For microstructural characteristics, they are mainly determined from the thermal gradient G and the growth rate R conditions during solidification, Fig. 2.22. G/R determines the morphology of solidification structure. For processing conditions which involve a high G/R value, the microstructure tends to be cellular which is the case for most metal AM processes. Under extremely high G/R condition, planar microstructure is to be expected but it is rarely observed. On the other hand, when G/R is small, dendritic or equiaxed dendritic microstructure will be observed. The microstructure size is mainly determined by the cooling rate which is expressed as $G \times R$. Slower cooling rate will generate bigger microstructure as it has more time to coalesce [119].

Many materials used in laser welding has their own thermal gradient and growth rate maps. One of the first applications of this map was used in the processing of superalloys due to their high industrial values. However, experimentally, this map is difficult to construct as the precise measurement of the thermal gradient and cooling rate are difficult to achieve during the short span of the solidification process.

Figure 2.22 Effect of temperature gradient G and growth rate R on the morphology and size of solidification microstructure [119].

Due to the localized heating and the layer-wise addition nature of metal additive manufacturing, majority of the heat flows downwards through the solidified material due to its higher thermal conductivity [120] (Fig. 2.23 (a)). Since grain growth tends to occur along the maximum heat flow direction during solidification [119], it is thus expected that most of the additively manufactured samples have a crystallographic texture of $\langle 001 \rangle$ along the build direction as shown in Fig. 2.23 (b). It causes anisotropic properties as well as large columnar grains which both negatively affect the industrial adoption of the components made by metal AM.

Figure 2.23 Schematics of heat transfer direction for selective laser melting [120]. Crystallographic texture orientation for nickel-based superalloy CM247LC built by selective laser melting [121].

Therefore, it is of great interest to alleviate this common $\langle 001 \rangle$ crystallographic texture and the columnar grains for metal AM and one of the most obvious solutions is to use heat treatment. Heat treatment can initiate grain recrystallization and grain growth, which can help to obtain a homogeneous polycrystalline microstructure.

Fig. 2.24 shows the effect of heat treatment on the SLM-built CoCrMo alloys. Images circled in blue are the microstructures built by SLM from both the top and side surfaces. It is obvious that all melt tracks and cellular structures are present after etching. The grains are elliptical along the build direction on the side surface and they appear to be predominantly in (001) orientation. The pictures circled in red are the microstructures after heat treatment. Both the melt tracks and cellular structures have disappeared due to recrystallization. The crystallographic texture is polycrystalline with no preferred orientation and equiaxed grains are obtained.

Fig. 2.24 (m) and (n) are the pole figures of the as-built and heat-treated CoCrMo samples respectively. For the as-built CoCrMo sample in Fig. 2.24 (m), majority of the grains have a (001) orientation as shown by the red dot in the center of the pole figure map. However, for the heat-treated sample in Fig. 2.2 (n), it does not have any preferred orientation as all the red dots are randomly distributed. Therefore, it shows that heat treatment can indeed break down the (001) crystallographic texture.

Despite the alleviation of preferred crystallographic texture and the columnar grains, there are several drawbacks. Firstly, it will cause microstructural coarsening. As shown in Fig. 2.24 (e) to (l), after heat treatment, fine cellular structures disappear, and the grain size increases. As a result, the material's strength deteriorates due to the lack of interfaces/obstacles to constrain dislocation movements. Moreover, heat treatment is an extra step and an additional cost. It will add as a further deterrent to industrial adoption.

Figure 2.24 Effect of heat treatment on the microstructure of SLM-built CoCrMo alloys. (a) to (i) and (c) to (k) are the as-built samples whereas (b) to (j) and (d) to (l) are their respective heat-treated counterparts. (m) and (n) are the pole figures of the as-built and heat-treated samples [122].

Another possible method of changing the common $\langle 001 \rangle$ texture is by optimizing the scanning strategies during fabrication. Research has shown the possibility of crystallographic texture control by manipulating the scanning strategy for a beta-type Ti-15Mo-5Zr-3Al alloy, shown in Fig. 2.25. Though the crystallographic texture along the build direction remains to be (001) for both scanning strategies, there is a change for texture on the other surfaces: x-y and x-z planes. When the laser scanning lines between adjacent layers are aligned in the same direction, the x-y and x-z planes have a (011) texture. However, when there is 90° of rotation between scanning lines of adjacent

layers, both x-y plane and x-z plane remain to be a (001) texture Fig. 2.25 (c) and (d). The authors did point out that the change in melt pool shape due to different scanning strategies might be the key for this phenomenon. Similar observations were made for SLM-built In738LC as well [115].

Figure 2.25 Effect of scanning strategy on the crystallographic texture development of SLM-built Ti-15Mo-5Zr-3Al alloy. (a), (c) inverse pole figure (IPF) images taken in the three orthogonal planes. (b), (d) {001} and {011} pole figures of the products measured in the y-z plane [116].

It was found in several publications, that the melt pool shape has a tremendous influence towards the grain morphology and/or texture for both additive manufacturing and laser welding [123-126]. For instance, by comparing computer simulation and experimental results, it is shown that the grain morphology and texture of Ti6Al6V can be successfully altered due to the change in melt pool shape for laser welding Fig. 2.26. In this example, a secondary laser was used following the movement of the melt pool. By doing this, the shape of the melt pool was successfully altered. Fig. 2.26 (a) and (c) are the simulated melt pool shapes occurred due to different processing parameters. Fig. 2.6 (b) and (d) show the corresponding experimentally observed grain structures. Clearly, different grain growth directions and grain morphologies were obtained as a result.

Figure 2.26 Relation between molten pool shape, heat flow and grain orientation. (a) & (c) simulated melt pool shape, (b) & (d) simulated grain structure for each thermal condition [127].

Interestingly, the same phenomenon is also observed in metal AM. By adjusting the scanning speed which inevitably caused a change in melt pool shape, site specific control of crystallographic grain orientation for EBM-built In718 was achieved, Fig. 2.27. It opens a new pathway for microstructural design.

Figure 2.27 examples of site specific crystallographic texture control for EBM-built Inconel 718 [128].

To further illustrate the effect of melt pool shape on grain orientation distribution, EBSD studies were conducted on two different melt pool shapes for SLM-built SS316L as shown in Fig. 2.28. Both samples have the same scanning strategy. However, for sample (a) (Fig. 2.28 (a) and (c)), it employs a lower energy input whereas for sample (b) (Fig. 2.28 (b) and (d)), a higher energy input was used which resulted in a keyhole shaped melt pool. It is obvious that cellular structures/dendrites always tend to grow perpendicular to the melt pool boundaries.

Due to the change in melt pool shape, the sample's crystallographic texture changed from a mixture of (001) and (011) for the sample with lower energy input to a (011)-dominating texture for the sample with higher energy input. Site specific crystallographic orientations were also obtained for point C, D and E in Fig. 2.28 (a'). Their respective pole figures are shown in Fig. 2.28 (e) to (g). It is interesting that for points C and D which have a (011) orientation along the z direction, they have a (001) orientation along the x direction. For point E, which has a (001) orientation along the z axis, it has a (011) orientation along the x axis.

It is found that the layered crystallographic texture of (001) and (011) developed in the lower power input sample has excellent mechanical and corrosion properties as compared to the sample built with higher power input which only has a single (011) texture. It demonstrates the possibility of microstructural control for the SLM process. With the same material and machine, by switching and scanning parameters, different types of crystallographic textures could be generated.

Though the effect of melt pool shape towards the formation of crystallographic texture is clearly demonstrated in this example. The effect of laser parameters towards the melt pool shape was insufficiently discussed. Thus the direct link between the laser processing parameter and the texture formation is weakly established.

Figure 2.28 Effect of melt pool shape on grain orientation distribution for SLM-built SS316L. (a) & (b) backscattered electron (BSE) images showing the morphologies of the boundaries of the columnar cells and melt pool boundaries. (a') and (b') are the respective enlarged views. (c) & (d) are the corresponding crystal orientation maps. (e) to (g) are the pole figures taken at each point of C, D and E [129].

It is to be noted that besides the melt pool shape's contribution, the crystallographic texture formation seems to be highly dependent on material's composition as well. For instance, besides the common $\langle 001 \rangle$ texture and a few $\langle 011 \rangle$ textures reported, a $\langle 111 \rangle$ texture was observed for SLM-built tantalum samples (Fig. 2.29). Clearly, for the selected area for EBSD studies shown in Fig. 2.29 (b), (111) is the dominant crystallographic texture.

However, the formation mechanisms for this type of texture was not fully discussed and explained. To the best of the author's knowledge, it is the only $\langle 111 \rangle$ crystallographic texture reported from the literature, and the formation mechanism is still unknown. Therefore, there is still a lack of understanding towards the texture formation for the SLM process.

Figure 2.29 (a) Optical microscopy image of SLM-built tantalum. (b) EBSD image of the selected area along the build direction [118].

In terms of grain shape modification, researchers have relied upon the columnar to equiaxed (CTE) transition model to control and/or explain their formations [130]. One of the first applications of the CTE model was on laser cladding for superalloy CMSX-4 [131]. As for additive manufacturing, it is proven to be successful for electron beam melting (EBM) fabricated In718 samples (Fig. 2.30).

Fig. 2.30 (a) shows the CTE criteria for In718. Typically, as the thermal gradient G decreases and solid-liquid interface solidification velocity R increases, grain growth is likely to switch from columnar to equiaxed. It will be columnar vice versa. By using a 3D simulation model to predict the respective G and R values, proper combinations of scanning parameters were adjusted to control the grain shape. In this case, the powder bed preheating temperature was found to have a huge influence towards the G and R combination. Therefore, by changing the powder bed temperature of the EBM process, columnar and equiaxed grains were obtained for different builds shown in Fig. 2.30 (b) and (c). It is believed that similar approach should be applicable to SLM process too.

Figure 2.30 (a) Columnar to equiaxed transition criteria for In718. (b) & (c) Change in grain shape by adjusting the printing parameter and strategies [132].

Besides the above-mentioned methods of modifying the crystallographic texture and grain size, researchers have also discovered the possibility of using two different lasers for microstructural control. For SLM-built SS316L in Fig. 2.13, the 400 W laser created a polycrystalline microstructure with an average grain size of $\sim 10^3 \mu\text{m}^2$, Fig. 2.13 (a). In contrast, the 1000 W laser generated a (001) crystallographic texture with an average grain size of $\sim 3 \times 10^4 \mu\text{m}^2$, Fig. 2.13 (c). Thus, both the crystallographic texture and the grain size are manipulated at the same time. It demonstrates the effectiveness of different lasers towards microstructural control. However, the detailed formation mechanisms of the different types of crystallographic textures and grain sizes were not explained in detail for this study.

Figure 2.31 Effect of two lasers on SLM-built SS316L. The 1000 W laser input results in a $\langle 001 \rangle$ texture whereas a 400 W generates a polycrystalline structure [133].

For SLM-built In718, the same phenomenon was also observed. In Fig. 2.32, a laser with lower power input of 250 W created regions of polycrystalline

microstructure. The other laser with a high power input of 950 W generated a region of (001) crystallographic texture. Like results obtained from the previous example of SLM-built SS316L, no detailed explanation of the texture formation mechanisms was provided for the current study. It is definitely of scientific interest to explain the above-mentioned phenomenon. If these results could be explained, they will facilitate the microstructural control for SLM tremendously.

Figure 2.32 Effect of two lasers on SLM-built IN718. EBSD analysis of a graded Inconel 718 sample featuring a single coarse columnar grained zone embedded in a fine grained matrix (a) Inverse Pole Figure (IPF) colored map of Y-Z section (b) The index map of IPF and the reference coordinate (c) Pole figures of the texture for Zone 2 [26].

In general, crystallographic texture control for the SLM process still remains at its infant stage. Though promising results have been obtained by several researchers, the real applicability towards the mechanical properties are still rather limited. Moreover, direct linkage between the laser processing parameters and the final microstructures needs to be established. The development of simulation work for prediction and control of the SLM-built part's microstructure is another area waiting to be enhanced.

2.5 Hot Cracking of Metal AM

Hot cracking is a spontaneous failure of an alloy during solidification. It typically happens at the end of solidification, and there are thin liquid films between solid grains [87, 134]. Hot cracking is usually identified as cracks, either on the surface or internally in the casting. An excessive hot cracking example for a casted valve is shown in Fig. 2.33 (a). The industrial value of metal parts can be severely affected by hot cracks. Hot cracking is also observed in the welding. Due to the specific regions that cracking initiates, it is further categorized into solidification cracking (in the weld fusion zone) and liquation cracking (in the heat affected zone) as shown in Fig. 2.33 (b) and (c). Regardless of the nomenclature, cracking has always been detrimental towards the mechanical performance of metal and alloys.

Figure 2.33 (a) Hot cracking example of a valve made by casting [135]. (b) Solidification cracking and (c) liquation cracking in aluminum circular-patch welds [136].

Certain features are consistent for all hot cracks. As hot cracking forms due to the presence of liquid film between solid grains, all cracks are intergranular in nature [137, 138]. As the molten metal solidifies, the liquid between different grains tends to solidify last. It is because the repulsive force between grain boundaries brings down the effective solidifying temperature and it is the reason for the existence of the liquid films. Moreover, at the end of solidification, liquid film tends to solidify into the shape of dendrite/cellular structure, it creates a typical smooth morphology on the fracture surface as shown in Fig. 2.34 (b).

Figure 2.34 (a) Cross section of a weld in 42CrMoS4 with showing a transverse crack. (b) classical hot crack surface or solidification crack of the weld of picture (a), direction of view marked with red arrow, showing classic hot cracking with free solidified dendrites [139].

Due to the severe consequence of hot cracking towards metal and alloy's performance, theoretical formulations were made with the hope of predicting and preventing hot cracking. Among all the models, the classic Rappaz-Drezet-Gremaud (RDG) criterion has proven to be very successful [140]. The RDG model considers the depression pressure Δp_{max} within the mushy zone induced by both solidification shrinkage (Δp_{sh}) and mechanical strain (Δp_{ϵ}):

$$\Delta p_{max} = \Delta p_{sh} + \Delta p_{\epsilon} = \frac{180(1+\beta)\mu}{\lambda^2 G} \int_{T_S}^{T_L} \frac{E(T)f_s(T)^2}{(1-f_s(T))^3} dT + \frac{180 R \beta \mu}{\lambda^2 G} \int_{T_S}^{T_L} \frac{f_s(T)^2}{(1-f_s(T))^2} dT \quad (Eq. 2.12)$$

with

$$E(T) = \frac{1}{G} \int f_s(T) \dot{\epsilon}(T) dT,$$

whereas G is the thermal gradient, β is the shrinkage factor, μ is the dynamic viscosity, λ is the characteristic microstructural length, R is the solid-liquid front growth velocity, $f_s(T)$ is the solid fraction, $\dot{\epsilon}(T)$ is the strain rate, $E(T)$ is the elongation and T_L is the liquidus temperature. T_S is the coherency temperature, below this value, liquid feeding problem becomes trivial, as liquid film breaks down into isolated drops. Compared to other hot cracking

models, The RDG model considers more factors such as solidification temperature range, viscosity, microstructural magnitude, shrinkage and strain factors.

Hot cracking is a critical problem for metal AM. It limits the variety of materials available for metal AM and it deteriorates the mechanical performance of the manufactured parts. Study has revealed the presence of liquation cracking for laser deposited Inconel 718 as shown in Fig. 2.35. The crack did not occur from the fusion zone, rather it stems from the HAZs since the 3rd layer, Fig. 2.35 (c). However, it is only possible to distinguish solidification cracking from liquation cracking in an interrupted single-scan fabrication. It is because for metal AM, due to the layer-wise cyclic heating characteristic, it is very difficult to distinguish the origin of the crack from the finished built part. Therefore, it would be more appropriate to use the term of hot cracking instead of merely solidification cracking itself.

Figure 2.35 Presence of liquation cracking for laser deposited Inconel 718 [141].

Hot cracking is a heavily reported problem for nickel-based superalloys due to their high industrial values [142-145]. Therefore, it is not surprising that both SLM and EBM have problems printing them, as shown in Fig. 2.36. On the left in the blue box, it is EBM-built superalloy showing the presence of

long hot crack, most of the cracks are high-angular cracks and the smooth surface indicates the presence of liquid film at the last stage of solidification. On the right in the red box, it is the SLM-built superalloy In738LC. The cracks seem to be shorter but more in quantities due to the smaller grain size. The representative EBSD graph surrounding the crack and the smooth surface of the liquid film is shown as well.

Therefore, regardless of which metal AM process employed, high angular grain boundaries (HAGB) are found to be more susceptible to cracking as compared to low angular grain boundaries (LAGB). Hot cracking is heavily dependent on the material's composition. The energy source types, such as electron beam or laser, have little to do with cracking minimization. The crack length seems to be related to the grain size of the built part. Moreover, liquid film was found to be a necessary condition for both studies.

Figure 2.36 On the left, EBM-built superalloy, (a) & (b) intergranular crack and (c) enlarged smooth fracture surface [146]. On the right, SLM-built Inconel 738LC, (a), (b) & (c) intergranular crack and (d) enlarged smooth fracture surface [147].

It is found from the above two publications that chemical heterogeneity helps to maintain the liquid film by lowering the solidus temperature. It was attributed to as one of the key factors for hot cracking initiation. For superalloy and Inconel, boron and/or zinc were identified as the key elements as shown

below, Fig. 2.37. Nevertheless, segregation within such a localized region can only be revealed by atom probe tomography technique.

Figure 2.37 On the left, atom probe tomography (ATP) shows the presence of borides near the grain boundary [146]. On the right, ATP displays that the grain boundary has extra zinc. Moreover, it also contains extra boron like the previous study [147].

In terms of minimizing hot cracks, several attempts were made. Changing scanning strategy achieved little success [70]. Chemical compositional modification was found to improve the cracking susceptibility [148]. It was hypothesized that an alloy's resistance to cracking can be enhanced by increasing the concentration of substitutional solid solution strengthening atoms within the lattice. The detailed composition of the original Hastelloy X (OHX) and the modified Hastelloy X (MHX) are listed in Table 2.2. Guided by the increase in strengthening coefficient, Mo and W's concentrations have been increased. On the contrary, Mn and Si were proven to be detrimental towards the hot cracking susceptibility by previous research.

Table 2.2 Composition of modified Hastelloy X (MHX) and original Hastelloy X (OHX). K is the elemental strengthening coefficients found from literature and Δc_i is the change in concentration [148].

Alloy	Ni	Cr	Fe	Mo	Co	Mn ^a	Si ^a	W	C
MHX wt.%	46.55 ± 0.27	21.80 ± 0.19	18.59 ± 0.17	9.40 ± 0.12	1.77 ± 0.05	0.22 ± 0.02	0.31 ± 0.02	1.05 ± 0.01	0.054 ± 0.01
OHX wt.%	47.87 ± 0.28	21.3 ± 0.19	19.5 ± 0.17	9.0 ± 0.12	1.04 ± 0.04	0.48 ± 0.03	0.32 ± 0.02	0.56 ± 0.03	0.057 ± 0.01
Δc_i (At. Frac)	-0.01	0.007	0.0004	0.003	0.007	-0.003	-0.0002	0.0016	-0.0001
k (MPa At. Fraction ^{-1/2})	—	337	153	1015	39.4	448	275	997	1061

The compositional modification did bring a positive influence on crack density as shown in Fig. 2.38. Clearly, for crack densities measured in both vertical and horizontal directions, the modified composition yielded a lower amount of cracks per unit area. Therefore, by controlling the concentration of substitutional solid solution strengthening atoms could indeed bring a beneficial effect towards the hot cracking minimization.

It is worth noting though, despite the positive change brought by the chemical composition modification, the hot cracks are still present within the as-built samples. Thus, complete elimination of cracking was not achieved via this method. Moreover, as the precise trace element control is very difficult, and elemental strengthening coefficient is not easy to calculate, thus there has not been any other report using this method till now.

Figure 2.38 Crack density of original Hastelloy X (OHX) and modified Hastelloy X (MHX) measured in vertical (V) build orientation, bottom plot, and horizontal (H) build orientation, top plot [148].

Another method used for hot cracking minimization was to introduce nanoparticles as nucleants [149]. It was observed in laser welding that cracking susceptibility improves as the grain size decreases [150]. Therefore, with the introduction of “lattice-matching” nano-nucleant, smaller grains were generated to share the residual strain.

Figure 2.39 Selective laser melting of Al7075 (a), (c), (e) without nano-particle nucleant and (b), (d), (f) with nano-particle nucleant [149].

Fig. 2.39 shows the effect of nano-particle nucleant on SLM-built Al7071. Without the nano particles, columnar grains with the presence of hot cracks are observed in Fig. 2.39 (e). However, by homogeneously distributing the nano-particles around the precursor powders Fig. 2.39 (b), grain refinement is achieved throughout the fabricated sample Fig. 2.39 (f). The grain size has reduced from $\sim 400 \mu\text{m}^2$ to $\sim 10 \mu\text{m}^2$. No cracks were observed within the build. As the grains become smaller, there are more grain boundaries to withstand the residual stress and help minimize hot cracks. It seems to be a more reliable method to eliminate the hot cracking issue for metal AM [149]. It should be noted that the nano-particles should share similar lattice parameter as the parent material. Thus, nucleants should be carefully selected for each material used for AM process.

2.6 Stainless Steel 316L

Belonging to the 300 series of austenitic stainless (FCC) steels, SS316L is one of the most widely investigated materials for metal AM [151-155]. This is due to its wide applications in marine, biomedical equipment and fuel cell [156-158]. Moreover, it has excellent weldability due to its chemical composition which is listed in Table 2.3 [159]. Compared to the common 304 or 316 grade stainless steel, SS316L has a very low content of carbon (<0.03 wt%), thus there is an “L” letter behind the series name. The low carbon content prevents the formation of chromium-rich carbides which are unfavorable for intergranular cracking minimization especially for welding process [160].

Table 2.3 Chemical composition for SS304, SS316 and SS316L [152].

Type	UNS	Composition, max wt %							
	Designation	C	Mn	P	S	Si	Cr	Ni	Mo
304	S30400	0.08	2	0.45	0.03	0.75	18-20	8-10.5	Nil
316	S31600	0.08	2	0.45	0.03	0.75	16-18	10-14	2-3
316L	S31603	0.03	2	0.45	0.03	0.75	16-18	10-14	2-3

Each element has its own specific purpose during the alloy design stage. Typically, when the chromium content is above 12 wt%, steel will become stainless due to the formation of chromium oxide layers on the surface of the metal part to prevent corrosion [160]. However, under certain heating conditions, chromium might form intermetallic compounds such as α' and carbides (mostly $M_{23}C_6$). “M” is mainly chromium but sometimes can be replaced by iron or molybdenum [161, 162].

On the other hand, nickel is primarily used to ensure the austenitic stability [163]. It also contributes towards the solid solution strengthening of austenitic steels. Together with chromium and iron, they form the main constituents for the 300 series stainless steels.

The original intention of manganese addition is to prevent solidification cracking. Manganese forms sulphide as it has high affinity with sulphur than iron [164]. Iron sulphite is detrimental towards the solidification cracking. Moreover, trace element control such as sulphur is rather difficult in the past. Thus, manganese is very important for this aspect.

For SS304, it does not have any molybdenum content. However, in order to improve the pitting corrosion of austenitic steels, 2-3 wt % chromium was replaced by molybdenum in SS316L [160]. As a result, SS316L could be used in a higher temperature regime and harsher environment exposed to corrosion as compared to SS304.

For the remaining elements, silicon is added for deoxidation during melting. It will form silicate upon reaction with oxygen. In fact, for SLM-built SS316L, amorphous silicate is also observed frequently. Sulphur is present in stainless steels as an undesirable impurity. However, it is found out the amount of sulphur has a tremendous influence towards the melt pool shape during laser welding and/or additive manufacturing. It is due to its associated change in surface tension values [165]. Like sulphur, phosphorous tends to form eutectics with iron, chromium and nickel which will deteriorate the alloy's properties. Manganese was added for this reason. Lastly, nitrogen is added for the solid solution strengthening effect. Even a minor addition can bring a drastic change in strength. However, too much nitrogen will cause cracking together with the presence of sulphur.

Therefore, throughout the years of industrial application, the composition of SS316L has been tuned almost to perfection. Its high weldability fits very well with metal AM process. Its solidification sequence will be further explained in the following paragraphs.

Figure 2.40 Phase diagram of commercial stainless steel 316L plotted by using ThermoCalc program [166].

Fig. 2.40 shows the phase diagram of SS316L. Being an austenite steel, SS316L is primarily consisted of face-centered cubic (FCC) γ phase when the nickel content is from 10 to 14 %. The body-centered cubic (BCC) δ or α phase is only present at very high or very low temperatures. From the phase diagram, assuming a nickel content of 13 wt %, the phase transformation will take place in the sequence of $L \rightarrow L+\gamma \rightarrow L+\gamma+\alpha \rightarrow \gamma+\alpha \rightarrow \gamma$. In other words, as the alloy cools down from its liquid state, austenite γ phase is firstly formed. As the temperature continues to drop, ferrite α phase starts to appear till all liquid becomes solid and γ , α phases coexist around 1400 degree Celsius. Lastly, all ferrite α phase will experience solid phase transformation to austenite γ phase. Due to the very low content of carbon, few carbides like $M_{23}C_6$ was observed in SS316L. However, it has been verified that under certain heat treatment conditions, precipitation of sigma σ phase can occur and it typically has a chemical composition of Fe-Cr with the addition of other elements [167, 168].

Other than the above-mentioned features, SS316L has a low stacking fault energy value of $\sim 20 \text{ mJ/m}^2$ which favours the formation of deformation-induced twinning [169]. A stacking fault is the region created when a perfect dislocation dissociates into two Shockley partial dislocations [170-172]. It is illustrated in Fig. 2.41 below.

Figure 2.41 Schematics of the relationship between Shockley partial dislocations and stacking fault in FCC material [173].

It is well known that the energy of a dislocation is proportional to the square of its Burgers vector b . Moreover, according to Frank's rule, for a perfect dislocation to dissociate into two partial dislocations with Burgers vectors of b_1 and b_2 , it has to satisfy the condition of $b^2 > b_1^2 + b_2^2$ [174]. For FCC systems, the perfect dislocation on (111) plane will dissociate into two Shockley partial dislocations according to the formula below [173].

$$\frac{a}{2} [10\bar{1}] = \frac{a}{6} [11\bar{2}] + \frac{a}{6} [2\bar{1}1] \quad \text{Eq. 2.13}$$

As shown in Fig. 2.41, when the perfect dislocation is dissociated into two partial dislocation lines, the region in between is termed as stacking fault. As the dissociated partial dislocations travel, they will come to a balance eventually between the repulsive forces of the partials and the attractive forces due to the stacking fault energy [175]. The stacking fault energy is thus defined as:

$$SFE = \gamma_{SFE} = \frac{Gb_1b_2}{2\pi d} \quad \text{Eq. 2.14}$$

G is the shear modulus, b_1 and b_2 are the Burger vectors of the partial dislocations, and lastly d is the partial dislocation separation distance [173]. It is clear from Eq. 2.14 that a higher stacking fault energy means it is less likely for a material to form a stacking fault as the partial dislocation separation will be quite small. Table 2.4 below lists the stacking fault energies of several common pure metals.

Table 2.4 Stacking fault energies of some common metals [176].

Material	Ag	Si	Ni	Cu	Mg	Al
SFE(mJ/m ²)	20-30	>42	90	70-78	125	160-200

Validated by experimental observations, that deformation twins are formed by glide of Shockley partial dislocations of the same sign on successive 1X1X1X planes [177]. Thus, stacking faults are the pre-requisite for deformation twinning formation. Materials like aluminium with high stacking fault energy are very difficult to encounter deformation twinning during plastic deformation. However, chemical composition is not the sole determining factor for stacking fault energy. For instance, iron irradiation, tensile strain rate and temperature can all influence the SFE values to a certain extent. Fig. 2.42 illustrates the types of deformation microstructures experienced by materials with different stacking fault energy values.

Figure 2.42 Schematic illustration of strain hardening curves for materials with different stacking fault energy values [178].

For materials with high SFE, dislocations can only move via dislocation gliding. It is very difficult for stacking faults and deformation twins to form. Therefore, there is no working hardening contribution from the deformation twins. The strain work hardening rate shows a constant decreasing trend, the blue curve in Fig. 3.42. However, for materials with a low SFE, plastic movement is solely accompanied by dislocation gliding only at the very early stage of deformation. Stacking faults and/or deformation twinning will be activated after a critical strain. Once the stacking faults and deformation twins are activated, the work hardening shows an improvement. Once the stacking faults and deformation twins have been exhausted, the working hardening will decrease again till fracture.

Conventionally for SS316L, majority of the work hardening mechanisms used involve nano-crystalline structures [179-181]. Thus, strength is improved at the expense of ductility. It is later found out that by employing a dynamic plastic deformation process followed by heat treatment, a nano-sized grains embedded with bundles of nanometer-thick deformation twins could be synthesised. Strength and ductility were enhanced concurrently, Fig. 2.43

[180]. As the strain dynamic strain increases, the strength increases with a reduction in ductility Fig. 2.43 (a). With the different heat treatment conditions, various combinations of strength and ductility could be achieved. Moreover, it also proves that twinning could bring huge benefits within the recrystallized fine grains.

Figure 2.43 Stress-strain curves of (a) SS316L samples made by dynamic plastic deformation with different strains. (b) The effect of heat treatment at various temperatures for 20 min [180].

As for SS316L built by metal additive manufacturing, various methods have been attempted such as SLM, EBM and LENS [43, 182-184]. Among all the methods, SLM process achieved the best stress-strain combinations. It also has its unique microstructure as compared to other conventional fabrication means.

It is because for EBM process, it needs to maintain a constant high-temperature powder bed throughout the build process. Therefore, detrimental sigma σ phase was found to occur for EBM-built SS316L. Moreover, due to the high temperature powder bed, it reduces the dislocation density and induces large grain sizes. All these make EBM process unsuitable to fabricate SS316L. The LENS technique usually involves a laser unit with a very high power input, thus, the intrinsic heat treatment generates similar results as the EBM-built SS316L.

Figure 2.44 Typical microstructure of a laser powder-bed-fusion (L-PBF) produced 316L stainless steel (SS) [88].

Fig. 2.44 displays a typical hierarchical microstructure obtained from SLM-built SS316L. From millimeter ranged grains to nanometer sized precipitations, SLM-built SS316L is highly heterogeneous. Compared to the conventional metal and alloys made by casting, SLM-built parts have a gradient transition of crystal orientations within each grain (grain boundary was defined as misorientation $> 10^\circ$), Fig. 2.44 (b). It indicates the presence of high amounts of geometrically necessary dislocations. Due to the high thermal gradient and fast cooling rates, atomic lattices do not have enough time for regular packing. Therefore, this orientation transition gradient occurs. Moreover, because of it, the low and high angle grain boundaries are highly extensive and irregular (Fig. 2.44 (g) & (h)).

Unlike alloys made by casting or molding, due to the unique temperature gradient and cooling rate conditions in SLM, the fabricated part tends to have a cellular microstructure Fig. 2.44(d). Under the scanning TEM, segregations of Mo and Cr were detected near the cellular boundaries. Moreover, it is found

that nano-inclusions were preferentially precipitated along the cellular walls, which will help dislocation pinning and promote deformation twinning formations. It should be noted though, the elemental segregation near the cellular structure's cell walls is highly dependent on the processing conditions. In this work, when two different SLM machines were used to fabricate SS316L, only one of the samples experienced this type of elemental segregation phenomenon. Fig. 2.45 shows the tensile properties of the SLM-built SS316L as compared to its counterparts made by other processing techniques.

Figure 2.45 Tensile properties of L-PBF 316L stainless steels [88].

Fig. 2.45 (a) shows the engineering tensile stress-strain curves of SLM-built SS316L compared to the as-cast and as-wrought samples. Clearly, both SLM-built tensile coupons (fabricated via two different machines) exhibited a higher strength and better ductility. Moreover, the uniform elongation and yield stress combination of the SLM-built SS316L surpasses majority of the samples fabricated via other means, Fig. 2.45 (b). It is believed from the work above, that the hierarchical microstructure provides the key strengthening mechanism towards the property enhancement for SLM-built SS316L. Therefore, SLM process is a very promising technique for manufacturing metal and alloys such as SS316L.

2.7 High-entropy Alloys

Compared to SS316L, high-entropy alloys belong to a new group of concentrated alloys. Since the discovery of metal-matrix composites and intermetallic compounds in the 1970s, the development of new alloys has always been evolved around one single base element. Unlike the traditional alloy design method, HEAs have multiple principal elements in equimolar or near-equimolar ratios [185]. They exhibit high strength and toughness, excellent wear resistance and high-temperature resistance, etc.

HEAs typically consist of at least five principal elements and instead of forming multi-phase microstructures with different intermetallic compounds, typically a simple solid solution (FCC or BCC) is obtained. The widely accepted explanation is that the high entropy of mixing among different elements helps to stabilize the overall microstructure [186]. Though it is proven lately that this factor alone is not enough to explain the phenomenon [187]. Other factors are being considered, e.g. valence electron density, enthalpy of mixing, differences in electronegativity, topological instability, but no one could give an appropriate justification at this point of time [188-190].

The most popular HEA system is CrMnFeCoNi, also known as the Cantor alloy [191]. However, since its discovery in early 2000, not much research progress was made. Recently, it is discovered that HEA has a very high fracture toughness and yield strength combination as shown in Fig. 2.27. The fracture toughness is even higher compared to majority of the commercial alloys such as Inconel, stainless steel, Nickel-based superalloy etc.

Therefore, this new type of alloy is a promising candidate with possibility to reinvent the alloy design strategies. Given its extraordinary properties, the HEA systems deserve more attention and research efforts. It is not only for the conventional manufacturing methods such as casting, but it should also be further explored for the metal AM field.

Figure 2.46 Ashby map showing fracture toughness as a function of yield strength for high-entropy alloys in relation to a wide range of material systems. The excellent damage tolerance (toughness combined with strength) of the CrMnFeCoNi alloy is evident in that the high-entropy alloy exceeds the toughness of most pure metals and most metallic alloys and has a strength comparable to that of structural ceramics and close to that of some bulk-metallic glasses [192].

Among all high-entropy alloy series, CrFeCoNi-based HEA is most widely researched [193, 194]. One example would be CrMnFeCoNi as mentioned above, a single-phase HEA that has an equal atomic ratio among all the elements. It is found to have extraordinary damage tolerance with tensile strengths above 1 GPa and fracture toughness values exceeding 200 MP·m^{1/2}. Furthermore, the mechanical properties are found to improve at cryogenic temperatures. It is proved that as the temperature decreases, deformation activities switched from planar-slip dislocation movement to mechanical nano-twinning [192, 195]. Therefore, this material is shown to be a very plausible candidate for extremely low temperature working environments.

Researchers have since tried to incorporate other strengthening methods to this new type of alloy. It is soon realized that a multi-phase HEA with a non-equal atomic elemental ratio might be able to offer better mechanical properties [196]. One representative example would be the HEA with a

composition of $\text{Fe}_{50}\text{Mn}_{30}\text{Co}_{10}\text{Cr}_{10}$ (atomic %). It was developed with the intention of having additional interphase and phase transformation strengthening effects.

Fig. 2.47 (a) shows that there are two phases (FCC and HCP) present in the alloy and this is achieved by changing the concentration of Mn from 45 to 30%. Chemical homogeneity is achieved both at the grain scale and the atomic level as shown by the ATP (atom probe tomography) mappings Fig. 2.47 (b). The introduction of manganese was inspired by the TRIP (transformation induced plasticity) steels [197-199]. In-situ studies have observed that phase transformation during deformation significantly improve the strength by increasing the dislocation storage capacity for metastable austenitic steels [200]. Therefore, the combination of phase transformation strengthening of FCC to HCP phase during deformation, interphase interface strengthening by FCC and HCP phases, and the solid solution strengthening due to homogeneous chemical composition all contribute to the excellent mechanical properties of the metastable high-entropy dual-phase alloys (TRIP-DP-HEAs) [196]. It offers a new pathway for alloy strengthening that other alloy systems could adapt and learn.

Figure 2.47 Elemental homogeneity among the two phases of $\text{Fe}_{50}\text{Mn}_{30}\text{Co}_{10}\text{Cr}_{10}$ (at%) HEA. (a) Energy-dispersive spectroscopy maps of the shown EBSD-mapped sample region. (b) Three-dimensional APT tip reconstructions of Fe, Mn, Co, Cr atom positions in a typical APT tip from the EBSD-mapped phase boundary. The crosses refer to the positions that the APT tips were taken from [196].

Fig. 2.48 shows the comparisons between TRIP-DP-HEAs with other single-phase HEAs. The TRIP-DP-HEAs have a better strength and a higher elongation compared to the typical single-phase HEA CrMnFeCoNi. Their properties are comparable when the grain size of TRIP-DP-HEA is ~7 times bigger compared to the single-phase HEA. The work hardening regime for the TRIP-DP-HEA is consistently higher compared to that of CrMnFeCoNi with similar grain sizes. This provides extra strength and elongation. It shows the great potential that TRIP-DP-HEAs have for the industrial applications. At the same time, it is believed there is still huge potential for material development of HEA.

Figure 2.48 Mechanical behavior of the TRIP-DP-HEAs compared to various single phase HEAs [196].

Besides the above two examples, refractory HEA and eutectic HEA developments have also attracted great research interests in the recent years [201-204]. Refractory HEAs were developed mainly with the aim of extending its high temperature applications. On the other hand, eutectic alloys such as AlCoCrFeNi_{2.1} has shown great promise for mechanical stress-strain performance as well [205]. Fig. 2.49 shows an example of eutectic HEA prepared by arc melting followed by cold rolling and heat treatment. It consists of two homogeneously distributed FCC and BCC/B2 phases respectively, Fig.

2.49 (a). Each phase was constructed via different elements. The FCC phase is primarily enriched in Fe, Co and Cr, whereas the BCC/B2 phase is made up by Al and Ni instead, Fig. 2.49 (e). Moreover, the distribution of BCC/B2 are either intergranular or intragranular within the FCC parent grain, Fig. 2.49 (f). Compared to the previously mentioned HEA sample, this dual-phase eutectic HEA possess a much higher yield and ultimate tensile strength, from ~ 1.2 GPa to 1.6 GPa. Elongation to failure is around ~ 20 %. Moreover, it is proven to perform well in a wide range of temperatures [203]. Despite the difference in terms of chemical composition and the design principle, the heterogenous microstructural distribution shows a great resemblance to the SLM-built SS316L shown previously in Fig. 2.44. Therefore, heterogeneity is proven to be one of the key strengthening means towards property enhancement.

Figure 2.49 Representative images of dual-phase eutectic high-entropy alloy AlCoCrFeNi_{2.1}. (a) to (d), EBSD, SEM and TEM images of the dual phase BCC, FCC morphology. (e) STEM mapping of the lamella structure showing preferential elemental segregation towards different phases. (f) Zoomed in TEM image of

intergranular (P2) and intragranular (P1) B2 phases. (g) Presence of annealing twins. (h) A schematic of the previously described microstructure. Scale bars, 20 μm in (a), (b), 2 μm in (c), 1 μm in (d) to (f) and 500 nm in (g) [205].

Several attempts have been made to fabricate HEA via metal AM, especially on the CrFeCoNi-based HEA systems. The primary purpose of these works so far is to investigate the feasibility of manufacturing HEAs via metal AM. Fig. 2.50 shows one of the first attempts to fabricate pre-alloyed CrFeCoNi powders via SLM [206]. The XRD profiles show a single FCC phase for both the fabricated and the annealed CoCrFeNi samples with two different layer thickness. Homogeneous elemental distribution is detected for all elements by EDS. However, built defects were observed within the SLM-built CoCrFeNi, especially when a higher layer thickness was employed.

Figure 2.50 (a) XRD patterns of SLM manufactured FeCoCrNi alloy for as fabricated and annealed samples with both 20 and 50 μm layer thickness. (b) SEM and EDS maps for 20 μm sample [206].

The Cantor alloy with the composition of CoCrFeNiMn was also attempted via SLM [207]. However, due to the high vapor pressure of Mn, about ~0.5 at. % of Mn was lost during the fabrication process. Like SLM-built SS316L, a heterogeneous microstructure was observed in the SLM-built CoCrFeNiMn

sample. Depending on the scanning parameters adopted, the tensile properties of the built part were quite different as shown in Fig. 2.51. The V2000 sample here was built to have a relative density of ~99.2% whereas the V2500 sample only has a relative density of 97.1%. Thus, the mechanical property worsens due to the presence of cracks and/or pores. Moreover, the ultimate tensile strength and elongation both improved for samples after heat treatment for 1h at 900 degrees Celsius. However, there is indeed a decrease for the yield strength values due to the disappearance of dislocations after heat treatment. Unlike the previous examples, the SLM-built CoCrFeNi did not exhibit a much improved property as compared to the casted counterpart.

Figure 2.51 Engineering stress-strain curves of SLM-built CoCrFeNiMn, the heat treated samples and the as-cast, as-recrystallized samples [207].

Selective electron beam melting (SEBM) technique was also employed to manufacture CoCrFeNi-based HEAs [208-210]. Due to the unique feature of SEBM, it has obtained different microstructures for AlCoCrFeNi as compared to the cast samples. For casting, the AlCoCrFeNi typically has a single BCC phase [211-214]. Fig. 2.52 displays the difference brought by SEBM compared to the as-cast samples.

Figure 2.52 (a) – (f) SEM-BSE images of the (a) cast and the SEBM (b) top and (c) bottom sections. The magnified images of Fig. 2.9(a) to (c) are shown in Fig. 2.9(d) to (f). (g) IPF maps and phase maps of the cast and the SEBM specimens obtained at the cross-section perpendicular to the build direction at the top and bottom sections [209].

In terms of microstructural size, SEBM bottom has the largest microstructure followed by the cast sample and lastly the SEBM top, Fig. 2.53 (a) to (f). It is attributed to the in-situ heat treatment effect of SEBM. During the fabrication process, the SEBM machine maintains a constant high-temperature build environment (~950 degree Celsius). Thus, for the SEBM bottom part, it is subjected to high temperatures throughout the entire build, like an in-situ heat treatment which promotes microstructural coarsening. On the contrary, for the SEBM top, once it is solidified there is no more heating nor heat treatment from the layers on top. Therefore, it preserves its refined microstructures.

Moreover, due to the in-situ heat treatment effect, SEBM built part no longer has only a single BCC/B2 phase. Rather, FCC segregated along the BCC/B2 grain boundaries was observed, Fig. 2.32 (g). It is more obvious for the SEBM bottom due to the prolonged heat treatment period. It is believed that the introduction of more ductile FCC phase helps to improve the work hardening and the elongation. Though the yield strength of the sample is reduced. This work proves that metal AM has the possibility of tuning the properties of HEA via its unique processing thermal history.

Compared to SLM and SEBM, laser engineered net shaping (LENS) was more frequently employed for material's development due to its ease of material change and less material is required for small sample fabrication [215]. For instance, blending of elemental powders was used to study $\text{Al}_x\text{CoCrFeNi}$ alloys phase transition and mechanical properties [216]. Fig. 2.54 (a) and (b) show the XRD results of phase transition from FCC to BCC as the amount of Al increases from 0.3 to 0.85. It is the same for both laser-deposited and arc melted samples.

Due to the difference in terms of chemical composition and phase constitution, the mechanical properties of these fabricated samples are also drastically different as shown in Fig. 2.54 (c) and (d). For both laser-deposited and arc melted samples, the tensile properties are very close for the same chemical composition. The $\text{Al}_{0.3}\text{CoCrFeNi}$ HEA has the lowest yield strength and ultimate tensile strength. It is due to the lack of strengthening phases. However, due to the ductile FCC phase, it has the best elongation results. As the aluminum concentration increases from 0.3 to 0.6 and lastly 0.85, more BCC/B2 phases were formed. It creates extra strengthening for the material, therefore, the strength of the material continues to raise as a result. The BCC phase also causes a reduction in elongation as there is insufficient slip systems for BCC compared to the FCC phase.

Figure 2.53 XRD profile of $\text{Al}_x\text{CoCrFeNi}$ alloy system by (a) direct laser sintering and (b) arc melting. True stress-strain curve of (c) direct laser sintered and (d) arc-melted $\text{Al}_x\text{CoCrFeNi}$ high entropy alloy system for Al concentration of $x = 0.3, 0.6, 0.85$ [216].

On top of the existing data on metal AM built HEAs, very few of them discussed the presence of cracking and its effect towards the mechanical properties of the final built part. However, in one particular study, it is observed that there is presence of crack along the grain boundary for a LENS-built $\text{Al}_{0.3}\text{CoCrFeNi}$ sample, Fig. 2.54. Though the detailed formation mechanisms of such cracks are not examined.

Cracking has little influence on the compression properties of the as-built sample, but it has great effects on the tensile properties, Fig. 2.54 (a). Both the compression and tensile curves have similar yield strength. However, the compression test has a much higher ultimate strength and elongation values. It is because that during tension, cracking reduces the material's load bearing abilities. It directly deteriorates its tensile performance. Therefore, tensile testing is a more holistic property measurement technique.

Figure 2.54 LENS built $\text{Al}_{0.3}\text{CoCrFeNi}$. (a) True stress-strain curves under tensile and compressive loading. (b) Sample after compression to a true strain of 1.0 and (c) SEM microstructure of the grain boundary crack in the deformed specimen [217].

In summary, early research works have shown that HEA is a very promising candidate for structural engineering applications. Especially for the CrFeCoNi-based HEA series. Current researches have been primarily focused on casting and/or rolling applications. The attempts on the metal AM techniques have been limited. Moreover, there is insufficient reports on the cracking phenomenon on the AM-built HEAs. Thus, there is still a lot of room for further development.

2.8 Research Gaps and Scope

From the previous literature reviews, SS316L is a proven material used by metal AM. However, limited microstructural control (crystallographic texture and grain size) was achieved together and justified properly. For CoCrFeNi-based HEA, researchers use hot isostatic pressing (HIP) to improve its densification [218]. Suggesting it might be susceptible to cracking.

Therefore, the scope of the present PhD study involves the microstructural control for SLM-built SS316L. Including both crystallographic texture and the grain size. With the help of a desirable microstructure, to achieve a strength-ductility improvement for the SLM-built SS316L. For the second part of this PhD, the hot cracking issue of HEA CoCrFeNi will be examined. Possible measures to minimize cracking will be attempted to yield good mechanical property for SLM-built HEA.

2.9 Research Roadmap and Approach

The overall research roadmap is shown in Fig. 2.55. For the first semester in year 2015, the main goal was to get familiarized with the SLM machine and understanding the basic work flow for the SLM process. After one semester's training, having the ability of fabricating parts with desired parameter inputs using precursor powders.

Year 2016 involves the intensive testing of various scanning parameters, including laser power, scanning speed, hatch spacing and the scanning strategy, etc. The material being investigated is SS316L due to its good weldability and rich literature data. By investigating the effect of various laser parameters, suitable scanning parameter and scanning strategy were selected for microstructural control. In this process, electron backscatter diffraction (EBSD) was extensively employed to reveal the grain information within the built parts.

For year 2017, mechanical testing was used to examine the effect of different microstructures towards the tensile properties. In order to justify the observed property discrepancy, transmission electron microscopy was applied for detailed microstructural observation and quantification such as dislocations and deformation twins.

For the second part of the PhD, hot cracking problem was observed in SLM-built HEA CoCrFeNi in year 2018. By using a vast range of processing

parameters, it is proven that hot cracking is a material's intrinsic property that cannot be cured solely by processing parameters. To precisely examine the chemical homogeneity surrounding the crack, atom probe topography was employed.

Lastly, chemical modification was attempted to minimize hot cracking and improve the mechanical property concurrently in year 2019. Localised testing method such as nano-indentation provided key insights to the effects of compositional modifications.

Research Roadmap

Figure 2.55 Research roadmap for the present PhD study.

Chapter 3 Materials and Methods

3.1 Powder Feedstock

The precursor gas-atomized powder of SS316L and HEA CoCrFeNi are shown in Fig. 3.1. The powder size ranges from ~20 to 63 μm . All powders are generally spherical in shape. However, the SS316L has more small satellites surrounding the big powders. Possible reason is due to the repeated recycling of the SS316L powders. Both powders are non-magnetic, so powder spreading will not be affected.

Figure 3.1 SEM images of (a) SS316L and (b) HEA CoCrFeNi powders.

For the preparation of $\text{Al}_x\text{CoCrFeNi}$ powder feedstock, tumbler mixer was used for the powder mixing. Pure aluminum powder was proportionally added into the pre-alloyed CoCrFeNi powder followed by 12 hours of rotational mixing. The overall powder content was limited to 1/3 of the mixing bottle's volume to create enough room for powder flow. Fig. 3.2 (a) shows a representative image of the blended $\text{Al}_x\text{CoCrFeNi}$ powders. The aluminum content was detected by the EDS mapping shown in Fig. 3.2 (b).

Clearly, the aluminum powders are well dispersed within the CoCrFeNi powders. Moreover, due to the different processing techniques, the aluminum

powders are not as spherical as the CoCrFeNi powders. They tend to be elliptical in shape.

Figure 3.2 (a) SEM image of blended pure aluminum powder and pre-alloyed CoCrFeNi powder. (b) EDS mapping of aluminum.

3.2 Selective Laser Melting Process

The selective laser melting machine used for the current experiment is the SLM Solutions 250 HL, Germany, Fig. 3.3. It employs two laser units. The first laser has a maximum power input up to 400 W with a Gaussian distribution. Its beam diameter is $\sim 80\ \mu\text{m}$. The second laser has a maximum power input up to 1000 W with a top-hat distribution. Its beam diameter is $\sim 200\ \mu\text{m}$. Two dimensions of substrates can be used for production, namely $100 \times 100\ \text{mm}^2$ reduced substrate and $250 \times 250\ \text{mm}^2$ big substrate. They can both be pre-heated up to $200\ ^\circ\text{C}$. Typical substrates used in this study are made of tool steel.

To keep an inert environment during the fabrication, argon gas was employed to fill up the entire chamber. Typically, the inside pressure is slightly higher compared to atmospheric pressure to reduce the powder splattering effect. A constant laminar gas flow is maintained above the powder bed to remove any over-heated undesirable waste. It is crucial towards the overall part quality.

The laser profile and the protective reflection lens should be frequently maintained for production consistency.

Figure 3.3 SLM Solutions 250 HL machine.

3.2.1 SLM File Generation

Due to the complexity of the SLM machine, there are many parameters which could be adjusted for production. Some examples would be the oxygen concentration, chamber gas flow rate, substrate temperature, laser focus, support structure, etc. However, for the scope of the current PhD study, only the laser power, scanning speed, hatch spacing, and the scanning strategy were heavily investigated. A wide range of laser power was used from 100 W to 950 W. The recommended maximum laser scanning speed by the machine manufacturer is ~ 10 m/s. However, the current study only employed a maximum laser scanning speed of 3 m/s for reliability and safety concerns. The hatch spacing is mainly influenced by the melt pool size which is in turn

determined by the laser power and scanning speed. The layer thickness is mainly controlled by the powder size. Generally, there is a ~40 % volume shrinkage after each layer's laser scan due to the material's consolidation and gas evaporation. Therefore, for the powder size range of ~20 to 63 μm , a 50 μm layer thickness was used for all experiments.

There are two types of scanning strategies which are available, namely the stripe and chessboard scanning strategies, Fig. 3.4. The definition of hatch spacing is the same for both strategies which is the distance between two adjacent scanning lines. However, for chessboard scanning strategy, it is defined by the number of cubes/boxes. Each cube is heated randomly to minimize heat accumulation and residual stress. For the stripe scanning strategy, it is governed by the stripe length which is the length of each scanning line. Each adjacent layer is rotated by an angle of 67° . 67 is an odd number and by using this number, the likelihood of two layers having the same scanning pattern is very small. It is beneficial towards the residual stress minimization.

Figure 3.4 Chessboard and Stripe scanning strategies for SLM fabrication.

A representative layer with a stripe scanning strategy under Slice Viewer is shown in Fig. 3.5. The stripe pattern is clearly observed in the overall image Fig. 3.5 (a). The zoomed in image in Fig. 3.5 (b) demonstrates the various scanning lines. Conventionally, boundary of each layer is consisted of 1 or 2 border scanning lines. The border lines determine the roughness of the built part. They usually have a lower laser power and slow scanning speed. For SS316L, the border lines used have a laser power of ~100 W and a scanning speed of ~440 mm/s. The hatching lines are the actual scanning lines. They will decide the density/internal quality of the built part. Occasionally, to ensure a good bonding between the border and hatching, at the end of each part's scan, there will be a fill contour line. The fill contour line is placed in between the border and the hatching lines.

Figure 3.5 Representative layer with a stripe scanning strategy.

After finalizing the scanning parameter and scanning strategy, they will be imported into the part fabrication shown in Fig. 3.6. The yellow platform is the reduced substrate. Red cylinders are the locations for screws. The fabricated part is normally placed with an angle with respect to the recoater/swiper. During the fabrication, part might experience side effects such as swelling or

deformation. By inserting an angle of rotation between the parts and the recoater, it reduces undesirable frictional forces which might damage the recoater.

Moreover, the separation among each part is also important towards surface finishing. During the SLM fabrication, each part is constantly heated by the cyclic heating. If two parts are too close to each other, it is detrimental for heat dissipation and the surface smoothness. Thus, by carefully designing the scanning parameter, scanning strategy and the part orientation, the SLM file will then be generated and sent for actual production.

Figure 3.6 Part orientation illustration.

3.2.2 Electron Discharge Machine (EDM)

After the completion of the built job, the fabricated samples are removed from the substrate via the electron discharge machine (EDM), Fig. 3.7. A series of fast recurring current discharges between two electrodes will occur within the metal wire in EDM. When the voltage between the two electrodes increases,

current generated will break down the surrounding metal workpiece which will then be carried away by the dielectric fluid.

Figure 3.7 Electron discharge machine (EDM).

3.2.3 Surface Grinding

The substrate is uneven after the EDM process. To recycle the substrate for next round of fabrication, surface grinding is needed Fig. 3.8. The substrate after EDM is fixed onto the surface grinder's platform via magnetic force. A lubrication fluid is applied between the rotating wheel and the substrate to minimize sputtering, heating and contamination. The hard, rotating wheel is lowered by about 50 μm each time until the surface is smooth again.

Figure 3.8 Surface grinding process.

3.2.4 Sand Blasting

The last step for substrate preparation is sand blasting. The sand blasting process roughens the substrate's surface for better part cohesion during the SLM process. Throughout the sand blasting process, fine sand particles carried by pressurized gas will hit the substrate continuously. The comparison images of the substrate before and after this process are illustrated in Fig. 3.9. Together with the recycled powder after sieving, a new SLM production can then take place.

Figure 3.9 Substrate (a) before and (b) after sand blasting process.

3.3 Microstructural Observation

Microstructural observation is critical to reveal and justify the mechanical properties. Depending on the purpose and microstructural scale, different techniques should be used accordingly. However, before the actual microstructural observation, relevant sample preparation procedures should be taken. For the current PhD work, all samples were firstly ground with SiC-paper of grit #320 and followed by MD-Largo (DiaPro Largo 9 μm suspension). They were then polished with MD-Dac (DiaPro Dac 3 μm suspension) and MD-Nap (DiaPro Nap 1 μm suspension). A mirror-like surface will be obtained after these processes for porosity examinations.

To reveal the microstructures, Ralph's solution (100 mL H_2O , 200 methyl alcohol, 100 mL HCL, 2 g CuCl_2 , 7 g FeCl_2 and 5 mL HNO_3) was adopted to etch the polished samples. An extra step of oxide polishing suspension (OPS) polishing was made before EBSD studies. For the TEM sample preparation, there are mainly two methods. The first method is to manually grind the sample to a thickness of $\sim 50 \mu\text{m}$. It is then forged into a circular shape with a diameter of 3 mm with a hole puncher. Dimple grinder is used with lubricant to create a concave shape. Lastly, ion milling is applied sequentially from 8° , 6° , and finally 2° till a hole appears in the thin region. The second method is to use FIB for site specific lift outs.

3.3.1 Light Optical Microscopy (LOM)

Optical microscope is usually the first step for microstructural examination. The OM equipment used in the current study is the Zeiss Axioskop 2 MAT. It is mainly used for density measurement and brief microstructural observation. For the density measurement, ImageJ software is used [219]. The work process flow is summarized in Fig. 3.10. The default image is shown in Fig. 3.10 (a). It is firstly converted to 8-bit image in Fig. 3.10 (b). A threshold is then applied to convert the image to black and white, Fig. 3.10 (c). The

ImageJ software offers many measurement options such as area fraction, standard deviation, perimeter etc. In this example, the density value was calculated to 94.7 %.

Figure 3.10 (a) Original image, (b) image after 8-bit processing and (c) image after further thresholding.

3.3.2 Scanning Electron Microscopy (SEM)

Compared to the optical microscope, SEM offers a greater resolution and many more functionalities. The equipment used for the current PhD work is a field emission scanning electron microscope (FESEM) JEOL 7600F, Fig. 3.11. For normal metallic object's microstructural observations, it typically has an accelerating voltage of ~15 kV, a probe current of ~8 and a working distance of ~15 mm. However, for magnifications above x10,000, it is recommended to use a low accelerating voltage of ~10 kV and a much smaller working distance of ~4.5 mm. Besides the advantage of observing smaller features in the micro to nano meter range, the backscatter images are also helpful for grain orientation differentiation and defects detections [52]. The FESEM is also equipped with an EDX detector. Therefore, elemental mapping could be conducted together with the microstructural observation.

Figure 3.11 FESEM JEOL 7600F.

3.3.3 X-Ray diffraction (XRD)

The XRD technique is mainly used for phase identification and brief crystallographic texture analysis. The equipment used is PANalytical Empyrean. Under normal working conditions, it is operated with a condition of 40 kV and 40 mA. For materials studied in this PhD work, the XRD scan typically ranges from 30° to 100° . The step size used is 0.01° and each test takes ~1.5 to 4 hours depending on the need of data quality.

As for the crystallographic texture analysis, the x-ray is switched from a continuous scan to point scan. Firstly, a 2θ scan is carried out to identify the various peaks. Then by setting the detector to the proper Bragg angle, 2θ , of the diffraction peak of interest, the stage is continuously inclined with from 0° to a specific angle χ . For each inclination, the stage is rotated 360° constantly around ϕ . The stage illustration is shown in Fig. 3.12. By collecting all diffraction intensities, the crystallographic texture for each peak will then be calculated.

Figure 3.12 Schematics of crystallographic texture measurement via XRD.

3.3.4 Micro CT Scan

SLM-built metal parts have many internal defects such as porosity and crack. It is proven that these defects have a tremendous influence towards the overall mechanical properties [71, 220]. However, normal characterization technique such as OM and SEM are not able to detect the 3D morphology of these defects. In contrast, micro CT Scan offers a method of revealing defects in 3D. The μ -CT machine used is the Skyscan 1173, Bruker, Belgium. A high voltage of 130 kV is used to achieve a resolution of $\sim 6.4 \mu\text{m}$. All μ -CT scan samples have a dimension of $3 \times 3 \times 8 \text{ mm}^3$.

The analysed sample is fixed onto a brass stage, Fig. 3.13. As the focused x-ray source is emitted onto the sample, the projection image will be collected by the behind detector. The CTVOX and CTVOL software will be used to assemble all 2D images and form the 3D structure. Due to the different response towards the emitting x-ray between the solid and defects, empty spaces such as crack and porosities can then be revealed.

Figure 3.13 Detailed view of experimental set up for μ -CT scan.

3.3.5 Electron Backscatter Diffraction (EBSD)

The electron backscatter diffraction (EBSD) is an important technique for AM built samples. It can be used to examine the grain orientation, misorientation and the preferred crystallographic orientations. Aztec software is used on the JEOL 7600F machine for EBSD studies. The sample stage is tilted to a 70° inclination with respect to the electron beam, Fig. 3.14 [221]. As the electron beam reaches the sample surface, some electrons will enter the sample, and some will backscatter. The escaping electrons may leave according to the Bragg angle and diffract to form Kikuchi bands. Each Kikuchi pattern correlates to a specific phase's unique orientation.

Figure 3.14 Illustration of Kikuchi pattern formation [221].

As for the indexing of the electron backscatter pattern (EBSP), conventionally it is done via the Hough transformation. The computer will detect each diffraction band and calculate the angle between different bands. By comparing the experimentally measured angular values and the theoretic values, the orientation will be determined. Recently, a new method of orientation identification is created by comparing the experimental EBSP and the simulated EBSP [222, 223]. It can reveal minor deformation such as those caused by residual stress. However, it is challenging to simulate EBSP, especially for alloys.

Besides orientation identification, EBSD can also use the statistical data to derive the preferred crystallographic orientations. It is often represented by the pole figures. Data construction on the pole figure is explained in Fig. 3.15. Assuming the crystal is placed in concentric with the unit sphere. For any crystal plane, the normal of the plane is projected to intersect the unit sphere. This point P is referred to as the pole. Therefore, there is a unique pole for any orientation. To reflect all orientation on a 2-dimensional image, the top hemisphere is projected with respect to point Q . Thus, all orientations within a sample can then be illustrated in the pole figure.

Figure 3.15 Indication of a crystallographic orientation representation on a pole figure [221].

Besides the functionalities offered by the Aztec software, MTEX software is used as well especially for grain-specific data representation [224]. It can also be used for texture analysis for the XRD data as well.

3.3.6 Transmission Electron Microscopy (TEM)

TEM technique is employed in the current PhD work mainly for dislocation and twinning observations. Compared to other characterization techniques, TEM provides nano-scale resolution of microstructural observation. Therefore, features like dislocations and twinning can be clearly revealed. TEM experiment requires a very thin sample in nanometer range such that high energy electron beam can penetrate through the sample. The phase identification is confirmed via the diffraction patterns.

The TEM samples in the present study were prepared mainly in two methods. Firstly, for general TEM samples, the samples were firstly ground down to $\sim 100\text{ }\mu\text{m}$ manually. It is then cut into a 3 mm disc using a hole puncher. Manual grinding will then thin down the sample to $\sim 50\text{ }\mu\text{m}$. A dimple grinder combined with a 3 μm paste is employed to create a dimple within the disc. Lastly, ion milling will be adopted slowly with a contact angle of 8° , 4° and 2° till a hole appears on the sample. For site-specific TEM sample of $\text{Al}_{0.5}\text{CoCrFeNi}$, FIB lift-out technique is used. A thin layer of platinum is deposited on the site-specific region before cutting surrounding the areas and finally retrieve the TEM lamella.

For the diffraction pattern analysis, CrystBox software is used [225]. It can automatically index the diffraction patterns. An illustration of the process flow of an FCC HEA TEM diffraction pattern is shown in Fig. 3.16. Firstly, the crystal's structure and lattice constants need to be inserted. Then the resolution/scale of the TEM image can either be read from the picture's scale bar or manually keyed in. The original diffraction pattern is shown in Fig. 3.16 (a). It subsequently goes beam detection, selection of diffraction spot

candidates, lattice fitting, vector selection and finally zone axis calculation. For this example, it is determined to be a (1 -2 1) zone axis.

Figure 3.16 TEM diffraction pattern indexing via CryTBox software.

3.3.7 Atom Probe Tomography (APT)

Compared to the previously mentioned characterization techniques, Atom Probe Tomography (APT) offers an atomic scale resolution for chemical analysis. Ions are destructively removed from the sample surface for imaging and quantification. By combining with time of flight mass spectrometry, their mass-to-charge ratio could be computed [226]. Three-dimensional information could be obtained via successive evaporation of the material. The process is schematically illustrated in Fig. 3.17.

Typically, needle-like field ion specimen is mounted on a cryogenically cooled goniometer. Field evaporation pulse will remove ions consecutively which will then be captured on the position-sensitive atom detector. The distance between the sample and the detector usually varies between 250 to 650 mm

[227]. APT is particularly useful for localised segregations surrounding dislocations and/or grain boundaries [228, 229]. In the present study, it is mainly used for segregation quantification and identification.

Figure 3.17 Schematic diagram of a three-dimensional atom probe. The active area of the single atom detector defines the area of analysis [227].

3.3.7 Cross-correlation EBSD (CC-EBSD)

Cross-correlation EBSD (CC-EBSD) is an analysis technique which aims to detect small strains and rotations through comparison of high-quality EBSD diffraction patterns. Conventionally, grain orientations are identified via Hough transformation and angle comparisons. It offers an angular resolution of 1° to 0.5° depending on the diffraction conditions. However, it is found that by comparing high-quality diffraction patterns (which has pixel sizes of $\sim 1300 \times 1300$), an unprecedented resolution of 10^{-4} for strains and 0.01° for rotations could be obtained.

During the data collection stage, all diffraction patterns were stored accordingly. For the subsequent analysis procedure, Cross Court 4 software was used for pattern cross-correlation. In total, 20 regions of interest (ROI) were selected for each pattern, Fig. 3.18. Only patterns with a confidence

index above 0.1 were included for study. For each grain, a reference pattern is chosen based on the highest confidence index value.

Figure 3.18 Representative regions of interest (ROI) selections.

Since Cross Court 4, an extra step of “remapping” was employed for strain calculations with huge rotational values. Firstly, the distortion matrix is computed from the displacements measured through cross correlation of patterns via Fast Fourier transformations. Then the normal and shear strains are obtained as the symmetrical components of the distortion matrix. Infinitesimal strain theory is employed for computing the rotational components. However, it is later found such computation procedures fail in the event of large rotational values. Therefore, the “remapping” procedure firstly “rotate” all crystal rotations to its original orientations. A set of new normal and shear strain values will then be computed. Lastly, finite strain theory is implemented to calculate the rotation values.

3.4 Mechanical Testing

Mechanical testing is an important step to determine the material's properties. The current PhD study predominantly employs indentation and tensile testing techniques. Indentation is a relatively easy and effective way of accessing the material's properties. Depending on the microstructural feature size, Vickers microhardness and nano indentation can be selected accordingly. In contrast, tensile testing is a more rigorous method of testing. Both the microstructure and defects can influence the testing results. Compared to the compression testing, it is found that cracks and porosities have a more profound effect for the tensile testing results [217].

3.4.1 Vickers Microhardness Indentation

Vickers microhardness indentation is typically used to acquire the microhardness values. The equipment used here is the Future Tech FM-300e microhardness tester, Fig. 3.19 (a). All measurements in the current PhD work uses a load of 1 kg and holding time of 15 s. Calibration of the machine is done before each experiment with a reference sample of 700 HV. At least 10 microhardness measurements were taken for each sample. A representative microhardness indent is shown in Fig. 3.19 (b).

Figure 3.19 (a) Future Tech FM-300e microhardness tester. (b) Representative microhardness indent.

The sample surface is polished to mirror-like surface for all microhardness testing. Due to the diamond shape of the indenter tip, the resultant indent should also have a similar morphology. Occasionally, due to the presence of defects, the indent with a weird shape must be discarded.

3.4.2 Nano Indentation

Compared to Vickers microhardness indentation, nano indentation offers a more precise, location-dependent hardness values in nano-meter range. An Agilent G200 nano-indenter was used in the current work. The testing method was chosen to be the continuous stiffness method (CSM). Compared to the conventional methods of nano indentation which only considers the force vs. displacement curve, the stiffness of contact can only be obtained from the unloading curve. However, for CSM, as the tip goes into the surface, there is a simultaneous oscillating force with a magnitude much smaller compared to the nominal load. By doing this, it provides an accurate measurement of the location of initial surface contact and continuous measurement of contact stiffness as a function of depth or frequency. Thus, eliminating the need of a unloading curve [230].

For the current PhD work, nano indentation is primarily used for the SLM-built HEA samples. Due to the presence of hot cracks, conventional microhardness indentation might interfere with the cracks. Thus, nano indentation is a preferred method of material property measurement. A representative indentation arrangement is displayed in Fig. 3.20 (a). A 7×7 matrix of indentations was placed in the area free of cracks. The relationship of nano indent with the grain orientation information can be revealed by the EBSD technique shown in Fig. 3.20 (b) and (c). Therefore, the orientation dependent property can also be studied via the nano indentation method. The scale bar in the present example is 100 μm .

Figure 3.20 (a) Nano indentation pattern arrangement, (b) nano indentations with respect to misorientation and (c) nano indentations with EBSD graph.

3.4.3 Tensile Testing

Compared to the indentation techniques, tensile testing offers a more holistic examination of the material's properties. An Instron Static tester (series 5569) was used for this work. Two different types of load cells were available for use, 50 kN and 5 kN. The ultimate tensile strength $\times$ the cross-sectional area should be above $\sim 10\%$ of the load cell for the results to be accurate.

The tensile coupons were machined from SLM-built blocks to eliminate the side effects from the scanning borders. The tensile testing set up and the specimen dimensions are shown in Fig. 3.21. Contact-based extensometer was used for accurate assessment of tensile strains. The tensile coupon has a gauge length of 10 mm, the gauge width is 3 mm and the thickness is 2 mm. All tensile testing was done with a strain rate of $\sim 1 \times 10^{-3} \text{ s}^{-1}$. At least 3 sets of specimens were tested for each experiment.

All tensile testing specimen was polished till #1000 grit sandpapers to reduce the detrimental effects from the rough side surface. For post-mortem microstructural observations, segments were taken $\sim 3 \text{ mm}$ away from the fracture surface for meaningful data evaluation.

Figure 3.21 (a) Tensile testing set up and (b) the tensile specimen dimensions.

Chapter 4 Applicability of the energy density formula for SLM-built SS316L

4.1 Introduction

Stainless steel 316L (SS316L) is an austenitic stainless steel with wide applications in marine, biomedical and structural industries [21]. It is one of the pioneer materials being employed in additive manufacturing [28]. Before the start this PhD work, majority of the SS316L samples built by SLM were using a laser power input lower than 200 W [231]. Table 4.1 shows a list of laser input values to manufacture SS316L by the year of 2015. The general conception back then was a lower laser power input tends to create a more uniform scan track. Moreover, due to the machine limitations, not all the SLM machines were equipped with a laser unit which can generate more than 200 W of power input. Therefore, it remains unclear if a higher laser power can yield a dense part at that point of time.

Table 4.1 Laser scanning parameters used to fabricate SS316L before year 2015 [232].

Power range (W)	Speed range (mm/s)	Beam size (mm)	Layer thickness (mm)	Scan spacing (mm)	Highest relative density	Reference
85–105	300	$\Phi(99\%) = 200$	20–60	112–125	98.8–99.2	[23]
104	300–800	200	30	130	99.3–99.5	[18]
100	300	$\Phi(99\%) = 180$	30	81–126	98.4–98.9 %	[24]
50	120	70	40	120	99+ %	[20]
105	380	$\Phi(99\%) = 200$	20–40	125	99.25–99.8	[9]
100	175–380	$\Phi(99\%) = 180$	60	126	95.8–98.8	[10]
105	380	$\Phi(99\%) = 200$	N/A	125	99.2	[9, 25]
100	300	$\Phi(99\%) = 180$	30	112–125	98.8–99.2	[22]
50	100–300	26–48	50	80	96.72–99.93	[12]
87	150	180	75	130	82	[2]
175	80–200	N/A	100	40–60	80.4–98.5	[11]

Moreover, though majority of the SLM machines employ a continuous laser, there are still machines which use a pulsed laser instead. Thus, the applicability of the energy density values $E = \frac{q}{v \times h \times t}$ (Eq. 2.1) between

different types of lasers is still unclear. For instance, it was found through experimentation that the optimal energy density value for a fully dense SS316L part made by a pulsed laser is $\sim 104 \text{ J/mm}^3$ [233]. However, it is unsure if this is the optimal value for continuous laser.

Lastly, the energy density is influenced by four determining factors. There are different combinations which can yield the same energy density value. Thus, it is worth investigating the microstructural consistency by changing other parameters while keeping the energy density constant.

In order to testify the above three questions, a set of laser scanning parameters were formulated accordingly as shown in Table 4.2. Firstly, a much higher laser power input of 380 W was applied. While keeping the layer thickness constant, laser scanning speed and the hatch spacing (distance between two adjacent laser scanning lines) were altered. The parameters were adjusted with the aim of maintaining a constant energy density input of $\sim 104 \text{ J/mm}^3$ as suggested by the pulsed laser machine [233]. A layer thickness of $50 \text{ }\mu\text{m}$ was chosen to suit the powder size of ~ 20 to $63 \text{ }\mu\text{m}$.

Table 4.2 SLM parameter for the fabrication of SS316L samples [43].

	Laser power [W]	Layer thickness [μm]	Scanning speed [mm/s]	Hatch spacing [μm]	Energy Density [J/mm^3]
S01	380	50	3000	25	101.33
S02	380	50	2500	30	101.33
S03	380	50	2000	35	108.57
S04	380	50	1750	40	108.57
S05	380	50	1500	50	101.33
S06	380	50	1250	60	101.33
S07	380	50	1050	70	103.40
S08	380	50	950	80	100.00
S09	380	50	850	90	99.35
S10	380	50	750	100	101.33
S11	380	50	700	110	98.70
S12	380	50	625	120	101.33

4.2 Results

4.2.1 Density Measurements

There were 24 samples built in total. Each parameter was built twice for comparison and validation purposes. Fig. 4.1 shows the as-built samples on substrate before EDM cutting. Cubes were fabricated with a dimension of $10 \times 10 \times 10 \text{ mm}^3$. Between successive printing layers, a rotation angle of 67° was used with the aim of residual stress minimization. 67 is an odd number and the likelihood of two layers having the same scanning lines on top of each other is extremely small by using this number.

Figure 4.1 As-built SS316L samples by SLM.

Density results are shown in Fig. 4.2 (a). There is a general decreasing trend in density measured using both the image analysis and Archimedes measurement methods. The smallest hatch spacing gives the best relative density result. All samples have a relative density higher than 99.1%, which is comparable and/or better compared to the previous literature data, Table 4.1. Therefore, this shows that 380 W laser power can fabricate highly dense

parts with the correct scanning strategy, schematically illustrated in Fig. 4.2 (b).

Figure 4.2 (a) Density graphs obtained from Archimedes and image analysis method. (b) Scanning strategy used for the present SLM build [43].

4.2.2 Porosity and Crack Distribution

To examine the porosity distribution and/or crack presence in the as-built samples, OM images were taken on representative polished samples as shown in Fig. 4.3. Clearly, as the hatch spacing increases from 25 μm (Fig. 4.3 (a)) to 120 μm (Fig. 4.3 (c)), the number of porosity increases. Pore size ranges from 10 to 20 μm . Smaller hatch spacing re-melts a substantial amount of the previous melt tracks. It is possible that this re-melting process helps to eliminate the trapped air as its solubility within the liquid decreases as temperature drops.

Besides the increment for porosity quantity as the hatch spacing increases, vertical cracks start to appear for the last few samples with bigger hatch spacing. The crack length typically ranges from $\sim 50 \mu\text{m}$ to 200 μm . It is worth noting that the vertical crack only starts to appear when the hatch spacing is 100 μm . The crack density increases as the hatch spacing further increases. Detailed crack formation mechanism is not yet understood. However, generally, SS316L is believed to be a material with good weldability and cracking is rarely observed.

Figure 4.3 The OM images of (a) S01 (b) S06 (c) S12 showing the pores. SEM images showing the topography of (d) S01, (e) S06 and (f) S12. The green arrows point towards the general scanning direction and the yellow arrows illustrate the two adjacent scanning lines [43].

The as-built top surface tomography SEM images are displayed in Fig. 4.3 (d) to (f). It clearly illustrates the increase in hatch spacing, and the scanning lines are indicated by yellow arrows. The sample with the smallest hatch spacing seems to have the smoothest surface due to its bigger overlapping area. There is a general melt pool curvature following the overall scanning direction (green arrow). As the melt pool solidifies after each laser scanning line, the semi-solid tends to follow the highest thermal gradient. Thus, there is a curvature present for each scan line.

4.2.3 Phase Identification

XRD analysis were performed on Sample 1 (hatch spacing of 25 μm), Sample 12 (hatch spacing of 120 μm) and the precursor powder. The respective XRD profiles are shown in Fig. 4.4 (a). Both samples exhibit mainly face-centered cubic (FCC) γ austenitic phase. Though, there is a small amount of body-centered (BCC) high-temperature δ ferritic phase present. Compared to the

powder diffraction pattern, the BCC (110) plane is merged together to the FCC (111) plane for the two fabricated samples. This is due to the presence of residual stresses within the built parts which leads to peak broadening. Moreover, inconsistent thermal shrinkage during cyclic heating also contributes to high residual stresses which may cause peak merge.

TEM study confirms the presence of BCC phase shown in Fig. 4.4 (b). Acicular needle-like dark fringes are identified by the electron diffraction pattern. The insert diffraction pattern confirms the $\langle 111 \rangle$ zone axis of the BCC phase. Besides the acicular shape, irregular shaped BCC phase was also detected. They typically have a size of $\sim 2 \mu\text{m}^2$. Other than the secondary BCC phase, dense dislocations were also discovered. During fast solidification process, the atoms do not have enough time for coherent packing which leads to high dislocation densities. It is worth noting that all BCC phases were found to form within the grains. No BCC δ phase was found passing across two grains.

Figure 4.4 (a) XRD profiles for S01, S12 and SS316L precursor powder. (b) TEM observation of BCC δ phase.

4.2.4 Microstructural Observation

The melt pool morphologies for Sample 1 and Sample 12 after etching are shown in Fig. 4.5. The melt pool boundaries (melt tracks) can be clearly observed. Few pores are present within the Sample 1 due to its high relative density Fig. 4.5 (a). The stripe scanning pattern consists of several stripes whereas each stripe is made of numerous scanning lines. During fabrication, the scanning lines will finish scanning within a single stripe before moving on to the adjacent stripe.

The variation in melt track morphologies can be explained by the rotation of successive scanning patterns which is of 67° . Taking Sample 1 as an example, as the scanning lines are parallel to the general scanning direction (or stripe sequence), the melt tracks are laid one upon another (Fig. 4.5 (a)(i)). As rotation takes place, there is an angle between the scanning lines and the general scanning direction, therefore the melt tracks are formed side by side each other. Finally, as the scanning lines are perpendicular to the general scanning direction, the melt tracks are closely packed against one another. The distance between adjacent melt track is roughly the same as the hatch spacing.

Figure 4.5 Melt pool morphologies for sample 1 and sample 12.

As for Sample 12 (Fig. 4.5 (b)), due to the wider hatch spacing employed, it is difficult to distinguish the relationship between the melt tracks and the scanning pattern. Nevertheless, the melt tracks are clearly visible. However, the melt pool seems to be deeper compared to Sample 1 due to the slower laser scanning speed used which creates a bigger melt pool. Also, adjacent melt pools are further apart to one another because of the bigger hatch spacing used. Vertical cracks are observed indicated by the white arrows. It should be noted that these vertical cracks are located within the center of the melt pools. Thus, they are not lack-of-fusion cracks.

To elucidate the relationship between these cracks and the grain morphology, EBSD studies were conducted. EBSD studies have proved that the cracks are intergranular in nature, Fig. 4.6. Both samples have a crystallographic texture of (001) along the build direction. Although, both samples were built via the same energy density value, the grain size was quite different. Sample 12 with a bigger hatch spacing of 120 μm (Fig. 4.6 (a)) has a much bigger average grain size compared to Sample 1 with a smaller hatch spacing of 25 μm (Fig. 4.6 (b)). Interestingly, the intergranular cracks are only present within the bigger grain-size sample. It is hypothesized that the sample with a bigger grain size are more prone to the effect of residual stresses. As the grain size increases, there are fewer grain boundaries to withstand the residual stresses due to localized heating/cooling. Cracking is therefore more likely to occur. More detailed explanation will be offered in Chapter 6.

Figure 4.6 (a) EBSD studies of (a) Sample 12 and (b) sample 1 [234].

Fig. 4.7 shows the SLM-built SS316L's microstructure after etching. Epitaxial growth is present as cellular microstructure grows across multiple melt tracks indicated by the blue arrow in Fig. 4.7 (a). The formation of these cellular structures is mainly contributed to the high thermal gradient during the SLM process. When viewed from different orientations, they appear to be either cellular, elliptical or longitudinal. However, for microstructural feature size characterization, only cellular and longitudinal microstructures can be used.

The typical cellular structure is shown in the enlarged Fig. 4.7 (b). The cell size is in the range of $\sim 1 \mu\text{m}$. It is well known that the microstructural size is closely related to the cooling rate. It is estimated that given a $1 \mu\text{m}$ feature size, the cooling rate should be $\sim 5.8 \times 10^5 \text{ K/s}$ [43]. Moreover, the melt tracks seem to have little influence towards the cellular microstructure's distribution.

Figure 4.7 SEM images of Sample 1 (a) showing the cellular microstructure. (b) Enlarged views of (a).

Inherently, it was also reported that cellular structure of size $\sim 0.5 \mu\text{m}$ is frequently observed in other SLM-built SS316L [88, 235, 236]. It is believed that the size of the cellular structures is closely related to the thermal conditions of the processing which is in turn related to the laser characteristics [88]. These fine sub-grain microstructures are believed to increase the material's strength due to the dislocations formed surrounding the cellular structures. They could effectively reduce the mean free path length for

dislocation movement which will then strengthen the material. These cellular structures are the characteristic features for metal AM.

Figure 4.8 TEM image showing the cellular microstructures of the S01 sample. The inset of SAED pattern indicates γ austenite matrix.

TEM studies were carried out to take a closer look of the dislocation structures in the as-built SS316L parts. Dense dislocation cell walls are observed in the $\langle 001 \rangle \gamma$ zone axis, Fig. 4.8. They are closely linked to the SEM images. Thus, it is obvious that the cellular structure cell walls are consisted of dislocations. TEM EDS analysis has shown that the dense dislocations are formed near to the Mo elements. The Mo atom is much bigger in size compared to the other types of atoms within the SS316L. Coherent lattice packing is difficult due to the difference in relative atomic sizes. Thus, dislocations will appear.

Besides the high dislocation density and a few BCC δ phase present within the FCC γ matrix, many nano inclusions are also observed in SLM-built SS316L. Fig. 4.9 illustrates the nano inclusion and the inserted diffuse ring pattern indicates its amorphous nature. It acts as an in-situ dispersion strengthening mechanism. Dense dislocations are observed around the

inclusions. They obstruct the dislocation movements and thus strengthening the material as a result. The inclusions in the present study are observed to have a size ~ 200 nm.

Figure 4.9 TEM image of a spherical inclusion. The inset of the diffuse ring pattern indicates that it is amorphous.

To confirm the elemental composition of the amorphous inclusion, TEM EDX was done and the detailed composition result is shown in Table 4.3. Clearly, the inclusion is mainly composed of silicon, oxygen chromium and manganese. It agrees well with the purpose of silicon addition, which is supposed to reduce the oxygen content within the sample.

A separate study confirms that the nano inclusion content/density is directly related to the residual chamber oxygen concentration. As the chamber residual oxygen content increases, the number of nano inclusions also becomes bigger. It is shown that there is a critical value that once the oxygen concentration surpasses, the tensile properties will be adversely affected [52].

Table 4.3 Amorphous oxide's chemical composition detected by TEM EDX.

Element	Weight%	Atomic%
O K	19.48	36.38
Si K	37.06	39.43
Cr K	18.24	10.48
Mn K	25.22	13.71
Totals	100.00	

The microhardness results are shown in Fig. 4.10. At least 10 indents were placed on each sample to achieve a reasonable standard deviation. There is a decreasing trend for microhardness from sample 1 to sample 12. It is believed that a smaller grain size generates a higher microhardness due to the grain boundary strengthening. The highest microhardness recorded is 220 HV and the lowest microhardness is 215 HV.

Figure 4.10 Vickers microhardness graph for samples from S01 to S12, with the annealed SS316L's microhardness range shown in the block below [43].

These microhardness values are within the expectations. All fabricated samples are harder compared to the annealed counterpart which typically has a microhardness in the range of 150 HV to 160 HV. It is mainly because of 3

reasons. Firstly, the SLM-built SS316L has a smaller grain size as compared to the annealed parts. Secondly, there is a huge amount of dislocations which will act as strengthening features. Lastly, there are many amorphous nano inclusions which could also act as dislocation pinning obstacles to strengthen the material.

4.3 Discussion

4.3.1 Laser Power Limitation for Energy Density Formula

From the introduction section, it is disclosed that majority of the previous SLM-built SS316L samples used a power input below 200 W. Thus, it is unclear if a higher laser input can still be applied for the energy density formula. Through this study, it is shown that a laser input of 380 W can still manufacture highly dense SS316L part with a relative density above 99 % according to the energy density formula.

For the relative densities, while keeping the energy density value constant, clearly a smaller hatch spacing helps to improve the relative density results through the re-melting process, Fig. 4.2. This is contradictory to previous research works whereas the hatch spacing is normally determined via the melt pool size. As a result, the hatch spacing used is typically in the range of ~80 to 120 μm . However, the current study proves that for SLM-built 316L, smaller hatch spacing could generate less porosities. Moreover, it also indirectly proves that the volumetric energy density formula alone is insufficient in predicting the relative density results of the SLM fabricated parts. It can only be used as a rough guide when designing the scanning parameters for the SLM process.

4.3.2 Correlation between Continuous and Pulsed Laser for Energy Density Formula

From this study, it is shown that the energy density value obtained from the pulsed laser machine shows a great applicability for the continuous laser machine. It further amplifies the use of the energy density values. Though the operation parameter definitions for the pulsed laser and continuous laser is rather different. For the pulsed laser, the main parameters besides the laser power input are the pulse duration and pulse separation distance. For the continuous laser, it's the scanning speed.

It is worth noting that the simplified energy density formula only considers the laser power input, hatch spacing, scanning speed and layer thickness. It has neglected the laser focus spot size which can be a major factor. It is coincident that the energy density value from the pulsed laser work has a laser spot size of $\sim 70\text{ }\mu\text{m}$. The current SLM machine has a laser spot size of $\sim 80\text{ }\mu\text{m}$. Thus, it is better to correlate an energy density value with similar laser focus spot size.

4.3.3 Microstructural Consistency for a Fixed Energy Density

Though all SLM-built 316L samples in the present study have a relative density above 99%, the energy density value does not guarantee porosity/crack distribution and microstructure consistence among the SLM-built parts.

In terms of the crystallographic textures, both Sample 1 (smallest hatch spacing and highest scanning speed) and Sample 12 (biggest hatch spacing and lowest scanning speed) exhibit a $\langle 001 \rangle$ texture along the build direction, Fig. 4.6. Moreover, the grain size of Sample 12 is ~ 5 times as big as Sample 1. The exact mechanism behind the difference in grain size is not clear yet.

However, it is speculated that as the scanning lines are very close to one another for Sample 1, the solidified material is constantly experiencing re-melting. As a result, the continuous grain growth will be adversely affected. Thus, a smaller average grain size is observed. The intergranular cracks experienced in Sample 12 is expected to be hot cracking yielded from residual stresses caused by the huge grain size. The detailed mechanisms will be discussed in Chapter 6 later.

As for the micro-hardness results, SLM-built samples are typically harder compared to the annealed counterparts due to the presence of higher amount of dislocations. Moreover, samples with a slower scanning speed tends to be softer, Fig. 4.10. One possible reason is that as the scanning speed decreases, the size of the melt pool increases. It in turn creates a relatively slower cooling rate, which leads to fewer dislocations. Also, the difference in grain size is another factor contributing to the difference in microhardness values.

4.4 Conclusions

This study mainly examined three questions about the applicability of the energy density formula for the SLM process. Firstly, it is proved that for the energy density formula, the maximum laser power input could be as high as 380 W. It offers a wider processing window for the energy density value. Moreover, the energy density value could be shared between a pulsed laser and a continuous laser. The only concern is the laser spot size, it is recommended to use an energy density value obtained by a similar laser spot size. Lastly, it is shown that given the same energy density value, the microstructure is inconsistent if any of the scanning parameters are varied. The main differences are the crack/porosity distribution and the grain sizes. For the present work, a smaller hatch spacing yielded a low porosity/crack content, it also has a smaller average grain size which improves the microhardness values.

Chapter 5 Simultaneously Enhanced Strength and Ductility for SLM-built SS316L

5.1 Introduction

Results from the previous chapter has demonstrated the possibility of using a higher laser power input (380 W) to fabricate SS316L samples with a high relative density. The next challenge is to explore the possibility of microstructural control and property enhancement for the SLM process. From the literature review studies in section 2.4, it is shown that the melt pool morphology has a tremendous influence towards the crystallographic texture formation. Therefore, the present study aims to create a laser scanning strategy that can generate melt pools of different shapes which can then be used to produce samples with different crystallographic texture with enhanced mechanical properties.

Figure 5.1 Design strategy for crystallographic texture control.

Fig. 5.1 displays the designed strategy for crystallographic texture control and property enhancement. Firstly, for the laser scanning strategy, majority of the literatures employed a single-scan melt pool strategy. For this strategy, as the second laser scanning line shines, the previously scanned track has already been fully solidified. It tends to create a long and shallow melt pool. Moreover,

the laser used usually has a Gaussian distribution with a rather small focus diameter ~ 40 to $80\ \mu\text{m}$. To change the melt pool morphology, we designed a multi-scan melt pool strategy. It employs a Top-hat laser with a focus diameter of $\sim 200\ \mu\text{m}$. Moreover, by choosing a smaller than usual hatch spacing, it tends to create a continuous, cumulative huge melt pool, Fig. 5.1 (a). A deep but short melt pool is generated instead. Three parameters were defined to quantify the melt pool morphology. They are the melt pool's rear length, width and height respective, Fig. 5.1 (b). Hopefully, through this method, different crystallographic textures can be generated according to Fig. 5.1 (c). Due to the difference in crystallographic texture, various deformation mechanisms could then be activated, namely dislocation slip and deformation twinning. Tensile properties will be manipulated as a result.

Table 5.1 SLM scanning parameters with a layer thickness of $50\ \mu\text{m}$.

Sample Number	100 W		200 W		380 W		570 W		760 W		950 W	
	Scanning speed [mm/s]	Hatch spacing [μm]	Scanning speed [mm/s]	Hatch spacing [μm]	Scanning speed [mm/s]	Hatch spacing [μm]	Scanning speed [mm/s]	Hatch spacing [μm]	Scanning speed [mm/s]	Hatch spacing [μm]	Scanning speed [mm/s]	Hatch spacing [μm]
01	800	25	1600	25	3000	25	3000	37.5	3000	50	3000	62.5
02	650	30	1300	30	2500	30	2500	45	2500	60	2500	75
03	550	35	1100	35	2000	35	2000	52.5	2000	70	2000	87.5
04	500	40	1000	40	1750	40	1750	60	1750	80	1750	100
05	400	50	800	50	1500	50	1500	75	1500	100	1500	125
06	325	60	650	60	1250	60	1250	90	1250	120	1250	150
07	275	70	550	70	1050	70	1050	105	1050	140	1050	175
08	250	80	500	80	950	80	950	120	950	160	950	200
09	225	90	450	90	850	90	850	135	850	180	850	225
10	200	100	400	100	750	100	750	150	750	200	750	250
11	175	110	350	110	700	110	700	165	700	220	700	275
12	160	120	325	120	625	120	625	180	625	240	625	300

To testify our hypothesis, a wide range of laser power inputs (from 100 W to 950 W) were attempted for SLM-built SS316L. The energy densities are kept the same ($\sim 104\ \text{J/mm}^3$) as proposed by Cherry et al [233] and the detailed scanning parameters are listed in Table 5.1. The 380 W parameters are borrowed from Table 4.1. As for the 100 W and 200 W parameters, the hatch spacing was kept as constant and the scanning speed is changed according to the energy density formula to yield the proposed energy density value. As

for the high-power laser parameters 570 W, 760 W and 950 W, the scanning speed was kept as constant instead. It is because the laser movement is controlled by the mechanical mirrors, there is a limit in terms of the maximum laser travelling speed. Thus, hatch spacing is altered to meet the energy density values.

These parameters were designed with a few purposes. Firstly, we would like to further stretch the laser power input range and examine their effectiveness for SLM-built SS316L. Secondly, the high-power laser inputs (from 570 W onwards) were planned with the aim of texture manipulation. Thirdly, it is of interest to see if the high-power inputs, which normally yield a bigger melt pool, will generate bigger grain size and coarser microstructure as a result.

5.2 Results

5.2.1 Relative Density and XRD Profiles

Archimedes method was used to measure the relative densities of the as-built SS316L samples. Fig. 5.2 displays the relative density results of all the fabricated samples designed in Table 5.1. For samples built with the 100 W laser power input, all samples have a low relative density from 95 % to 97 %. The first few samples of the 100 W batch have especially bad density values. Further analysis confirms the poor relative density results stem from the lack-of-fusion defects resulted from insufficient melting. The first few samples have a fast scanning speed which inevitably yielded in a shallow melt pool that cannot fully penetrate the powder bed layer thickness.

The samples built with a 200 W and 380 W all have a relative density above 99 %. Their density values show a great resemblance to each other. The density values are consistent for all builds. As for samples built with 570 W, 760 W and 950 W, the first 5 samples within each laser power exhibit high relative density values which are above 99 %. However, as the hatch spacing

increases further from sample 6 onwards, the relative density deteriorates to ~98.5 % eventually. Possible reason is that as the hatch spacing increases, there is insufficient melting between adjacent melt pools. It further proves that the maximum laser power could be stretched up to 950 W for the energy density formula.

Figure 5.2 Relative density result of SLM-built SS316L with various laser parameters.

To reveal the effects of laser power input towards the phase constitution, the top surfaces of first sample from each batch and the recycled powder were tested by XRD experiment. Their respective XRD profiles are displayed in Fig. 5.3. From the XRD results, all samples have mainly FCC phase. It is different from the previous study whereas samples were built by the 380 W. Further analysis shows that the BCC phase has disappeared in the recycled powder possibly due to the heat treatment effect. The virgin powder does have certain amount of BCC phase as shown in Fig. 4.4 (a). However, it is believed that as the powder went through multiple fabrication processes, the hot as-built samples act as in situ heat treatment sources. As a result, solid phase

transformation took place and no BCC remains. Thus, no BCC phase is present in this work.

From the XRD results in Fig. 5.3, 100 W sample has a similar polycrystalline XRD profile as the recycled powder. It indicates that there is no preferred crystallographic texture within the sample due to its high porosity content. Despite all samples are of FCC phases, 200 W and 380 W samples have the strongest (100) peak whereas 570 W, 760 W and 950 W samples have the strongest (110) peak. Therefore, from these graphs, it is speculated that these two batches (200 W, 380 W and 570 W, 760 W, 950 W) have different preferred crystallographic textures.

Figure 5.3 XRD profiles of SLM-built SS316L with different laser power inputs.

Before the close examination of the preferred crystallographic textures developed within the samples. It is important to validate if the desired melt pool shapes were achieved by the proposed single-track and multi-track scanning strategies. Due to the close similarities for the XRD profiles between

different batches, only the first sample from the 380 W and 950 W batches were selected for a more detailed inspection.

As the SLM fabrication is a cyclic heating process, the melt pools are constantly subjected to re-melting from the layer on top. Their shape might be altered during the re-melting. As a result, only the top layer was investigated to examine the melt pool morphology. With reference to the scanning lines on the top layer, the sample is polished either perpendicular and/or parallel to the scanning lines to study the melt pool's shape. The results after etching are shown in Fig. 5.4.

Perpendicular to the laser travelling direction, the 380 W laser has a melt pool size of $\sim 300\text{ }\mu\text{m}$ width and $\sim 50\text{ }\mu\text{m}$ depth, Fig. 5.4 (a). The red cross and dot represent that the laser is travelling in and out of the planes. The distance between adjacent melt tracks is $\sim 25\text{ }\mu\text{m}$ which matches the hatch spacing used for the fabrication. Due to the high extent of re-melting, the melt pool is relatively wider and shallower compared to most of the melt pools from the literature.

As for the 950 W laser, no melt pool was detected perpendicular to the laser travelling direction, Fig. 5.4 (b). There is a huge blank area with a depth of $\sim 200\text{ }\mu\text{m}$. Melt pool only starts to appear below this region. In contrast, parallel to the laser traveling direction, a melt pool with $\sim 600\text{ }\mu\text{m}$ width and $\sim 300\text{ }\mu\text{m}$ depth was observed, Fig. 5.4 (c). It is an abnormally large melt pool for the SLM process. A substantial amount of material has been re-melted. Therefore, for the 950 W sample, the individual laser scans have merged together to form a continuous melt track for each laser scanning stripe.

Figure 5.4 Melt pool morphologies perpendicular to the laser scanning lines for (a) 380 W and (b) 950 W sample. (c) is the melt pool shape parallel to the laser scanning line.

5.2.2 Crystallographic Texture Control for SLM-built SS316L

To reveal the crystallographic texture and grain size of the 380 W and 950 W samples, EBSD studies were carried. An area of $\sim 1 \text{ mm} \times 1.2 \text{ mm}$ were examined, and the results are shown in Fig. 5. 5.

Figure 5.5 EBSD inverse pole figure (IPF) coloring map with respect to build directions and their respective pole figures for (a) & (c) 380 W sample and (b), (d) 950 W sample. Scale bar is 200 μm .

Fig. 5.5 shows the EBSD graphs along the build direction. The colour legend (Fig. 5.5 (a)) depicts a red colour for the $\langle 001 \rangle$ orientation, green colour for the $\langle 011 \rangle$ orientation and the blue colour for the $\langle 111 \rangle$ orientation. Clearly, the 380 W sample has a preferred $\langle 001 \rangle$ crystallographic texture as most of the grains are red whereas 950 W sample has a preferred $\langle 011 \rangle$ crystallographic texture since most of the grains are green. Fig. 5.5 (c) and (d) are the pole figures of the 380 W and 950 W samples. From left to right, each individual circle shows the normalized orientation intensity along the $\langle 001 \rangle$, $\langle 011 \rangle$ and $\langle 111 \rangle$ orientations. Clearly, for 380 W sample, the highest intensity occurs at the $\langle 001 \rangle$ orientation (a red dot at the center of the $\langle 001 \rangle$ orientation), Fig. 5.5 (c). For 950 W sample, the highest intensity is in $\langle 011 \rangle$ instead.

The melt pool boundaries of the 950 W sample are highlighted in black lines with reference to the SEM image for clarity. Majority of the grains grew perpendicular to the melt tracks; therefore, the grains were observed to follow a zig-zag growth manner. In contrast, the grains in 380 W sample mostly grow straight following the build direction. Despite its smaller melt pool size for 380 W sample, it is shown to have a larger average grain size of $\sim 310 \mu\text{m}^2$ as compared to $180 \mu\text{m}^2$ of the 950 W sample. It is against the conventional thought whereas a bigger melt pool will induce a bigger average grain size. It is worth noting that for the 380 W sample, grains can grow through multiple melt tracks as each melt pool is only $\sim 50 \mu\text{m}$ deep. The grains in 380 W sample can be as long as $\sim 200 \mu\text{m}$. However, for the 950 W, no grains were observed to grow through melt tracks. Fine equiaxed grains are present near 950 W sample's melt pool boundaries. Clearly, there are different grain growth mechanisms for these two samples.

Moreover, to investigate the microstructural stability of the as-built parts, heat treatments at 650°C were carried out for 950 W and 380 W samples (Fig. 5.6). They were held in vacuum condition for 2 hours followed by furnace cooling [237]. There is little sign of grain growth for both samples. Crystallographic textures of both samples were certainly not affected by the

heat treatment process. Thus, the microstructure and properties of the SLM-built SS316L parts in this work are supposed to be thermally stable at 650 °C, that is higher than one third of its melting point. It extends the working range of the SLM-built SS316L from room temperature to ~650 °C.

Figure 5.6 EBSD IPF coloring maps with respect to build directions for 380 W and 950 W samples in (a) & (c) the as-built state and in (b) & (d) the heat-treated state. Scale bar is 200 μm [238].

5.2.3 Monte Carlo Simulation of Grain Growth

To elucidate the formation mechanisms of different crystallographic textures for the 380 W and 950 W samples, Monte Carlo simulation was conducted with the open source Stochastic Parallel PARTicle Kinetic Simulator (SPPARKS) [239, 240]. The Monte Carlo Potts model that involves spins (or

grain identifiers) on a discrete lattice was employed. A random number is allocated for each lattice at the beginning. As the simulation progress, lattice will experience a spin or a change in number. Both the lattice selected for the spin process and the spin process itself are subjected to a varied probability according to the pre-defined external conditions. When two neighboring lattices have the same number, they are then a grain.

The overall bonding energies between adjoining unlike spins (adjacent grains) is computed as:

$$E = \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^L (1 - \delta(q_i q_j)). \quad \text{Eq. 5.1 [239]}$$

N is the total number of lattice sites, q_i and q_j are spins at lattices sites i and j. L is the number of neighbors of each lattice site. For the whole simulation process, the overall bond energy is always decreasing. Therefore, grains are constantly growing or coarsening. A mobility factor (the likelihood for lattice to experience spin), F is specified as:

$$F = F_o \exp \left(\frac{-Q}{k_B T(t, i)} \right) \quad \text{Eq. 5.2 [239]}$$

Q is the activation energy for grain boundary motion, and F_o is a user defined prefatory. K_B is Boltzmann's constant, and $T(t, i)$ is the temperature inputs at specific time and location. The Monte Carlo acceptance probabilities of spin flip is then calculated as:

$$P = \begin{cases} F \exp \left(\frac{-\Delta E}{k_B T_s} \right) & \text{if } \Delta E > 0 \\ F & \text{if } \Delta E \leq 0 \end{cases} \quad \text{Eq. 5.3 [239]}$$

Therefore, if the overall bonding energy is smaller than 0, which means the grains are growing, the probability of spin happening is equal to F. However, if the overall bond energy is greater than 0, it will then be subjected to an extra probability of $\exp \left(\frac{-\Delta E}{k_B T_s} \right)$, the probability of the spin to happen is lower. This

ensures the overall energy of the system to decrease with each calculation step and thus grain growth proceeds.

The original application for welding's grain growth model in SPPARKS is app-potts-weld-jom. However, it is found from literature, that only the rear part of the melt pool has effects on the grain growth whereas the front part has little influence [123]. Therefore, the original solver was slightly modified to exclude the front part of the melt pool. A new melt pool shape was defined under weld_type = 0. Detailed codes of the modification are listed below for easy reference.

```

1. /*New method to create only the rear part of melt pool.*/
2. else if(weld_type == 0) {
3.   int WorkingHAZ = (int) (Haz - Wwidth)/2.0;
4.   if (time > StartWeld) {
5.     nx = domain->boxxhi/domain->lattice->xlattice;
6.     ny = domain->boxyhi/domain->lattice->ylattice;
7.     nz = domain->boxzhi/domain->lattice->zlattice;
8.     Mobility = 0.0;
9.     y_weld = (int) (vel * (time - StartWeld));
10.    int x = xyz[i][0];
11.    int y = xyz[i][1];
12.    int z = xyz[i][2];
13.
14.    // Specify the rear part of the melt pool
15.    if (y >= (y_weld - Wlength - WorkingHAZ - Wcap) && y <=
        y_weld - Wlength * 0.5 + deep_length/2.0 && x >= (nx/2 -
        Haz/2) && x <= (nx/2 + Haz/2)) {
16.
17.      if (pow(((x - nx/2)/(Wwidth * 0.5)),2) + pow(((y - (y_weld
        - Wlength/2.0))/(Wlength * 0.5 + Wcap)),2) + pow(((z -
        nz)/(float)ellipsoid_depth),2) <= 1)
18.
19.        {MobilityRear = 1.1;}
20.      else {
21.        for (int k = 0; k <= WorkingHAZ; k++) {
22.          if (pow(((x - nx/2)/(Wwidth * 0.5 + k)),2) + pow(((y -
        (y_weld - Wlength/2.0))/(Wlength * 0.5 + Wcap + k)),2) +
        pow(((z - nz)/((float)ellipsoid_depth + k)),2) <= 1) {
23.            MobilityRear = exp(-k * exp_factor);
24.          }}}}
25.
26.      if(MobilityRear > MobilityFront) {Mobility = MobilityRear;}
27.      else {Mobility = MobilityFront;}
28.      if(Mobility > 1.0 || Mobility < 0.0){
29.        spin[i] = (int) (nspins*random->uniform());
30.      }}}}

```

To capture the characteristics of the various melt pools, three key parameters were incorporated into the simulation: width, depth and rear length. The first two values are determined from the Fig. 5.4. The rear length of melt pool was captured either from finite element simulations or observation of its ripple pattern. The ratios of melt pool width, height and rear length are 6:1:35 and 2:1:3.6 for 380 W and 950 W samples, respectively. The simulation results are displayed in Fig. 5.7.

Figure 5.7 Monte Carlo Simulation of grain growth for (a), (c), (e) 380 W and (b), (d), (f) 950 W samples.

The isometric views of the simulated results in Fig. 5.7 (a) and (b) show the overall grain morphology surrounding the melt pools. For the front views in Fig. 5.7 (c) and (d), it is apparent that grains tend to grow straight from bottom to top within the 380 W melt pool. However, in the 950 W melt pool, grains would like to grow perpendicular to the melt pool boundary. Due to the symmetry of an FCC material, this growth phenomenon tends to create a (011) orientation with respect to the build direction. Moreover, there is a cluster of equiaxed grains within the centre of the melt pool as different grains meet one another. It prevents the columnar grains from further growth. Fine equiaxed grains are also present at the periphery of melt pool boundary, which is consistent with the experimentally observed data. Therefore, the experimental observation of $\langle 011 \rangle$ crystallographic texture formed in 950 W samples (Fig. 5.5 (a) and (b)) is well consistent with the simulation results.

However, for the top view of the Monte Carlo simulation, 380 W sample shows a more uniform grain distribution, but the 950 W sample shows heterogeneous grain morphologies. It is slightly different from the experimental observation. It is possible that for the actual fabrication, the overlap between adjacent laser tracks re-melts majority of the previous track. Yielding a more homogeneous microstructure for the 950 W sample. Despite the minor differences, the Monte Carlo Simulation provides a reasonable justification for the different crystallographic textures formed.

5.2.4 Microstructural Observation

Before the examination of the tensile properties, a brief microstructural observation is done via OM. Fig. 5.8 shows the OM images of the 380 W and 950 W samples after etching. The OM images of 380 W and 950 W samples viewed from XY-plane (top surface) are shown in Fig. 5.8 (a) and (d). The difference in scanning length and hatch spacing can be clearly observed. The

laser scanning lines are highlighted by the yellow arrows. For 950 W sample, it has a shorter scanning length of 0.5 mm to prevent the balling effect (overheating) as compared to 1 mm which is utilized by 380 W sample. The angle of rotation between subsequent layers is $\sim 67^\circ$ as shown in Fig. 5.8 (d). Due to the enormous size of the melt pool in 950 W sample, it is possible to see melt pools from 2 different layers consistently at the same plane. However, the same is not true for 380 W sample.

The melt pool size (viewed from side surface) of 950 W sample is several times bigger than the 380 W counterpart as shown in Fig. 5.8 (b) and (e). Under a higher magnification, the epitaxial growth of the cellular microstructure is evident in 380 W sample as it grows across the melt pool boundary Fig. 5.8 (c). The growth direction of the cellular structures are represented by the green arrows whereas the melt tracks are highlighted by the yellow dotted lines. In contrast, only obscure, misaligned cellular microstructure is observed in 950 W sample Fig. 5.8 (e).

To date, the exact formation mechanism of this type of microstructure is not fully understood yet. However, several possible reasons are proposed. Firstly, it might be caused by the in-situ heat treatment effect from the bigger melt pool, so that elemental segregation is less severe. Therefore, the microstructure feature is less obvious. Secondly, the strong Marangoni effect might have disrupted cellular structure's original growth trajectory, causing the non-uniform growth direction. As a result, it is impossible for long cellular structures to form under stable growth environments.

Besides the difference in microstructure features, it is observed that after electro-etching, the 950 W sample has many black dots. These black dots are not present within the 380 W sample and they are believed to be induced by pitting corrosion. It is likely that during melting process, the huge melt pool preferentially segregates the molybdenum atoms to the melt tracks. As a result, the pitting corrosion resistance of the melt pool decreases within the melt pool. During the electro-etching process, pitting corrosion took place

randomly within the melt pool. More detailed analysis should be done to validate this hypothesis.

Figure 5.8 OM images of top and side views for (a) & (b) 380 W sample and (d) & (e) 950 W sample. SEM images of side views for (c) 380 W sample and (f) 950 W sample. Scale bar for (a), (d) is 200 μm ; (b), (e) is 50 μm ; and (c), (f) is 10 μm [238].

TEM study was carried out for the as-built 950 W sample, and it clearly has more dislocations than the 380 W sample as shown in Fig. 4.8 and Fig. 5.9. There are several possible reasons which could lead to the formation of more dislocations within the 950 W sample. Firstly, as shown in Fig. 5.8 (e), the cellular structures in the 950 W sample are not well aligned to one another. This could lead to lattice incoherency and facilitates the formation of geometrically necessary dislocations. Moreover, the large melt pools and huge re-melting regions in the 950 W sample may create more segregation. The bigger atoms such as Mo could be pinned into the cellular structure's cell walls and generate more dislocations as a result.

Regardless of the formation mechanisms, the higher dislocation density in 950 W sample will certainly help to create a higher yield strength. Moreover, it was reported that the presence of dislocations are the pre-requisite for the appearance of deformation twinning [104]. It is expected that the high dislocation density within the 950 W sample will facilitate the formation of

deformation twinning. It is possibly one of the reasons for the earlier initiation of deformation twins in the 950 W sample.

Figure 5.9 Cellular structure of the as-built 950 W sample [238].

5.2.5 Tensile Properties

To elucidate the effect of various scanning parameters on the mechanical properties of the SLM-built SS316L, tensile tests were conducted on the first sample of each laser power input. The engineering stress-strain curves are shown in Fig. 5.10. The engineering stress-strain curves show that 100 W sample has the worst tensile properties both for its strength and ductility, and it is because of its poor relative density. Interestingly, for samples with similar XRD profiles, their tensile properties are also very close to one another. It suggests that these tensile properties are predominantly dictated by their crystallographic features. 570 W, 760 W and 950 W samples have a higher strength and a better ductility compared to 200 W and 380 W samples. Though, their relative densities are both above 99.0%.

For all SLM-built samples, their engineering yield strength, ultimate tensile strength and elongation are all higher compared to wrought, annealed

counterpart (the yellow dotted lines) [241]. It is especially so for the yield strength, due to smaller grain size and higher amount of retained dislocations. Since the mechanical properties are very similar to the XRD profiles, only 100 W, 380 W and 950 W samples will be discussed for clarity hereafter. The dotted lines in the present figure will be further explained in the Discussion section later.

Figure 5.10 Engineering stress-strain graphs for SLM-built SS316L with different laser power inputs.

Work hardening rate curve normalized by shear modulus (74 GPa) is shown in Fig. 5.11 [242]. The work hardening curve is an effective measure to study the work hardening capability of these samples for their high ductility values. All work hardening curves display a general decreasing trend and the work hardening regimes fall within 0.01 to 0.03G, which is comparable to other FCC metals having deformation twins [243, 244].

A closer examination of the work hardening rate graphs shows that work hardening started earlier for 950 W sample at a true strain of ~ 0.020 compared to ~ 0.025 for 380 W sample. Moreover, despite the earlier initiation for 950 W sample, it goes through a longer regime for the work hardening. It is believed to be the root cause for its improved mechanical properties.

Therefore, to justify its property enhancement, there are two factors to consider: (a) the earlier work hardening for the 950 W sample and (b) the associated longer work hardening range. These factors will be further discussed in the Discussion section.

Figure 5.11 True strain-hardening rate normalized by the shear modulus as a function of true strain

5.3 Discussion

5.3.1 Microstructural Formation Mechanisms

The present work illustrates the possibility of crystallographic texture and grain size controls for the SLM-built SS316L. Firstly, it is demonstrated that a wide range of laser power inputs are suitable for SLM-built SS316L (200 W to 950 W). However, the 100 W laser power input is insufficient to fully melt the precursor powders. Secondly, the crystallographic texture can be engineered from a <001> texture to a <011> texture with careful parameter selection and suitable melt pool morphologies. However, contrary to the common conception, the 950 W sample which has a larger melt pool size generates a smaller average grain size as compared to the 380 W sample.

The smaller average grain size for 950 W is expected to be caused by the strong Marangoni effect and high recoil pressure which are induced by the high-energy laser source. As a high-power laser input is used, a bigger melt pool is yielded. Therefore, more liquid is subjected to convection due to the differences in terms of density and surface tension, known as Marangoni effect [245]. Moreover, due to the high laser intensity, there is a lot of evaporation activities above the centre of the melt pool. The evaporated gaseous phase exerts a downward pressure (recoil pressure) which further enhances the Marangoni convection [77]. The constant, fast movement of the molten liquid within the melt pool is unfavourable for continuous epitaxial growth. Thus, despite a bigger melt pool size, the 950 W sample still has a smaller average grain size.

By analyzing the as-built EBSD graphs using MTEX software, it is found that the crystallographic texture indexes along the $\langle 001 \rangle$ direction for 380 W sample, $\langle 011 \rangle$ direction for 950 W sample were determined to be ~ 3.6 and ~ 2.1 respectively. Thus, the 380 W sample does have a slightly stronger texture. Possible reason for this might be the formation of small trace equiaxed grains at the melt pool boundaries of the 950 W sample. These equiaxed grains are typically polycrystalline in nature. They will reduce the texture strength of the 950 W sample.

It should be emphasized that laser power alone cannot determine the kind of crystallographic texture achieved. Proper combination with suitable scanning strategy is required. It was reported that a 400 W laser source created a random crystallographic texture and a 1 kW laser source induced a (001) crystallographic texture for the same material of SS316L [133]. Though, the details of scanning strategy were not disclosed in the previous work. Therefore, melt pool shape is the only direct indicator for the crystallographic texture formation.

Thus, despite the minor difference, the Monte Carlo simulation provided some insight into relationship between the melt pool shape and the grain morphology within the fusion zone. Built on the present study and with the

aim of extending our existing knowledge, Fig. 5.12 is a crystallographic texture selection map for laser melting/welding. By hypothetically varying the melt pool shape, different types of crystallographic textures and grain sizes are generated as a result.

Figure 5.12 Crystallographic texture selection map from varying melt pool geometries by kinetic Monte Carlo simulations [238].

The vertical axis L/W represents the ratio between the length and width of the melt pool and the horizontal axis H/W is the ratio between the height and width of the melt pool. With the increment of L/W and reduction of H/W ratios, a long and shallow melt pool ($L/W = 8$ and $H/W = 1/8$) tends to create a (001) crystallographic texture. In contrary, as the melt pool becomes short and deep ($L/W = 1$ and $H/W = 1$), a (011) crystallographic texture is more likely to occur. Five representative grain growth figures are listed in Fig. 5.12 (I) to (V).

However, it should be noted that the above simulation mainly considers a single-phase material and no phase transformation is included. The crystallographic orientation of the material below the melt track is also assumed to be a fine polycrystalline material. No thermal gradient and growth rate data are added in the calculation.

Though, there is a reasonable correlation between the simulation and the experimental observation for this work. A more sophisticated model is required for the metal AM process. A combination of the thermal history simulation and the grain growth simulation are needed to mimic a realistic environment. This method has been demonstrated to be effective for laser welding [124, 125]. Hopefully, with the advance of simulation, the formation mechanisms of a <111> crystallographic texture could be understood in the future [118].

5.3.2 Work Hardening and Deformation Twinning Initiations

In terms of the earlier initiation of work hardening for 950 W sample, it is expected to arise from its higher dislocation density. Due to the misaligned cellular structures observed in 950 W sample (Fig. 5.8), more geometrically necessary dislocations are expected to form for crystal's compatibility. As a result, the mean free path length for dislocation movement is adversely hindered. Therefore, it will experience yielding and work hardening earlier compared to the 380 W sample.

Moreover, it is known that the presence of dislocations is a pre-requisite for the appearance of deformation twinning [104]. Therefore, 950 W sample is supposed to experience deformation twinning earlier as well. As known, the deformation twinning stress σ_{tw} could be calculated from Eq. 5.4 below [175].

$$\sigma_{tw} = 2 \times \gamma_{sf} / (b_p \times m_{average}) \quad \text{Eq. 5.4}$$

γ_{sf} is the stacking fault energy ($\sim 20 \text{ mJ/m}^2$) [169], b_p is the burgers vector for Shockley partial dislocation ($\sim 0.146 \text{ nm}$), and m is the Schmid factor. In this work, area-normalized Schmid factors for 950 W and 380 W samples were determined to be 0.451 and 0.459 respectively from their EBSD maps (Fig. 5.5). It makes $\sigma_{tw(950 \text{ W})} = 607 \text{ MPa}$ and $\sigma_{tw(380 \text{ W})} = 597 \text{ MPa}$. Plotting these values back to the original tensile stress-strain graphs in Fig. 5.10, they indicate that deformation twinning starts at 9 % engineering strain for 380 W sample and 7 % engineering strain for 950 W sample. Therefore, 950 W not only starts working hardening earlier due to the dense dislocations, it also experiences deformation twinning earlier because of the different crystallographic orientations.

5.3.3 Work Hardening Durations

Despite its earlier initiation of deformation twinning, 950 W sample goes through a longer period of the work hardening process. It is later found to be facilitated by the higher quantity of deformation twins formed in the deformed 950 W sample. Twinning has a superior dislocation storage density compared to the conventional grain boundaries. Dislocations cannot pass through normal high-angle grain boundaries, and subsequently dislocation clusters are formed surrounding the grain boundaries. It gives the materials a higher strength but reduced ductility as fracture is more likely to happen around the dislocation pile ups. However, coherent twinning interface offers a different mechanism when interacting with dislocations. Dislocation can either pass through or glide along the twin boundary by dissolving into Shockley partial dislocations. It greatly improves the materials' dislocation storage capacity and enables the material to have a higher strength and better elongation [102].

SS316L has a relatively low stacking fault energy which is favorable for deformation twinning formations [169]. In this work, post-deformation EBSD study was carried out to capture the deformation twins. Fig. 5.13 (a) and (c)

are the EBSD IPFs for deformed 380 W and 950 W samples on the top surface. Like the as-built samples, the deformed 380 W sample have larger average grain size compared to the deformed 950 W sample. Moreover, they remain the respective crystallographic textures of (001) and (011). Fig. 5.13 (b) and (d) are the respective band contrast maps, and the deformation twins are highlighted in red. Despite the limitation in EBSD resolutions ($0.5\ \mu\text{m}$), deformation twins in micron size were successfully captured.

Figure 5.13 EBSD IPF coloring map for the top view of deformed (a) 380 W and (c) 950 W samples. Their respective band contrast maps superimposed with red-colored deformation twins (b), (d). Inverse pole figures consisted of grains with and without deformation twins parallel to the tensile direction (e) and (g). The inverse pole figures of as-built (f) 380 W and (h) 950 W samples parallel to the tensile direction. The dotted contour lines represent the Taylor factor values. Scale bar for (a), (c) is $50\ \mu\text{m}$ [238].

950 W sample seems to have more grains experiencing deformation twinning compared to 380 W sample. It is contradictory to conventional notion that grains with a bigger size tends to experience more deformation twins. Thus, this phenomenon must stem from the difference in crystallographic textures. Fig. 5.13 (e) and (g) display the inverse pole figures along the tensile direction. Grains with and without deformation twins are highlighted in red and black colours respectively. The blue dotted contour lines represent the Taylor factor values, M . It is obvious that most of the grains that do not experience

deformation twinning have a Taylor factor value of $M < 2.6$. Those grains that experience deformation twinning tend to accumulate near to the $\langle 111 \rangle$ orientation along the tensile deformation direction. These results correlate well with previous findings from other austenitic steel studies [246-248]. Fig. 5.13 (f) and (h) show the as-built 380 W and 950 W samples' inverse pole figures with respect to the tensile deformation direction. Due to its (001) crystallographic texture within 380 W sample, most of the grains aligned within the $M < 2.6$ region which is unfavourable for deformation twinning to take place. In contrast, for 950 W sample, there is a good portion of grains located outside the $M < 2.6$ region and near to the $\langle 111 \rangle$ orientation along the tensile direction. It facilitates deformation twinning to happen within more grains and thus improve the mechanical properties.

Figure 5.14 Tensile graphs of 380 W and 950 W along the build direction. (b) & (c) Inverse pole figures of 380 W and 950 W samples with respect to tensile direction [238].

To check the mechanical property's consistency, tensile experiment along the build direction is also tested as shown in Fig. 5.14 (a). The (011) textured 950 W sample still has a better combination of strength and ductility as compared to the (001) textured 380 W sample. Though, the strength values of both samples along build direction are lower compared to the horizontal direction.

As shown in the inverse pole figures, due to the presence of cube texture in 380 W sample, majority of the grains have a Taylor factor smaller than 2.6 which is unfavorable for deformation twinning, Fig. 5.14 (a). It should be noted though, that due to the small size of tensile coupon, no extensometer was applied during the testing. However, we still can conclude that 950 W sample has superior mechanical properties on both strength and ductility in comparison to 380 W sample along both horizontal and vertical directions. In addition, the vertical direction is slightly weaker than the horizontal direction for SLM-built SS316L parts.

Figure 5.15 TEM micrographs showing the dominant deformation mechanisms in the two representative SLM-built SS316L samples with different crystallographic textures. (a) TEM image showing two adjacent grains with $\langle 001 \rangle$ and $\langle 321 \rangle$ orientations in the deformed 380 W sample. Grain boundary (GB) is indicated. The right three arrows point to the single-thin twin lamellae. (b) TEM image showing dislocations and stacking faults that exist between two single twin lamellae in the deformed 380 W sample. (c) Enlarged TEM image of the enclosed region in (b) showing a nano-twin and surrounding stacking faults (SFs) along $\langle 011 \rangle$ zone axis. (d) TEM image showing many multiple twins indicated by arrows in the deformed 950 W sample along $\langle 011 \rangle$ zone axis. (e) TEM image showing the multiple nano-twins in the deformed 950 W sample. (f) HRTEM image of the enclosed region in (e) showing the nano-twin lamellae with twin boundaries (TBs) and SFs. Scale bars for (a), (b), and (d) are 200 nm, (c) and (e) 50 nm, and (f) 5 nm [238].

To confirm the influence of crystallographic texture towards deformation twinning and examine the nano-scale microstructural features, TEM studies

were carried out. Fig. 5.15 (a) shows two adjacent grains with two different orientations of (001) and (321) respectively from the deformed 380 W sample. No twins were observed within the (001) orientated grain. With a cubic texture of (001)[100] developed in 380 W sample, it further confirms that grains with an orientation close to (001) alignment along the tensile direction are unfavourable for deformation twinning to occur. However, within the non-(001) orientated grains, separate single-twin lamellae with tens of nanometres in width are popularly seen in 380 W sample (Fig. 5.15 (a)-(c)). Moreover, Fig. 5.15 (b) and (c) display many dislocations and stacking faults that exist between twin lamellae, which are ought to be strongly interacted with each other during plastic deformation. In contrast, much more multiple deformation twin lamellae were observed in the deformed 950 W sample (see Fig. 5.15 (d)). The multiple nano-twin lamellae and the stacking faulted regions are shown in Fig. 5.15 (e). High-resolution transmission electron microscopy (HRTEM) image in Fig. 5.15 (f) reveals the nano-twin lamellae and stacking faults at atomic scale. The stacking faults made of partial dislocations occurred owing to the dislocation/twin interactions. It is evidenced that twinning is the dominant deformation mechanism in the (011) textured 950 W sample and the formation of nano-twins could be the major reason that accounts for the simultaneously enhanced strength and ductility.

Besides the influence of deformation twinning, the contribution of grain refinement towards overall strength enhancement is rather minimal. According to classical Hall-Petch relationship, $\sigma_y = \sigma_0 + \frac{k_y}{\sqrt{d}}$ whereas σ_y is the yield strength, σ_0 , k_y are material-specific constants, and d is the average grain diameter. From EBSD graphs in Fig. 5.5, by estimating grains as circles, the average diameter for 380 W and 950 W samples are 13.2 μm and 11.6 μm respectively. For SS316L at room temperature, k_y has a value in the range of ~450 to 700 $\text{MPa}\cdot\mu\text{m}^{1/2}$ [249]. By substituting in the relevant values, the $\frac{k_y}{\sqrt{d}}$ term for 380 W and 950 W samples are ~8.1 MPa and ~12.6 MPa respectively. Thus, the effect of grain refinement towards overall strength increment is negligible. Therefore, the dominant microstructural feature for

strength enhancement lies within the nano-scale deformation twins. Due to the existence of varied crystallographic texture, the work hardening duration differs because of the quantity of deformation twin formations.

5.4 Conclusions

In conclusion, the strength and ductility of SS316L has been simultaneously improved in this work. By using suitable laser power and scanning strategy, single-scan melt pool and multi-scan melt pool were generated via the Gaussian and Top-hat profiled lasers respectively. As a result, melt pools of different geometries were created. From the previous studies on single laser tracks, we know that slow scanning generates deep but irregular melt pools while fast scanning creates discontinuous balling phenomena [123, 250]. Therefore, majority of the previously optimized laser scanning parameters fall in between with regular, shallow melt pools. This in turn contributes to the formation of (001) crystallographic texture along build direction for SLM-built metal parts. In this work, the multi-scan melt pool strategy can produce a stable, deep melt pool with a width to height ratio of 2:1. Accordingly, a desirable (011) crystallographic texture may form instead of the common (001) crystallographic texture.

Aided by the kinetic Monte Carlo mesoscale simulation approach, it is shown that a long, shallow melt pool promotes the formation of (001) texture; whereas a short, deep melt pool favors the occurrence of (011) texture. Therefore, both experimental and simulation works prove that melt pool morphology has a tremendous influence towards the crystallographic texture formation within the additive manufactured samples. It is also worth noting, a bigger melt pool does not necessarily have a bigger grain size. Convection flows within the melt pool are expected to influence its grain growth behavior too. As a result, 950 W sample not only has a deformation-twinning favored $\langle 011 \rangle$ crystallographic texture, it also has a smaller grain size. Via simple “Hall Petch” calculations, it is derived that the strength improvement yielded from smaller grain size is not significant when compared to the deformation

twins. Thus, for alloys with low stacking fault energies, crystallographic texture control holds the key for their mechanical property enhancement.

Finally, the high-power 950 W sample not only improves the mechanical performance, it drastically reduces the manufacturing time. With the increased laser power input, a bigger hatch spacing can be used. Therefore, fewer scan lines are needed per unit area. It shows great potential for industrial adoption due to faster built rate and better mechanical performance.

Chapter 6 Hot Cracking of SLM-built High-entropy Alloy CoCrFeNi

6.1 Introduction

The use of high-entropy alloys in metal additive manufacturing is still quite limited to date. Due to its exceptional high fracture toughness, it is a difficult material to work with using conventional tooling processes [251]. Metal AM offers the advantage of near-net shape forming capability. High-entropy alloy CoCrFeNi is often regarded as the base material for different HEA systems [194]. Thus, it is a suitable candidate to explore the feasibility of using HEAs in AM. Moreover, it might be used as a fracture-resistant alloy specifically designed for AM. Previous research work on SLM-built CoCrFeNi has demonstrated the possibility of printing this material, but the mechanical property did not meet the desired level [206]. Therefore, the current study will examine the root cause of deteriorated SLM-built CoCrFeNi's property.

Pre-alloyed HEA CrFeCoNi was printed by SLM. A range of scanning parameters was tested. Firstly, by keeping the laser power constant, energy density was varied from 50 to 180 J/mm³. 60 samples with various processing parameters were built. None of the samples has a relative build density higher than 99%. The optimal energy density was determined to be 110 J/mm³. Secondly, two different scanning strategies, namely chessboard and stripe/bi-directional, with varying scanning lengths were deployed. For chessboard scanning strategy, laser scanning takes place randomly within the chessboard to minimize the residual stress. The process parameters for 6 samples built with the optimal energy density is listed in Table 6.1. At least two samples were built for each parameter.

For the three samples built via the chessboard scanning strategy, the only difference is the number of cubes printed for each layer. Given that each sample has a dimension of 10 × 10 × 10 mm³, the laser scanning length for samples with 4, 16 and 64 cubes are 5, 2.5 and 1.25 mm respectively. For

the stripe scanning strategy, the laser scanning length is equal to the strip length.

Table 6.1 Process parameters for SLM-built HEA CoCrFeNi.

Sample	Scanning Pattern	No. of Cubes	Stripe Length (mm)	Power (W)	Energy Density (J/mm^3)	Hatch Spacing (mm)
C1	Chessboard	4	-	150	110	0.1
C2		16	-	150	110	0.1
C3		64	-	150	110	0.1
S1	Stripe	-	10	150	110	0.1
S2		-	2	150	110	0.1
S3		-	0.5	150	110	0.1

6.2 Results

6.2.1 Relative Density Measurement

Fig. 6.1 shows the macroscopic view of the representative CoCrFeNi samples built by SLM using different parameters from Table 6.1.

Figure 6.1 Macroscopic view of SLM-built CoCrFeNi samples with various scanning parameters.

The side surfaces after fabrication is rather smooth. The size of the scanning line can be gauged by viewing the top surface of the as-built samples. As the scanning length decreases for stripe scanning strategy and number of cubes increases for the chessboard scanning strategy, the top surface morphology becomes rougher.

To examine the relative density values of the as-built samples, optical images of the polished cross sections along the build direction are shown in Fig. 6.2. Their respective average relative density values computed from a few dozen images are stated on the top left corner. The relative densities were calculated via ImageJ described in Chapter 3. The pores and cracks are highlighted in red.

It is obvious that majority of lack-of-fusion cracks due to insufficient melting between successive layers are only present in C1 and S1 samples. Though they have the same laser power and hatch spacing, C1 and S1 have longer scanning lengths. It is speculated that the longer melt pool's Plateau-Rayleigh instability might have contributed to this cracking [252].

Figure 6.2 Optical images of SLM-built HEA CoCrFeNi. Pores and cracks are highlighted in red and their relative densities are shown on the top left corner.

Generally, as the length of the melt pool or liquid becomes longer, it is more difficult to maintain its cylindrical shape. Therefore, the instability tends to create droplet-like separations within the melt pool. When this happens, the laser power cannot fully penetrate those bigger droplets and lack-of-fusion cracks will occur. Like SLM-built SS316L samples, spherical porosity is also observed within the current HEA. Unlike SS316L, some of the spherical pores in SLM-built CoCrFeNi are much larger in size. They are in the range of ~30 to 80 μm for S3 sample.

Other than the presence of lack-of-fusion cracks and the spherical pores, numerous vertical cracks were observed for all as-built samples. These cracks are in the range of 100 to 200 μm . The nature and distribution of these cracks will be disclosed in the following paragraphs.

6.2.2 Nature and Distribution of Cracks

To examine the nature of the cracks, chemical etching was done on the polished cross sections of sample C2, Fig. 6.3.

Figure 6.3 OM images of light-etched SLM-built HEA CoCrFeNi

All vertical cracks seem to align themselves along the grain boundaries which is a typical feature of hot cracking. The extent of cracking is clearly revealed in Fig. 6.3. To better understand the extend of cracking, OM images were assembled together to display the whole area for C2 and S3, which have the better relative densities among the 6 samples, Fig. 6.4.

Figure 6.4 Assembled OM images for C2 and S2.

Clearly, cracking is present throughout the whole build. The width and length of the polished samples are ~10 mm. The maximum crack length is ~200 μm as shown in Fig. 6.2. It is a huge contrast compared to the polished surface

of the SLM-built SS316L sample. To reveal the nature of cracking, large-area EBSD studies were conducted on the C2 and S3 samples, Fig. 6.5.

The EBSD scans of C2 and S2 are shown in Fig. 6.5 (a) and (b). It is noted that the grain size of SLM-built CoCrFeNi samples is extraordinarily large, columnar grains can epitaxially grow up to ~3 mm in length and ~200 μm in width. In comparison, SLM process typically generates a grain length of less than 0.1 mm for AlSi10Mg [114], and ~0.2 mm for SS316L, Inconel 625 and CoCrMo [117, 238, 253]. One close match is pure molybdenum with a grain length of ~2 mm, which also suffered from extensive intergranular cracking in the as-built stage [254]. Besides the huge grain size, it is discovered that lack-of-fusion cracks, circled in black in Fig. 6.5 (a) severely affect the grain growth trajectory. The spherical pores circled in red in Fig. 6.5 (b) has little influence on the grain growth path. Since majority of the spherical pores are formed at the last stage of solidification due to the reduction of gas solubility within the liquid metal, they not expected to interrupt the grain growth.

Detailed band contrast maps and EBSD figures surrounding the cracks are shown in Fig. 6.5 (c) and (d). The cracks appeared to be the black lines on the grey band contrast maps. Obviously, all cracks are intergranular in nature. They do not necessarily have to be in the form of straight lines. Rather, they tend to follow the adjacent grain's morphology.

Figure 6.5 EBSD graphs for (a) C2 and (b) S2 along the build direction. Detailed scan of (c) C2 and (d) S2 crack distributions.

Besides the presence of numerous intergranular cracks, both samples exhibit a strong (011) crystallographic texture. To retrieve statistically convincing misorientation data, the misorientation between grains for Fig. 6.5 (a) and (b) are computed and shown in Fig. 6.6 (a). It is a typical misorientation distribution for the metal AM process. The low angular grain boundaries ($<15^\circ$) presents in the majority of all misorientations. Moreover, ~ 70 cracks were randomly selected for detailed EBSD studies for sample C2 and S2. It was found that all cracks are indeed intergranular and majority of the adjacent grains' misorientations lies from 40° to 50° (Fig. 6.6 (b)). It is a direct evidence that SLM-CoCrFeNi are susceptible to intergranular cracking.

Figure 6.6 (a) Misorientation distribution of SLM-built CoCrFeNi. (b) Misorientations of randomly selected hot cracks [234].

6.2.3 Tensile Properties of SLM-built CoCrFeNi

To examine the tensile properties of the SLM-built HEA CoCrFeNi, representative C and S samples are shown in Fig. 6.8. Each printing parameter was at least tested for 3 times. It shows that the yield strengths (Y_s) are 556.7 ± 23.6 and 572 ± 7.48 MPa, the ultimate tensile strength (UTs) are 676.7 ± 20.5 and 691 ± 15.9 MPa, and the elongations to failure are $12.4 \pm 2.1\%$ and $17.9 \pm 0.9\%$ for C and S samples respectively, which has shown to be superior to the previous work with the same layer thickness [206]. Moreover, S samples performed better with smaller deviations in terms of strength and ductility in comparison with C samples.

Figure 6.7 Representative engineering stress and strain curves for S2 and C2 samples.

Since both samples have similar crystallographic texture and grain size, the only possible difference between the two is the crack quantity and distribution. Therefore, to elucidate the reasoning for the different mechanical performance of C and S samples, μ -CT data and the corresponding cross-sectional OM images are shown in Fig. 6.9 (a) to (b). With the same scanning parameters but a different scanning strategy, C sample contains more cracks/pores compared to S sample. Moreover, for S sample, the cracks are randomly distributed which is a common phenomenon for metal AM fabricated parts [21].

However, for C sample, the cracks align themselves along the build direction. This phenomenon is validated in the OM images with the aligned cracks are circled in red. It is worth noting that the chimney-like cracks were only present under the chessboard scanning strategy with stripe sizes of 1.25 and 2.5 mm. It does not appear under the stripe scanning strategy (stripe sizes from 0.5 mm to 10 mm) nor the chessboard scanning strategy with a stripe size of 5 mm. For the appearance of the “chimney-like” cracking, it is believed that as the stripe length becomes shorter for chessboard scanning, more scanning regions were created. Due to the random scanning sequence among these regions, each region was heated in isolation and limited heat can be dissipated away horizontally (majority of the heat is conducted away from

below). Therefore, it resulted in an increase in thermal gradient but a decrease in cooling rate which favors the growth of columnar grains. As the grains continue to grow, cracks are likely to follow along the build direction and the “chimney-like” cracking occurred.

Figure 6.8 Figure 2. μ -CT images with their corresponding cross-sectional OM images of the (a) C and (b) S samples. The chimney-like crack in C sample is circled in red dashed line. The tensile fracture surfaces of (c) C and (d) S samples with hot cracks highlighted by white arrows. Enlarged view of the cellular structure's smooth surfaces for (e) C and (f) S samples [234].

For tensile fracture surfaces shown in Fig. 6.9 (c) and (d), more elongated cracks are detected in C sample and they are believed to cause its property deterioration and deviation. Typical smooth surfaces of cellular structures are shown in Fig. 6.9 (e) and (f). The cellular size is $\sim 1 \mu\text{m}$. It indicates that the

cracks are formed at the last stage of solidification with the presence of liquid film. Together with the intergranular nature, these are evidences that the cracks occurred within SLM-built CoCrFeNi are hot cracking.

6.2.4 Chemical Homogeneity

Numerous studies have suggested that chemical heterogeneity is one of the key factors assisting the formation of hot cracks. Thus, EDS mapping after light etching was conducted to observe elemental segregation at the micron scale, Fig. 6.9. The EDS mapping was performed on the etched cellular structures. The cellular structures have a dimension of $\sim 1\ \mu\text{m}$ which is consistent with feature size observed on the tensile fracture surfaces Fig. 6.8 (e) and (f).

Though, no elemental segregation was detected for SLM-built CoCrFeNi samples under EDS. The presence of cellular structures indicates the possibility of dense dislocation cell walls. It is likely that during solidification, cellular structures form due to the fast cooling rates. The incoherent alignment among the cells contribute to the formation of dislocations. However, the resolution of the EDS mapping is not enough to detect atomic elemental segregation nor the dislocations.

Figure 6.9 EDS mapping of SLM-built CoCrFeNi sample from the top surface.

To detect elemental segregation in the atomic scale, atom probe tomography test was conducted near the hot crack in Fig. 6.10 (a). The site of tip selection is less than 1 μm away from the hot crack.

Figure 6.10 (a) SEM image showing that APT specimens were acquired on the periphery of a hot crack. (b) SEM image showing an APT specimen tip with a dimension of ~ 50 nm. (c) APT reconstruction volumes showing atom distribution of the 4 constituting elements (Co, Cr, Fe and Ni) [234].

The APT tip specimen with a radius of ~ 50 nm was analyzed (Fig. 6.10 (b)). Compared to other commercial alloys such as Ti6Al4V, the atom probe tomography took more time for the current HEA sample due to its high toughness. Moreover, this sample is easily fractured due the data acquisition. Fig. 6.10 (c) reveals that distribution of the 4 constitute elements is uniform and their atomic ratios remain to be consistent. Obviously, no elemental segregation is seen at the intergranular crack. Thus, it is suggested that the hot cracking could not be attributed to elemental segregation for this SLM-built HEA. There must be other reasons for the extensive hot cracking happened in this SLM-built HEA.

6.3 Discussion

Clearly, there are several prominent features of SLM-built HEA CoCrFeNi. Firstly, extensive hot cracking is evident and little segregation is present both at the microscale and the nanoscale. Secondly, it generates huge grain size of ~3 to 4 mm in length. As known, lacking alloying content for grain nucleation will cause formation of big-sized grains in metals and alloys [255]. Thus, both CoCrFeNi and pure molybdenum built by SLM might undergo limited constitutional undercooling during rapid solidification of AM process which leads to large columnar grains. Moreover, we found that epitaxial grain growth was broken down in the periphery of the lack-of-fusion cracks. However, small spherical pores have little influence on the grain growth. As observed by Leung et al. that spherical pores were mainly formed at the last stage of solidification due to the reduction of gas solubility as molten metals cooled down [85]. Therefore, epitaxial columnar grain growth is unlikely to be affected.

6.3.1 Crack Initiation and Propagation

To examine the root cause of the hot cracking issue in the present work, we need to firstly understand its initiation mechanisms. The hot cracking formation process for metal AM is illustrated in Fig. 6.11. After each laser scan, the top powder feedstock becomes liquid. Fusion zone starts to solidify from the bottom where the temperature is the lowest. During solidification, cellular structures will grow from the bottom towards the grain center. It is experimentally validated that when the grain boundary misorientation is above a certain critical value, the repulsive force between the grains will lower the coalescence temperature of the trapped liquid [256]. Thus, for high angular grain boundaries, there is usually trapped liquid metal within them.

Figure 6.11 A generic schematic illustration of the hot cracking mechanism in AM process

Due to the presence of residual stress, either from thermal shrinkage or mechanical strain, crack tends to initiate from the grain boundary. It is because the liquid/semi-solid trapped within the grain boundaries generally has a weaker fracture resistance. Thus, majority of the residual stresses will be concentrated on them. Once the residual stress is above a critical value, fracture will occur which will then lead to a crack initiation.

Despite the crack initiation, not all cracks will propagate. The unsolidified liquid (semi-liquid) on the top layer, may fill up any openings through liquid feeding. Therefore, this schematic explains (1) why hot cracks are all intergranular in nature. It is because at the last stage of solidification, grain boundaries are the weakest links in the material subjected to residual stress/strain. (2) The smooth features of fracture sites in hot cracking. As the hot cracks occur near the grain boundaries at the last stage of solidification, there is still liquid film present. The smooth features are the solidified cellular structure/dendrite.

Sometimes, if there is insufficient liquid feeding due to high viscosity and/or fast solidification rate, the cracks can also be terminated by the deposited layer on top.

Figure 6.12 Crack morphology of the SLM-built CoCrFeNi annotated with the black dotted line for melt track, red arrows for cellular structure/dendrite growth direction, and continuous blue lines for grain boundaries.

Fig. 6.12 shows a closer examination of the crack propagation pathway along the build direction for the SLM-built CoCrFeNi. Once a hot crack is initiated, it cannot grow forever. Its propagation is highly dependent on its geometrical relationship with the melt pool. It was previously mentioned that hot cracks tend to follow the morphology of the grain boundaries. In this case, the middle crack has changed its growth direction for 3 times. For ease of interpretation, the grain boundaries are highlighted in blue solid lines. The melt tracks are noted by dotted black lines. Lastly, the cellular structure's growth direction is represented by the red arrows.

As the middle crack initiates from melt pool 1, it switched its growth direction 2 times before it continues to grow in melt pool 2. From melt pool 2 to melt pool 3, it changed its growth direction again. Finally, when it reaches melt pool 4, it meets a converging grain boundary and it stopped propagation. It is worth noting that, after each melt pool boundary, the cellular structures either grow in the same direction as those below the melt pool or they will switch by an angle of 90° perpendicularly due to cubic crystal nature of the FCC material. Thus, hot crack can only propagate with the presence of diverging grain boundaries.

6.3.2 Residual Stresses with SLM-built CoCrFeNi

Figure 6.13 TEM image showing a large number of dislocations within the as-built cellular microstructure. Cell boundaries are indicated by white arrows. A selected area diffraction (SAED) pattern is shown with a $\langle -1\ 1\ 0 \rangle$ zone axis.

Since residual stress is believed to be the root cause for this hot cracking, it is important to understand the residual stress levels within the as-built CoCrFeNi sample. TEM study was carried out. Fig. 6.13 shows dislocation structures from the $\langle -110 \rangle$ zone axis. The dendrite/cellular structure's boundaries are highlighted by white arrows. The SAED pattern confirms the $\langle -110 \rangle$ zone axis. Unlike the usual cellular structures observed from the as-built SS316L Fig. 2.44, the interior of the as-built CoCrFeNi's cellular structure is not clean. Dense dislocations are present within the cells. It directly proves the presence of plastic deformation induced by high residual stress in the SLM-built CoCrFeNi. Therefore, it is very likely that high residual stress level might be the key for hot cracking in SLM-built CoCrFeNi.

6.3.3 Effect of Grain Size to Hot Cracking

To quantify the effect of large grain size towards the high residual stress level within the built parts, the classic RDG model listed reviewed in Chapter 2 is employed.

$$\begin{aligned} \Delta p_{max} = \Delta p_{sh} + \Delta p_{\varepsilon} = & \frac{180(1+\beta)\mu}{\lambda^2 G} \int_{T_S}^{T_L} \frac{E(T)f_s(T)^2}{(1-f_s(T))^3} dT \\ & + \frac{180 R\beta\mu}{\lambda^2 G} \int_{T_S}^{T_L} \frac{f_s(T)^2}{(1-f_s(T))^2} dT \end{aligned} \quad (Eq. 2.12)$$

with

$$E(T) = \frac{1}{G} \int f_s(T) \dot{\varepsilon}(T) dT$$

Like the original calculations made by the RDG model, the strain rate $\dot{\varepsilon}$ is assumed to be a constant value of 10^{-2} s^{-1} [140, 257]. Therefore, besides the other constants, the main challenge is to compute the integral values using the solidification path data. To validate and testify the proposed hypothesis, three materials' solidification data were involved as shown in Fig. 6.14. SS316L is typically regarded as a very easy material to work with in metal AM. However, it is found lately that with the use of a high power laser, extensive cracking occurred [258]. On the other hand, Al7075 has long been regarded as a material unsuitable for welding. It is reported recently that introduction of nanoscale grain nucleation successfully prevented hot cracking [149].

The SS316L and Al7075 solidification paths were adapted from previous researches whereas the HEA CoCrFeNi data was computed from the Pandat software. Among the three materials, Al7065 has the longest solidification range of $\sim 180^\circ\text{C}$ whereas CoCrFeNi has the shortest solidification range of $\sim 20^\circ\text{C}$. Typically, materials with long solidification range is more prone to hot cracking as it takes more time to solidify [259]. It is more likely for liquid film to form surrounding the grains. However, the solidification path data cannot explain the current HEA's hot cracking phenomenon.

Figure 6.14 Solidification paths of SS316L, CoCrFeNi and Al7075 [149, 260].

For the calculation procedures, the solidification path curve data is firstly imported into Matlab. It is then discretized with an interval of 1 Kelvin each for the temperature axis. The “trapz” function in Matlab is used for the integral calculations. Lastly, substituting in the relevant parameters, the depression pressure values are calculated. From Eq. 2.12, a longer solidification interval does contribute to a higher depression pressure. All materials’ constants used in the calculation are listed in Table 6.2 blow.

Table 6.2 Material Property values used for pressure drop calculations.

	CoCrFeNi	SS316L	Al7075
λ [m]		10^{-6} [43]	
G [K/m]		10^6 [114]	
v_T [m/s]		10^{-3} [132]	
β	0.17	0.17 [82]	0.19 [261]
μ [kgm ⁻¹ s ⁻¹]	$3.15 \cdot 10^{-2}$ [262]	$1.49 \cdot 10^{-3}$ [82]	$6.42 \cdot 10^{-3}$ [263]

To keep the SLM working conditions the same, the λ , G and v_T are kept as constants. The v_T is estimated from the columnar grain shape of the SLM-built samples. No thermal shrinkage β data was found for HEA CoCrFeNi. The value of SS316L is used instead due to their close atomic weight and element constitution. The dynamic viscosity of HEA Al_{0.1}CoCrFeNi is used for CoCrFeNi due to their close chemical composition as well [262]. The coherency temperature T_s is taken as the temperature when $f_s(T) = 0.93$ as suggested by [87].

Due to the different nucleation tendencies and existing experimental data, it is assumed that for cross section along the build direction, the largest average grain size can be obtained for SLM-built CoCrFeNi, SS316L and Al7075 are 10^6 , 10^6 , and $10^4 \mu\text{m}^2$ respectively [258, 264]. To incorporate the effect of grain size, the strain rate $\dot{\epsilon}$ is proportionally decreased as the lateral grain size decreases.

Figure 6.15 Hot tearing propensity with respect to their grain size and typical depression pressures for the chosen SLM-built alloys.

Fig. 6.15 is the calculated depression pressures with respect to the grain size for SS316L, CoCrFeNi and Al7075. It is observed that as the grain size decreases, the contribution of mechanical strain Δp_{ε} decreases exponentially. It is found that once the corresponding grain size exceeds a characteristic depression pressure value, hot cracking will start to occur. It is worth noting that, when the grain size is close to the transition point for SS316L, only minor cracking appeared (Fig. 4.5). The transition point sample is the sample 12 built via 380 W from Chapter 4. The same trend is also validated for the SLM-built Al7075 fabricated from literature. Though, no previous grain size data of SLM-built CoCrFeNi is available, based on the above-mentioned results, it is conceived that hot tearing for the SLM-built CoCrFeNi could be overcome when its average grain size is below $10^4 \mu\text{m}^2$.

6.4 Conclusions

In conclusion, this work presents the issue of hot cracking for SLM-built HEA CoCrFeNi sample. Extensive hot cracks were found for the as-built sample regardless of the processing parameter variations. It causes the relative density of all builds to be below 99%. Through the EBSD studies, all cracks are found to be intergranular in nature and majority of the cracks lie in the grain boundaries with a misorientation of 40° to 50° . Together with the examination of the tensile fracture surface, smooth surfaces indicating the presence of liquid film are observed. Thus, it is a problem of hot cracking.

Unlike those hot cracking problems observed in the superalloys, there is little elemental segregation. For the current study, neither EDS mapping nor atom probe tomography detected any segregation. Rather the TEM study of the as-built sample discovered huge amounts of dislocations. It indicates the presence of high residual stresses within the sample. The classical RDG model was used to explain the effect of grain size towards the residual stress level and the occurrence of hot cracking for the SLM process.

It is found that the huge grain size (up to 3 mm in length) of the SLM-built CoCrFeNi is the root cause for the presence of hot cracking. Since all elements with this HEA have similar atomic numbers, there is a lack of constitutional undercooling for grain nucleation. Thus, the grain size of the present material is several times bigger compared to the commercial alloys processed by SLM under similar conditions. Therefore, grain size reduction is a critical issue for SLM-built CoCrFeNi samples.

Chapter 7 Grain boundary segregation assisted prevention of hot tearing in $\text{Al}_x\text{CoCrFeNi}$

7.1 Introduction

Chapter 6 demonstrates the presence of hot cracks in SLM-built CoCrFeNi. The large grain size induced residual stress is believed to cause the cracking. To fabricate a HEA with high strength and high ductility, these hot cracks need to be alleviated. Moreover, other strengthening mechanisms should be introduced to the CoCrFeNi-based HEAs for its property improvement. For crack minimization, several methods listed in Chapter 2.5 have successfully reduced number of cracks. However, for the present HEA, it is a single-phase solid solution and no elemental segregation was detected. The main challenge is to create extra constitutional undercooling for grain nucleation. In terms of the property enhancement, interphase interface strengthening is proven to be effective [196]. Combined with the fast solidification rate of the SLM process, it can generate refined interlocking mechanisms which is expected to strengthen the material effectively.

With the above assumptions in mind, compositional modification needs to be done. From existing literature data, aluminum seems to be a plausible addition for the CoCrFeNi-based HEAs. It can initiate phase transformation from FCC to BCC with its concentration increment [186]. With the correct balance between the FCC and BCC volume percentage, the desired strength-ductility combination could then be achieved. Moreover, aluminum has a much bigger atomic size compared to the four elements in CoCrFeNi. It is supposed to help to create lattice distortion and create more constitutional undercooling for nucleation. Therefore, it is hypothesized that aluminum addition could reduce the residual stress level within SLM-built CoCrFeNi alloys through secondary phase formation. Moreover, the secondary phases could possibly strengthen the material through their refined microstructures.

Since the preparation of pre-alloy powder needs a considerable lead time, the present study used powder blending between pure aluminum powder and the pre-alloyed CoCrFeNi powders. The pure aluminum powders were proportionally added into the CoCrFeNi powders. A tumbler mixer was used for powder blending for 12 hours. In total, there are three batches of samples built using this method. They are namely Al_{0.1}CoCrFeNi, Al_{0.5}CoCrFeNi and Al_{1.0}CoCrFeNi. These samples were fabricated with the intension of explaining the effects aluminum addition towards crack minimization and property improvement for CoCrFeNi HEAs.

The representative powder morphologies after blending is shown in Fig. 7.1. Due to the nature of powder blending, the aluminum powders (red in color) are not fully, homogeneously distributed within the powder mixer. Possible influencing factors towards chemical homogeneity are powder size distribution, container rotational speed and volume percentage of powder in the container etc. Therefore, powder blending could never achieve a chemical homogeneity comparable to the pre-alloyed powder. However, it is indeed an effective way to quickly access the compositional suitability for AM. It is believed that under the current SLM processing conditions with a laser power of 150 W and slow scanning speed of 270 mm/s, it provides extra time for alloys to remain in the liquid state. As a result, there is extra time for elemental redistribution within the melt pool for better compositional homogeneity.

Figure 7.1 SEM images of powder bending for Al_{0.5}CoCrFeNi.

7.2 Results

7.2.1 Crack Density and Nature of Cracking

The samples of $\text{Al}_{0.1}\text{CoCrFeNi}$, $\text{Al}_{0.5}\text{CoCrFeNi}$ and $\text{Al}_{1.0}\text{CoCrFeNi}$ after fabrication are displayed in Fig. 7.2. The rectangular blocks were later machined to tensile coupons via EDM machine. Due the limited blended powder, each material was only built to a sample height of ~4 mm. By visual inspection, there is no obvious cracks present on the as-built sample's surface. However, crack features are apparent on the polished cross sections, Fig. 7.3.

Figure 7.2 Macroscopic view of the SLM-built $\text{Al}_x\text{CoCrFeNi}$.

All images were taken on the top surface of the as-built samples. The SLM-built CoCrFeNi sample is displayed as a reference, Fig. 7.3 (a). Compared to the base CoCrFeNi sample, $\text{Al}_{0.1}\text{CoCrFeNi}$ has more cracks, $\text{Al}_{0.5}\text{CoCrFeNi}$ has much fewer cracks and both the crack density and the crack size increase for $\text{Al}_{1.0}\text{CoCrFeNi}$, Fig. 7.3 (b) to (d).

Figure 7.3 Number of solidification cracks for (a) pure CrFeCoNi, (b) CrFeCoNi with 0.1 Al (at.%) addition, (c) CrFeCoNi with 0.5 Al (at.%) addition and (d) CrFeCoNi with 1.0 Al (at.%)

To investigate the difference in crack density and distribution among these samples, EBSD studies were carried out for $\text{Al}_{0.1}\text{CoCrFeNi}$ and $\text{Al}_{1.0}\text{CoCrFeNi}$ samples, Fig. 7.4. Clearly, there is a fundamental difference between the cracking mechanisms. The $\text{Al}_{0.1}\text{CoCrFeNi}$ sample has a similar crack nature as CoCrFeNi as all cracks are intergranular, Fig. 7.4 (a) and (b). The cracks tend to grow along the high angular grain boundaries. In contrast, the $\text{Al}_{1.0}\text{CoCrFeNi}$ sample has a much smaller average grain size, Fig. 7.4 (c) and (d). Instead of having only intergranular cracking, it consists of a mixture of intergranular and intragranular cracks. The addition of aluminium seems to create a huge grain refinement effect for this sample. All grains are equiaxed in this EBSD graph.

Figure 7.4 Top surface crack morphology of SLM-built (a) & (b) $Al_{0.1}CoCrFeNi$ and (c) & (d) $Al_{1.0}CoCrFeNi$.

7.2.2 Phase Transition with Aluminum Addition

To examine the phase constitution, XRD testing was conducted for the top surfaces of each sample. The results are displayed in Fig. 7.5. From bottom to top, the tested materials are $CoCrFeNi$, $Al_{0.1}CoCrFeNi$, $Al_{0.5}CoCrFeNi$ and $Al_{1.0}CoCrFeNi$. The FCC phase is depicted by the green sphere and the BCC/B2 phase is depicted by the blue stars. The XRD results show a clear phase transition from FCC to BCC/B2 as the aluminum content increases, that is consistent with previous literatures [186]. Both the $CoCrFeNi$ and $Al_{0.1}CoCrFeNi$ samples have only a single FCC phase. The BCC phase starts to appear in the $Al_{0.5}CoCrFeNi$ sample. Lastly, for the $Al_{1.0}CoCrFeNi$ sample, it has completely transformed into a single BCC/B2 phase. Therefore, excluding the consideration of cracking, the $Al_{0.5}CoCrFeNi$ sample should have the best combination between strength and ductility as it has a dual phase microstructure.

Figure 7.5 XRD results of CoCrFeNi, Al_{0.1}CoCrFeNi, Al_{0.5}CoCrFeNi and Al_{1.0}CoCrFeNi. The zoomed in image of the (111) peak of the FCC phase.

It is interesting to inspect the distribution of aluminum especially for the Al_{0.1}CoCrFeNi sample since there is no phase transition took place. The zoomed-in image of the FCC (111) peaks displays the difference among CoCrFeNi, Al_{0.1}CoCrFeNi and Al_{0.5}CoCrFeNi. As the aluminum content increases, the FCC (111) peak shifts to the left from 43.9° to 43.8° and finally 43.6°. They translate to a lattice constant of 3.568 Å, 3.576 Å and 3.591 Å for CoCrFeNi, Al_{0.1}CoCrFeNi and Al_{0.5}CoCrFeNi respectively.

Therefore, before the formation of BCC phase, the aluminum atoms are dissolved into the CoCrFeNi's FCC matrix. Due to its larger atomic size, it expands the original lattice matrix as a result. As the number of aluminum atoms increases, the default FCC matrix can no longer hold these Al atoms. As a result, they transformed into the BCC crystal structure. In this study, the Al_{0.5}CoCrFeNi sample is found to be a transition point. For this composition, the BCC phases just started to form. It is believed that by a careful addition, a duplex HEA could be achieved via this method.

7.2.3 Microstructural Observations

EBSID studies were carried out on the regions away from cracks for all four samples on the top surface, Fig. 7.6. As the aluminum content increases from CoCrFeNi to Al_{0.5}CoCrFeNi, there is no apparent change in terms of grain size for the top surface. The average grain size is $\sim 8 \times 10^3 \mu\text{m}^2$. However, for the Al_{1.0}CoCrFeNi sample, the grain size decreases drastically to $\sim 80 \mu\text{m}^2$. It was originally suspected that excessive aluminium content will creates additional constitutional undercooling which will induce grain nucleation.

Figure 7.6 EBSD IPFs of the top surface of SLM-built (a) CoCrFeNi, (b) Al_{0.1}CoCrFeNi, (c) Al_{0.5}CoCrFeNi and (d) Al_{1.0}CoCrFeNi.

Ideally, with the knowledge of the grain size data, depression pressure vs grain size curves could be plotted to elucidate the effect of grain size towards the cracking. However, without accurate materials data such as shrinkage factor and viscosity values, it is extremely difficult to determine the exact depression pressure for solidification cracking like Fig. 6.15. Thus, the exact grain size transition point is yet to be known for these materials.

To examine the distribution of BCC/B2 phase inside the FCC grains, detailed EBSD scans were conducted on the top surface of $\text{Al}_{0.5}\text{CoCrFeNi}$ sample, Fig. 7.7. IPF + IQ map in Fig. 7.7(a) displays the existence of cellular structures. Areas for EDS mapping and cross-correlation EBSD are also highlighted as reference. Clearly BCC/B2 phase is only present surrounding the FCC cellular boundaries due to segregation at the last stage of solidification, Fig. 7.7(b). Interestingly, the BCC/B2 grains have distinct orientations even when they are in the same grain. It is vastly different from the arc-melted sample with similar chemical compositions [265].

Figure 7.7 Detailed EBSD graph of the top surface for $\text{Al}_{0.5}\text{CoCrFeNi}$ containing BCC/B2 network. (a) IPF + IQ map along the build direction. Regions used for EDS and cross-correlation EBSD later are highlighted respectively. (b) Phase + IQ map. (c) Image Quality overlaid with BCC/B2 IPF map. (d) Phase boundaries with Kurdjumov-Sachs and Nishiyama-Wasserman orientation relationships. (e) Theoretical and experimental pole figures of BCC/B2 phase within Grain 1 in (d) plotted with respect to the parent FCC grain orientation.

To examine the crystallographic orientation relationships between FCC and BCC/B2 phases, four well-defined relationships were considered: Bain, Kurdjumov-Sachs (KS), Nishiyama-Wasserman (NW) and Pitsch. It is found that with a tolerance angle of 2.5° , majority of the phase interfaces either obey a Kurdjumov-Sachs (KS) or Nishiyama-Wasserman (NW) relationship, Fig.

7.7(d). It is worth noting that some of the BCC/B2 grains obey none of the above-mentioned crystallographic orientations. They are thus likely to be formed through chemical segregation rather than phase transformation. Generally, with the presence of stresses following a fixed direction during phase transformation, there should be a preferred variant selection. To examine the variant selection preferences, all theoretical variants obeying KS and NW relationships were plotted in pole figures Fig. 7.7(e) with respect to the FCC orientation in Grain 1, Fig. 7.7(d). The same procedure was conducted for all BCC/B2 grains within Grain 1. The BCC/B2 orientations in pole figure have a strong resemblance with the theoretical predictions. Therefore, there is no preferred variant selection during the phase transformation process. Considering the complex heating/cooling cycles in SLM-built samples, it is understandable that stress should be present for all directions. Therefore, the beneficial effect of residual stresses towards phase transformation should not be ruled out. On the contrary, it is reported that with a similar composition, no BCC phase was detected via XRD for casted samples. The BCC phase only appeared after high-temperature heat treatment [266]. Thus, the phase transformation phenomenon in the current sample is likely to be the result of both “in-situ annealing” and the residual stresses.

EDS mapping was conducted on the SLM-built $\text{Al}_{0.5}\text{CoCrFeNi}$ sample, Fig. 7.8. Clearly, Nickel and Aluminum co-segregate into the cell boundaries whereas Iron and Cobalt segregate inside the cellular structures. From the SEM-EDX, there is no segregation happening for Chromium, which is inconsistent with APT data later, likely due to the overlapping peaks in EDX measurement. Chemical analysis was conducted for minor element detection in combination to SEM-EDX. The chemical analysis results for CoCrFeNi and $\text{Al}_{0.5}\text{CoCrFeNi}$ are listed in Table 7.1.

Table 7.1 Chemical analysis for CoCrFeNi and $\text{Al}_{0.5}\text{CoCrFeNi}$

at%	Co	Cr	Fe	Ni	Si	Al
CoCrFeNi	24.66	24.61	24.25	24.76	1.72	
$\text{Al}_{0.5}\text{CoCrFeNi}$	22.08	21.75	22.90	22.08	1.60	9.59

Figure 7.8 EDX elemental distribution for SLM-built $Al_{0.5}CoCrFeNi$.

From the chemical analysis, a minor amount of silicon was detected within the sample. It is expected to be the impurities introduced during the powder atomization stage. The remaining elements are within their respective expected ranges.

7.2.4 Tensile Properties

Tensile testing was carried out for all the above-mentioned samples. However, since the cracks are too prevalent for the $Al_{1.0}CoCrFeNi$, no data was recorded. The tensile results are displayed in Fig. 7.9. The $CoCrFeNi$ sample was taken from the previous chapter's results.

Figure 7.9 Tensile results of $CoCrFeNi$, $Al_{0.1}CoCrFeNi$ and $Al_{0.5}CoCrFeNi$.

The $\text{Al}_{0.1}\text{CoCrFeNi}$ sample has a lower yield strength as compared to the CoCrFeNi . Moreover, the presence of cracking prevents any further elongation and it merely extends for $\sim 2\%$. In comparison, $\text{Al}_{0.5}\text{CoCrFeNi}$ registered both a higher yield and ultimate tensile strength as compared to the base CoCrFeNi sample while maintaining a similar ductility value.

The fracture surface of the CoCrFeNi sample has been displayed previously in Fig. 6.8. The rest of the fracture surfaces are shown in Fig. 7.10. The $\text{Al}_{0.1}\text{CoCrFeNi}$ sample has a very similar fracture surface to the CoCrFeNi sample. Smooth surface of liquid films which is typical feature of hot cracking is easily to be observed. For the $\text{Al}_{0.5}\text{CoCrFeNi}$, it mainly consists of the ductile dimple fracture surface. It explains its higher ductility compared to other samples. Almost no ductility was recorded for $\text{Al}_{1.0}\text{CoCrFeNi}$ sample and typical brittle fracture was detected on its fracture surface. Therefore, too little aluminum addition will result in more hot cracks whereas extra aluminum will induce brittle fracture due to the formation of BCC phase. Both scenarios are undesirable towards the mechanical performance.

Figure 7.10 Fracture surface of the $\text{Al}_{0.1}\text{CoCrFeNi}$, $\text{Al}_{0.5}\text{CoCrFeNi}$ and $\text{Al}_{1.0}\text{CoCrFeNi}$ samples.

7.3 Discussion

7.3.1 Cracking mechanisms for $\text{Al}_{0.1}\text{CoCrFeNi}$ and AlCoCrFeNi

Before the investigation of cracking minimization for the SLM-built $\text{Al}_{0.5}\text{CoCrFeNi}$ sample, the mechanisms of the increased cracking for $\text{Al}_{0.1}\text{CoCrFeNi}$ and $\text{Al}_{1.0}\text{CoCrFeNi}$ samples need to be clarified. The intention of introducing aluminum to CoCrFeNi was either to create additional stress relieving measure through phase transformation. Also, the aluminum atoms are expected to generate extra constitutional undercooling which could assist grain nucleation. Therefore, the material could be strengthened with a smaller grain size in the as-built state. However, both the above-mentioned samples ended up with more cracking.

For $\text{Al}_{0.1}\text{CoCrFeNi}$ sample, the cracks are very similar to the base CoCrFeNi material. They both exhibit intergranular cracks with similar grain sizes. It is known that hot cracking susceptibility depends on both semi-solid/liquid's viscosity (liquid backfilling) and the material's high-temperature load bearing abilities. It is reported that the viscosity values for CoCrFeNi based HEAs are rather high [234]. The addition of a small amount of aluminum is unlikely to make it higher and provide a huge influence. In terms of high-temperature load bearing abilities, study suggested for $\text{Al}_x\text{CoCrFeNi}$ alloys that it is proportionally correlated to the room-temperature properties [267]. Therefore, nano-indentation was conducted to examine the material's room-temperature mechanical properties. It is a suitable technique for this purpose as the small indentation zone could effectively avoid the influence of hot cracks. At least 16 indents were placed on CoCrFeNi and $\text{Al}_{0.1}\text{CoCrFeNi}$ separately and the representative graphs are shown in Fig. 7.11.

Figure 7.11 Nano-indentation results of the CoCrFeNi and Al_{0.1}CoCrFeNi phase.

An indentation depth of 2000 nm was preset for both samples whereas CoCrFeNi requires a load of ~320 mN and Al_{0.1}CoCrFeNi only needs a load of ~275 mN. Therefore, the Al_{0.1}CoCrFeNi sample registered a lower hardness value. This phenomenon is mostly neglected or unreported from previous researches. However, in the current work it is believed to be the key reason for the increased hot cracking observed inside the SLM-built Al_{0.1}CoCrFeNi sample (Fig. 7.3 (a) & (b)). Given its similar grain size as the base CoCrFeNi sample, the residual stress level should be rather close. Due to the material's softening and its lower load bearing capability, more cracks will thus form.

As for Al_{1.0}CoCrFeNi sample, the cracking formation mechanism seems to be different. It is a brittle fracture as shown in Fig. 7.10. Despite its smaller grain size, cracks are found to be thicker and more extensive. To examine the propensities of solidification cracking, the solidification paths of the current Al_xCoCrFeNi system were computed via Thermo Calc using TCHEA3 database, Fig. 7.12. Despite the contradictory opinions for the applicability of solidification range towards the solidification cracking tendencies [268,269]. There is still useful information that could be derived from such calculations.

Figure 7.12 Solidification paths of $Al_xCoCrFeNi$ calculated via Thermo Calc.

The solidification temperature ranges for $CoCrFeNi$, $Al_{0.1}CoCrFeNi$, $Al_{0.5}CoCrFeNi$ and $Al_{1.0}CoCrFeNi$ are 16°C, 57°C, 291°C and 297°C respectively. It is commonly believed that a longer solidification range renders a material more susceptible towards hot tearing [140]. Other than the solidification temperature range calculation, the expected phases under Scheil equilibrium condition is also derived. Both $CoCrFeNi$ and $Al_{0.1}CoCrFeNi$ are consisted of only FCC matrix, and B2 phase was supposed to form for $Al_{0.5}CoCrFeNi$ after the solidification of primary FCC phase. As for $Al_{1.0}CoCrFeNi$, the primary phase is B2 and FCC phase is supposed to appear afterwards. It should be noted though, that no FCC peak was detected for the SLM-built $Al_{1.0}CoCrFeNi$ in XRD experiment in the current work though. The fast cooling experienced in SLM likely suppressed the formation of FCC phase in the $Al_{1.0}CoCrFeNi$ sample.

Therefore, according to the solidification temperature range data, both $Al_{0.5}CoCrFeNi$ and $Al_{1.0}CoCrFeNi$ should experience more cracking as compared to $CoCrFeNi$ as they have a much longer solidification stretch. Moreover, the $Al_{1.0}CoCrFeNi$ sample has a B2 primary solidification phase which is known to be highly brittle. It is suspected that once a porosity or lack-of-fusion crack is present during solidification, it could cause fracture rather easily within the B2 phase. It is believed to be the reason for its extensive hot cracking. As for the $Al_{0.5}CoCrFeNi$ sample, the later introduction of B2 phase

did not create cracking, but rather help to minimize the residual stress levels that will be further discussed in the later sections.

7.3.2 Spinodal decomposition within the interdendritic regions

To understand the crack minimization mechanism in SLM-built $\text{Al}_{0.5}\text{CoCrFeNi}$, its microstructural constitution needs to be examined in more details. Special emphasis should be placed upon the dislocation distributions as they are a direct indication of plastic activities within the sample. To do so, TEM study was carried out on $\text{Al}_{0.5}\text{CoCrFeNi}$, Fig. 7.13.

Figure 7.13 Transmission electron microscopy (TEM) images of $\text{Al}_{0.5}\text{CoCrFeNi}$. (a), (b) Bright and dark field images of dendrite and interdendritic regions. Selected area electron diffraction (SAED) patterns from the dendrite and interdendritic regions are highlighted in blue and red respectively. (c) High-angle annular dark-field (HAADF) image of dislocation distributions observed from FCC $\langle 1 -1 2 \rangle$ zone axis. (d) Enlarged view of interdendritic region. (e) HRTEM image of phase interface between FCC and BCC/B2.

Bright and dark field images of dendrites and interdendritic regions are shown in Fig. 7.13(a) and (b). The dendrite has a size of $\sim 1.5 \mu\text{m}$ which is consistent

with previous BSE image, Fig. 7.8. SAED patterns taken from dendrites and interdendritic regions are highlighted in blue and red respectively. When FCC phase is fixed in its $\langle 011 \rangle$ zone axis, the BCC/B2 phase is close to its $\langle 111 \rangle$ zone axis. To confirm the presence of B2 phase, SAED pattern from its $\langle 0-11 \rangle$ zone axis was obtained. The presence of weak superlattice diffraction spots confirms that B2 is indeed present. It is consistent with the Scheil equilibrium calculations. To capture the dislocation distributions and the B2 morphology, high-angle angular dark field (HAADF) images were taken. Fig. 7.13(c) and (d) were taken from the FCC $\langle 1-12 \rangle$ zone axis. Clearly, dense dislocations were observed in the dendritic FCC phase. Indicating the presence of plastic activities under high residual stress. The BCC/B2 region remains rather uniform in colour, absent of dislocation activities. However, since the experiments were not conducted under the controlled two-beam diffraction conditions, a direct comparison of dislocation densities between the two samples are not possible. Besides the dislocations, several dark patches were also observed in both FCC and BCC/B2 regions. It is reported from previous research with a similar composition that these dark patches are found to be AlN precipitates [270].

An enlarged image of the BCC/B2 interdendritic region is shown in Fig. 7.13(d). Homogeneously distributed bright and dark rods are found with an interspacing of ~ 10 nm. It is a characteristic feature of spinodal decomposition and has been previously observed from casting samples [270]. Through further inspection, this feature is present throughout the BCC/B2 region. HRTEM image near the FCC and BCC/B2 interface is shown in Fig. 7.13(e) taken from the BCC $\langle 111 \rangle$ zone axis. Clearly, the FCC (bright region) does not consist of a uniform lattice. It is to be expected as the fast solidification rate in SLM creates extra dislocations and orientation gradients within grains. On top of the nonuniform lattice, dark fringes were found in the BCC/B2 region. They might be the superimpose of BCC and B2 lattices along the TEM lamella.

To differentiate and capture the exact chemical compositional transition from FCC to B2 and BCC, atom probe tomography experiments were conducted.

It was shown in Fig. 6.10 that chemical homogeneity remains to be homogeneous for SLM-built CoCrFeNi along the grain boundaries. Similar experiment was firstly done for Al_{0.1}CoCrFeNi to examine its chemical homogeneity, Fig. 7.14.

Figure 7.14 Atom probe tomography of Al_{0.1}CoCrFeNi and its 1D chemical concentration profile.

Clearly, no elemental segregation was detected for Al_{0.1}CoCrFeNi sample. Aluminum atoms are homogeneously distributed among the FCC matrix. However, for Al_{0.5}CoCrFeNi segregation around phase interfaces was observed, Fig. 7.15.

Figure 7.15 Atom probe tomography of Al_{0.5}CoCrFeNi. (a) Elemental chemical distributions for various elements containing a phase interface. (b) Iso-surface for 15 at.% Chromium. Histograms for (c) FCC/B2

interface, (d) B2/BCC interface and (e) 1D concentration profiles are created according to the indications in Fig. 7.15(b).

Consistent with the EDX result in Fig. 7.8, Aluminum and Nickel segregate into the B2 region, Fig. 7.15(a). Unlike the EDX results, Cobalt and Silicon were found to be enriched in FCC matrix together with Chromium and Iron. It is worth noting though, the Silicon segregation is rather small. Moreover, from thermodynamic calculations, silicon does not contribute to any phase formation activities. To further differentiate various phases, iso-surface for 15 at.% Chromium was computed in Fig. 7.15(b). Two phase interfaces were detected, namely FCC/B2 interface and B2/BCC interface. Their respective histograms were displayed in Fig. 7.15(c) and (d). To track the difference between various phases, 1D concentration profile was plotted from FCC to B2 and then BCC phase, Fig. 15(e). For FCC phase, the elemental constitution is very close the base material. As it transits to B2, the FCC/B2 interface has a width of ~3 nm which is consistent with the previous TEM observations, Fig. 7.13(e). The B2 phase has a high concentration of Nickel and Aluminum with the lowest Chromium amount within all major elements. Therefore, the B2 phase is concluded to be an ordered NiAl phase. For the B2/BCC interface, due to the close lattice constants, the phase interface is much smaller ~1 nm. It is mainly Chromium enriched which is consistent with previous findings for casting process [271]. The BCC phase is thus the disordered Cr-enriched phase. As a result, the SLM-built $\text{Al}_{0.5}\text{CoCrFeNi}$ consists of primary FCC phase within the dendrite/cellular structures. The interdendritic regions are consisted of spinodal decomposed B2 and BCC phases. Their formation procedures and contribution towards stress minimization is further illustrated in the next section.

7.3.3 Residual stress reduction in $\text{Al}_{0.5}\text{CoCrFeNi}$

To explain the effects of observed microstructures towards residual stress minimization, their thermodynamics of formation should firstly be clarified.

The quantity of various phases under equilibrium condition was plotted against temperature shown in Fig. 7.16(a) (an enlarged view is shown in Fig. 7.16(b)). Under the equilibrium solidification condition, the ordered NiAl B2 phase will form first. It is then followed by the FCC phase while the disordered Cr-enriched BCC phase is the last to form. Later on, during the solid-state transformations, the FCC phase will then spinodally decomposed into the B2 and BCC phases. It is evident as the concurrent increment in phase amounts of B2 and BCC as the FCC content decreases.

Figure 7.16 $Al_{0.5}CoCrFeNi$'s phases quantities plotted against temperature calculated via Thermo Calc.

Therefore, there are mainly two events during the solidification of $Al_{0.5}CoCrFeNi$. Firstly, during the solidification stage, aluminum is segregated into the interdendritic and grain boundary regions due to their lower solubility within the parent FCC phase. As the dendrites have already been solidified, the interdendritic/grain boundary regions are still in liquid or semi-solid state due to the segregation and lower coalescence temperatures. As the Al-enriched regions start to solidify, ordered B2 NiAl will firstly appear followed by the FCC phase. Then, the FCC phase will spinodally decomposed into the ordered B2 NiAl and disordered Cr-enriched BCC phase. Since BCC lattice has a lower atomic packing density from FCC lattice, given a fixed number of atoms, lattice expansion is to be expected. It could relieve the residual stresses within the material since they are mainly tensile in nature. Moreover, the spinodal decomposition is also beneficial towards stress minimization within the B2 regions. To validate these assumptions, cross-correlation EBSD

(CC-EBSD) studies were conducted for residual stress analysis for the $\text{Al}_{0.5}\text{CoCrFeNi}$ sample. CC-EBSD is a suitable tool for this situation because it provides unprecedented resolution of $\sim 10^{-4}$ for elastic strains and 0.01° for rotations. In contrast, normal EBSD procedure which employs a standard Hough transformation only offers a precision of $\sim 0.5^\circ$ [272].

The CC-EBSD studies were conducted from the top surface of the as-built sample as shown in Fig. 7.17. An extra step of “re-mapping” was introduced to minimize the effect of large grain rotations. Clearly, for the normal residual strains, majority of them are constrained surrounding the BCC/B2 grains. Taking “normal ϵ_{11} ” strain as an example, to the righthand side is the positive direction (indicated as red) and to the left is negative (indicated as blue). All the parent FCC grains have a greenish color which indicates no or low residual strain levels. As for the BCC/B2 grains, they are highly strained with an absolute value up to 0.08. Moreover, it is found that the residual strains within each BCC/B2 grain is seldom uniform. There is always a strain gradient inside the BCC/B2 grains as highlighted by the black dotted circles. It indicates a nonuniform deformations to accommodate the residual strains from the adjacent parent FCC phase. The normal strains following other directions show similar behaviors. As for the shear residual strain, taking “shear ϵ_{12} ” strain for instance, the parent FCC phase has a higher value. It is because compared to the BCC/B2 phase, the FCC phase has more slip planes to accommodate external strains. Thus, most of the plastic deformation happens through gliding or shearing. The maximum absolute value of FCC strain is always lower compared to the BCC/B2 phase though. As the CC-EBSD technique assumes that there is no stress for the out-of-plane direction, the other shear strains involving the out-of-plane direction are significantly lower compared to shear ϵ_{12} .

Figure 7.17 Cross-correlation EBSD (CC-EBSD) of the Al_{0.5}CoCrFeNi sample for residual strain determinations. For normal strains, right, upward and out-of-plane directions are set as the positive directions. For the shear strains, the positive direction follows the arrows on each respective cubic illustration.

To better capture the plastic activities due to residual strain between different phases, the geometrically necessary dislocation (GNDs) map is calculated and plotted in Fig. 7.18. Similar to the normal strains, the BCC/B2 grains registered a higher dislocation content. The parent FCC grains mostly have a GNDs density of $\sim 10^{14}$, which is a typical value for FCC materials. As for the BCC/B2 grains, their GNDs density is about one order of magnitude higher compared to the FCC grains. This is expected because during the solidification process, the FCC parent grain always solidifies first while the interdendritic BCC/B2 grains are still in its liquid or semi-solid state. Upon complete solidification, the BCC/B2 phase has a lower homologous temperature (lower melting point, Fig 7.12)) comparing to the parent FCC phase. Therefore, during the cooling stage, the high-temperature load-bearing ability of the BCC/B2 grains is weaker than the parent FCC grains. As the residual stress starts to build up due to thermal contraction, more plastic deformation or grain rotation will occur for the BCC/B2 grains. They act as an effective residual stress/strain absorber and minimize the detrimental effect of residual stress/strain towards hot cracking.

7.4 Conclusions

In conclusion, with the aim of crack minimization and property enhancement, three batches of samples were fabricated, namely $\text{Al}_{0.1}\text{CoCrFeNi}$, $\text{Al}_{0.5}\text{CoCrFeNi}$ and $\text{Al}_{1.0}\text{CoCrFeNi}$. It is found that only $\text{Al}_{0.5}\text{CoCrFeNi}$ shows the promise of crack minimization and property enhancement. For $\text{Al}_{0.1}\text{CoCrFeNi}$, aluminum addition results in material softening. As a result, the material's load bearing ability decreases. Under the same amount of residual stress during SLM fabrication, it experiences more hot cracking as compared to the base material CoCrFeNi . On the other hand, $\text{Al}_{1.0}\text{CoCrFeNi}$ sample has a smaller average grain size among all the samples. However, the high aluminum content changes the primary solidification phase to B2 instead of FCC. As the brittle B2 phase has little resistance towards fracture during solidification, with the presence of thermal stresses and porosities, extensive intergranular and intragranular cracks were obtained.

Compared to other samples, $\text{Al}_{0.5}\text{CoCrFeNi}$ has a unique microstructure. It is formed firstly through aluminum segregation into the interdendritic and grain boundaries. Then the Al-enriched regions will solidify as ordered NiAl B2 phase and FCC phase. The FCC phase will then go through spinodal decomposition to form ordered NiAl B2 and disordered Cr-enriched BCC phase. It is found that these BCC/B2 phase could act as effective strain absorbers to alleviate the tensile residual stresses. This is done both through the lattice expansion of the B2/BCC phase and the high-temperature deformations.

Chapter 8 Conclusions

It is demonstrated in this PhD work that selective laser melting process holds great potential of microstructural control through the layer-wise fabrication manner. Stainless steel 316L has been manufactured as a representative example. By combining suitable laser power input and scanning strategy, single-scan melt pool and multi-scan melt pool result in drastically different melt pool shapes. Monte Carlo simulations have validated that the melt pool shape has a direct influence towards the crystallographic textures formed. Typically, as the melt pool approaches a morphology of length over width ratio of 8 and height over width ratio of 1/7, a $\langle 001 \rangle$ crystallographic texture is expected. On the other hand, when the melt pool has a length over width ratio of 1 and height over width ratio of 1, then a $\langle 011 \rangle$ crystallographic texture is likely to form.

For materials with low stacking fault energies such as stainless steel 316L, $\langle 011 \rangle$ crystallographic texture favors the deformation twinning as compared to the typical $\langle 001 \rangle$ crystallographic texture. As a result, the $\langle 011 \rangle$ textured sample performs better both perpendicular and parallel to the build direction for tensile testing. The tensile strength and ductility are found to increase by ~16% and ~40% respectively. It offers a unique way of manufacturing components with better strength and ductility concurrently.

In terms of extending the material library for metal additive manufacturing, hot cracking has been identified as one of the biggest obstacles. Majority of the hot cracking issues has been focusing on superalloys previously due to their high industrial value. As a result, chemical heterogeneity surrounding grain boundary was determined to be a key factor promoting hot cracks. However, by employing a novel high-entropy alloy CoCrFeNi, it is found out that hot cracking exists despite chemical homogeneity remains at the atomic scale. The large grain size resulted high residual stress was believed to be the root cause for hot cracking instead.

To minimize the hot cracks within SLM-built CoCrFeNi, aluminum was proportionally added. With a minor amount of Al_{0.1}CoCrFeNi, material becomes softer and its load bearing ability decreases, which leads to more cracks. When high amounts of aluminum are introduced for Al_{1.0}CoCrFeNi, the primary solidified phase changes to a brittle B2 phase. It is more prone to hot cracking due to its low fracture resistance. Interestingly, the Al_{0.5}CoCrFeNi composition decreases hot cracks. Its unique phase formation sequence introduces the ordered NiAl B2 phase and the disordered Cr-enriched BCC phase at the hot cracking susceptible grain boundary regions. These secondary phases effectively alleviate the large tensile residual strains. As a result, the hot cracking issue of the material is improved significantly.

Chapter 9 Future Work

Building upon the existing knowledge from the present work, there are several aspects that could be further explored in the future. Firstly, the crystallographic texture control methods developed in the present work could be further employed for other metal and alloys. Though, deformation twinning does not exist for materials with high stacking fault energies. However, it is expected that materials properties which are depended on crystallographic orientation such as electrical conductivity could be manipulated to suit various needs.

Secondly, pre-alloyed $\text{Al}_{0.5}\text{CoCrFeNi}$ powders should be used for the SLM fabrication as well. Though samples built with blended powders have shown promising tensile properties, there is inevitably the presence of chemical heterogeneity within the as-built samples. There is a general belief that the pre-alloyed powders can produce products with better qualities compared to the blended powders. Thus, it should be fabricated for validation purposes.

Lastly, physical material data of the new high-entropy alloys should be investigated. Unlike commercial alloys which has been widely studied and examined, HEA's material data base is very limited. It severely hindered the material development process. For instance, thermophysical information is severely lacking to simulate and/or predict the microstructure experiencing fast cooling process for SLM.

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