In-situ alloying of beta titanium for implant application via laser powder bed fusion

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IN-SITU ALLOYING OF BETA TITANIUM
FOR IMPLANT APPLICATION VIA LASER
POWDER BED FUSION

HUANG SHENG
SCHOOL OF MECHANICAL & AEROSPACE ENGINEERING

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APPLICATION VIA LASER POWDER BED FUSION

HUANG SHENG

SCHOOL OF MECHANICAL & AEROSPACE ENGINEERING

A thesis submitted to the Nanyang Technological University in partial fulfillment of
the requirements for the degree of Doctor of Philosophy

2021

Statement of Originality

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

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Huang Sheng

Supervisor Declaration Statement

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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Yeong Wai Yee

Authorship Attribution Statement

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

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The contributions of the co-authors are as follows:

- Prof. Yeong provided the initial project direction and edited the manuscript drafts.
- I prepared the manuscript drafts on topics related to *in-situ* alloying.
- Dr. Sing prepared the manuscript drafts on topics related to multi-metal processing.
- Dr. Tey collected accurate information on multi-metal processing using methods other than laser powder bed fusion.
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- Prof. Yeong suggested the research direction and edited the manuscript drafts.
- I wrote the drafts of the manuscript. The manuscript was revised together with Dr. Sing, Delooze, and Wilson.
- I performed the experiments and analysis on samples' quality, phase constituents, element composition, microstructure, tensile properties and fractography.
- Dr. Sing performed the experiment and analysis on material's biocompatibility. Tensile test experiment and materials fabrication were done with the assistance of Dr. Sing.

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Abstract

By manufacturing biomedical β -Ti alloys with Laser Powder Bed Fusion (LPBF), the “stress shielding” problem can be alleviated through compliance matching between bones and the implant. The “stress shielding” effect occurs when the stiffness of an implant is higher than that of the bone. This will lessen the load being bore by the bone, leading to bone resorption and ultimately implant loosening. For the author’s research, manufacturing of β -Ti using LPBF was done by *in-situ* alloying due to its relatively lower cost, compositional flexibility as well as the potential to achieve compositionally graded parts. In this method, the required proportions of two or more constituent powders are mixed, fed through the hopper, spread over the powder bed and scanned by laser to obtain the alloyed component. However, research gaps still exist in the field of *in-situ* alloyed β -Ti via LPBF. For instance, the effect of biocompatible β stabilizer addition in an *in-situ* alloyed β -Ti is not well studied. Moreover, the relatively high melting point of biocompatible β stabilizer (e.g. Ta & Nb) led to porosity-inclusion dilemma, where the progressively higher energy density input (E_d) effectively reduces the content of unmelted inclusion, but leads to the undesirable formation of keyhole induced porosity in the alloy. The inability to build a part with sufficient quality led to limited understanding on the fracture behaviors of *in-situ* alloyed β -Ti, which is otherwise essential for the structural reliability of an implant.

To address the research gaps, the effects of Ta addition were investigated using *in-situ* alloyed Ti-Ta alloys. With processing using the same laser parameters, the addition of Ta led to defects evolution from keyhole induced porosity to incomplete fusion of melt pools. Ti30Ta (wt.%) provides the optimal mechanical properties for

orthopaedic applications due to its lowest elastic modulus (E) ~ 73 GPa while having the highest yield strength (YS) ~ 950 MPa. The addition of Ta refines the lath/acicular phase size which strengthens the Ti-Ta alloy up to Ti30Ta. However, the usage of Ta led to the issue of unmelted particles due to its high melting point (T_m) of 2997°C . Hence, the study proceeded with the usage of Nb, which has lower T_m of 2468°C and at the same time possesses similar β stabilizing characteristics as compared to Ta. Ti34Nb (wt.%) was chosen due to its similar β stabilizing tendency as Ti30Ta, in which both are near β compositions. Thereafter, a new laser scanning approach was proposed and its feasibility to resolve the porosity-inclusion dilemma was concluded. The combination of high P (~ 650 W or 950 W), high V_L (~ 650 mm/s or 950 mm/s), a top-hat profile laser and a suitable stripe scanning strategy is ideal for fabricating a fully dense Ti34Nb sample with limited content of unmelted Nb inclusions. These parameters result in a slow moving, large melt pool, with a small aspect ratio and melt pool angle, in a single stripe. This ensures uniform mixing of constituents and eliminates keyhole porosities. Nevertheless, the poor ductility associated with Ti34Nb in this thesis led to initial suspicion of insufficient athermal ω suppression due to the lack of β -stabilizer. This led to further study on the fracture behaviors of Ti41Nb (wt.%) and its correlation with the structural characteristics of the material. The formation of layered composite-like mesostructure with alternated Nb deprived region and matrix region was observed, due to the inherent fast cooling rate of LPBF that limits the melting and diffusion of Nb. The crack interactions with the composite-like mesostructure strongly affects the fatigue crack growth (FCG) rate and fracture toughness in an anisotropic fashion. At high ΔK ($> 7 \text{ MPa}\sqrt{\text{m}}$), the FCG underwent severe deflection in the Nb deprived region and slows down the FCG rate. Meanwhile,

crack deflection occurs along the interface of Nb deprived region and matrix region during fast fracture. This improved the fracture toughness of the resultant alloy by almost two-fold despite its brittle failure response in a tensile test.

All in all, the findings in this thesis contributed to the scientific knowledge that is essential to propel the application of *in-situ* alloyed β -Ti.

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List of Figures

Figure 1 E of various implant materials as compared to human cortical bone [6]	2
Figure 2 Strength and Elongation of Designed β -Ti Alloys [11].....	5
Figure 3 Elastic Modulus of Designed β -Ti Alloys [11]	5
Figure 4 Various causes for failure of implants that leads to revision surgery [8]	6
Figure 5 Basic workflow of AM process.....	7
Figure 6 (Left) LPBF machine with a human beside for size comparison, and (Right) Schematic of LPBF process.....	8
Figure 7 Biocompatibility of metals: (a) cytotoxicity of pure metals and (b) relationship between polarization resistance and biocompatibility of pure metals, CoCr alloy and stainless steels. [11]	10
Figure 8 Research overview.....	16
Figure 9 Schematic of SLM build chamber and process. The white fonts illustrate the machine components while the black fonts illustrate the key processing parameters [40].....	18
Figure 10 Macro-morphology of (a) keyhole and (b) conduction melt pools [76]..	24
Figure 11 Optical micrographs of as-built samples revealing the microstructure: (a) Ti6Al4V, (b) (Ti6Al4V)-2Fe, (c) (Ti6Al4V)-3Fe, and (d) (Ti6Al4V)-4Fe. The BD is indicated by the white arrows [102].....	31
Figure 12 Backscattered electron SEM images showing the Pd powder (bright region) “doped” on Ti6Al4V powder [107]	33
Figure 13 Back scattered electron SEM images showing (a) microstructure and (b) magnified region of as-LPBF fabricated Ti6Al4V-0.2Pd where Pd rich region can be seen as bright region [107].....	33

Figure 14 E variation of as-quenched Ti-based alloy with the addition of β stabilizer [23].	41
Figure 15 SEM-EDS image of polished Ti-42Nb tensile test specimen (a) 10x SE mode (b) 50x SE mode (c) 1000x BSE mode and (d) EDS mapping of region shown in (c).	46
Figure 16 The microstructure of the Ti-22Al-25Nb specimens after undergoing different heat treatment conditions: (a) 1250 °C, 2.5 hrs; (b) 1250 °C, 4 hrs; (c) 1350 °C, 2.5 hrs; (d) 1350 °C, 3.5 hrs [146].	59
Figure 17 Electron backscatter diffraction (EBSD) mapping showing the effect of heat treatment on SLM as-built parts from 950 °C ($L_1 + \beta$ field) down to room temperature, forming finer α grains with increasing cooling rate: (a) cooling with a 5 °C min ⁻¹ , (b) cooling with a 100 °C min ⁻¹ . The scale bars indicate a length of 50 μ m. Black lines in EBSD mapping indicate HAGBs ($>10^\circ$) [148].	60
Figure 18 The effect of melt pool depth-to-width ratio on pore formation [160] The effect of melt pool depth-to-width ratio on pore formation [160].	68
Figure 19 Micrograph of AlSi25 sample produced at 400W and 2000 mm/s, some melt pools are marked by dotted lines, and keyhole porosity is indicated by red arrows, BD is building direction [161].	69
Figure 20 Typical defects of in-situ alloyed Ti-Nb binary alloy with increasing E_d (a) porosity (b) unmelted Nb [122].	70
Figure 21 SEM of Ti40.5Nb at different E_d (a) 39 J/mm ³ (b) 214 J/mm ³ [122].	70
Figure 22 OM images revealing the quality of LPBF built Ti-Ta alloys via in-situ alloying: (a) CP Ti (b) Ti10Ta (c) Ti30Ta and (d) Ti50Ta.	83

Figure 23 XRD patterns of LPBF-built in-situ alloyed Ti-Ta alloys with different Ta contents.	85
Figure 24 Line EDS analysis on Ti10Ta part: (a) Line EDS analysis across lath- α boundary (b) Result of line EDS analysis.	87
Figure 25 SEM BSE images revealing the microstructure of LPBF built Ti-Ta alloys via in-situ alloying: (a) CP Ti, (b) Ti10Ta, (c) Ti30Ta and (d) Ti50Ta, with the right portion showing a SE image. (e) High magnification image of the matrix region in Ti30Ta showing fine acicular- α'' phase. (f) High magnification image of Ta poor region in Ti30Ta showing lath- α' phase. (g) High magnification image of matrix region in Ti50Ta showing fine acicular- α'' phase (h) High magnification image of Ta-poor region in Ti50Ta showing lath- α' phase. The red arrows highlight some of the Ta-rich areas/unmelted Ta.	90
Figure 26 EBSD mapping with IPF-Z coloring (BC showing minor phases): (a) CP Ti (IPF coloring for HCP), (b) Ti10Ta (IPF coloring for HCP and BC for unmelted Ta), (c) Ti30Ta (IPF coloring for orthorhombic and BC for unmelted Ta), (d) Ti50Ta (IPF coloring for BCC and BC for HCP), (e) Low magnification BSE image of CP Ti, (f) Higher magnification EBSD mapping for Ti50Ta to highlight lath- α phase. The white arrows highlight some of the Ta-rich areas/unmelted Ta.	91
Figure 27 Pole figure with in-plane axis parallel to the BD (a) Ti (HCP) (b) Ti10Ta (HCP) (c) Ti30Ta (Orthorhombic) and (d) Ti50Ta (BCC).	95
Figure 28 SEM BSE images revealing prior- β grain nucleated from unmelted Ta particle.	97
Figure 29 Mechanical properties of Ti-Ta alloys with different Ta wt.% (a) E (b) UTS (c) YS and (d) ϵ_f	98

Figure 30 Vickers microhardness value of Ti-Ta alloys with different Ta wt.% (a) x-y plane (b) y-z plane.	99
Figure 31 Fractography of (a) CP Ti (b) Ti10Ta (c) Ti30Ta (d) Ti50Ta.	99
Figure 32. Ti34Nb powder mix for in-situ alloying.	107
Figure 33. Schematic representations of (a) Gaussian and top-hat laser profiles, (b) Schematic of single track and single stripe scanning and (c) The scanning strategy employed. The black arrow in (b) indicates the laser scan paths and directions associated with each scan type.....	108
Figure 34 Schematic of model to study melt pool evolution during laser scanning.	111
Figure 35 Images of (a) In-situ alloyed parts built via LPBF and (b) Machined customized tensile coupon. (c) Schematic representation of the customized tensile coupon.....	114
Figure 36 XCT reconstruction showing the 3D porosity and unmelted Nb distribution in the 350W, 650W and 950W samples. Pores and unmelted Nb are marked in green and red, respectively. OM images of the corresponding samples show the 2D appearance of these defects.....	116
Figure 37 Sphericity distribution of Nb inclusions corresponding to 350W, 650W and 950W samples.	117
Figure 38 Representative SEM images of porosity defects: keyhole porosities corresponding to 350W sample and gas porosity corresponding to 350W, 650W and 950W samples.	117

Figure 39 (a) Composition of the three LPBF printed Ti-Nb samples analysed by EDS and (b) their XRD patterns. The error bars represent confidence interval of 99.7%.

..... 119

Figure 40 (a) 3D representative microstructures of 350W, 650W and 950W samples imaged in the BSE mode. Microstructures of the 350W samples (b) near the end of laser scan track, and (c) middle of laser scan track. d) High magnification BSE image of unmelted Nb in the 650W that is enclosed within a yellow rectangle in (a). Dashed lines in (a) are used as guides to show the melt pool boundary..... 121

Figure 41 Texture distribution represented by the (100) pole figure for (a) 350W (b) 650W and (c) 950W samples. 123

Figure 42 Representative grain orientation maps (IPF-Z coloring), obtained using EBSD for (a) 350W (b) 650W and, (c) 950W samples. (d) Pole figure for 350W. LAGB ($2^{\circ} - 15^{\circ}$) are depicted with gray while HAGB ($> 15^{\circ}$) with black lines. The white arrows in (c) indicate the presence of unmelted Nb inclusions. 124

Figure 43 Grain width (short axis of columnar grain) distribution of the as-printed samples..... 124

Figure 44 Representative SEM images of the single tracks (top and cross section view) corresponding to (a) 350W (b) 650W and (c) 950W samples and that of single stripe (top layer, cross section view) corresponding to (d) 350W, (e) 650W, and (f) 950W samples. The maximum angle of melt pool boundaries are measured as the angle tangential to the melt track profile at the intersection between melt track profile and the re-melt layer. 127

Figure 45 A confocal microscopy scan showing the topology of the top surfaces for (a) 350W (b) 650W and (c) 950W samples. The red arrows illustrate the stripe

scanning path of laser (not to be scaled and meant for illustration purposes only). The black lines highlights several frozen ripples within a single stripe scan.	129
Figure 46 Simulated temperature profile snapshots, which represents the melt pool evolution in a single stripe during laser scanning with printing parameters corresponding to (a) 350W and (b) 950W samples. The x-z cross section of the simulated profiles at the locations corresponding to that observed in experiments for parameters corresponding to (c) 350W and (d) 950W samples. y-z cross sections of the same location for (e) 350W and (f) 950W samples. The 200 μm scale bar is applicable for c-f.	133
Figure 47 Tensile stress-strain response and the change in normalized strain hardening rate with true strain of 350W and 950W samples. All values are quoted with confidence interval of 99.7%.	137
Figure 48 Post facto EBSD mapping of the side surfaces of tensile-tested (a) 350W and (b) 950W samples showing twin boundaries overlaid on band contrast. (c) Post facto BSE micrograph of the side surface of tensile-tested 950W sample. (d) Misorientation angle distribution from EBSD analysis in (a) and (b). The representative fracture surface of (e) 350W and (f) 950W sample. The yellow arrows are used to indicate the slip band traces. The BD and tensile direction (TD) are indicated wherever applicable.	138
Figure 49 Plot of dendritic growth, R, and the thermal gradient, G, for Ti34Nb. The range of values of G and R in the melt pools of 350W and 950W samples are superimposed on the plot to assess the possibility of CET.	142
Figure 50 Schematic of stray grain formation due to unmelted Nb particles.	142

Figure 51 Schematic of rotating stripe strategy with stripe scanning corresponding to (a) normal h normal V_L stripe scanning strategy and (b) fast h fast V_L stripe scanning strategy.....	153
Figure 52 (a) Schematic of CT specimens and tensile coupons on a LPBF substrate and (b) Dimensions of the customized tensile coupon.	154
Figure 53 XCT reconstruction showing the 3D unmelted Nb and porosity distribution in the L20, H20, L40 and H40 samples. Quantification of unmelted Nb and porosity in each sample is summarized in a bar chart. Unmelted Nb and pores are marked in blue and red, respectively. All values are quoted with a confidence interval of 99.7%.	159
Figure 54 Phase and elemental constituents of the in-situ alloyed Ti41Nb alloy via LPBF.	161
Figure 55 (a) BS image depicting mesostructure of Ti41Nb. (b) Thresholded image of (a) to highlight banded mesostructure.	162
Figure 56 (a) BS image and (b) grain orientation mapping with IPF-Z coloring to depict the mesostructure of the in-situ alloyed Ti41Nb part. (c) and (d) magnifies the matrix region and Nb depleted region respectively in (a), representing the microstructure of the part. (e) SAED image and (f) bright field TEM image of ω_1 and ω_2 variant, representing the nanostructure of the part. The yellow arrows in (c) and (d) point towards incompletely diffused Nb particle. The white arrows in (d) point towards α'' laths which appear as faint streaks. The white discontinuous circle in (e) is the selected area for dark field TEM image. The zone axis (ZA) of TEM image is given at the bottom of image (e).	163

Figure 57 (a) Grain width distribution and (b) texture distribution represented by the {100} pole figure of in-situ alloyed Ti41Nb via LPBF.	164
Figure 58 Representative tensile stress-strain response of horizontal and vertical tensile coupon.	166
Figure 59 The representative fracture surface of (a) horizontal and (b) vertical tensile coupon. (c) and (d) are the EDS maps corresponding to Nb of fracture surface (a) and (b) respectively. The red dotted circle is used to highlight the cleavage fracture along an elongated grain. The yellow arrows are used to indicate the incompletely diffused Nb particles.	167
Figure 60 Post facto BSE micrograph on the side surface of tensile-tested (a) horizontal and (b) vertical tensile coupon. Post facto EBSD mapping on the side surface of tensile-tested (c) horizontal and (d) vertical tensile coupon. The EBSD maps (c) and (d) were taken from the region covered by the boxes with discontinuous outline in (a) and (b) respectively. The 3D boxes in (d) with discontinuous outline represent the crystallography orientation associated with each grain. The BD and tensile direction are indicated wherever applicable.	169
Figure 61 Representative Paris curve for lay, $\perp$ and $\parallel$ CT specimen, where FCG rate per cycle, da/dN , is plotted as a function of the applied stress intensity factor range, ΔK , in each sample.	171
Figure 62 EBSD band contrast map on the fatigue precracked region of (a) lay (b) $\perp$ and (c) $\parallel$ CT specimen.	172
Figure 63 BSE micrograph on the high ΔK fatigue precracked region of (a) lay (b) $\perp$ and (c) $\parallel$ CT specimen. (d) and (e) are the magnified SE images of (b) and (c) respectively, which aid in the differentiation of secondary cracks and slip traces.	

White arrows in (a), (b) and (c) point the slip traces. Yellow discontinuous arrows in (d) and (e) point the secondary cracks.. The red box in (a) indicates the sawtooth-like crack. Red shading on CT specimen illustration located at the bottom left corner of (a), (b) and (c) shows the corresponding location of BSE micrograph.	174
Figure 64 Optical micrograph on the fatigue fractured surface of (a) lay (b) $\perp$ and (c) $\parallel$ CT specimen. The shaded region on the illustration of CT specimen located at the top right corner of each image shows the location where the fractography is extracted from.	176
Figure 65 Fracture surface of the fast fracture region associated with (a) lay (b) $\perp$ and (c) $\parallel$ CT specimen. The shaded region on the illustration of CT specimen located at the bottom left corner of each image shows the location where the fractography was extracted from.	178
Figure 66 FCG mechanism in the high ΔK region associated with Lay, $\perp$ and $\parallel$ CT specimens.	182
Figure 67 (a) Schematics showing the fast fracture behavior of lay, $\perp$ and $\parallel$ CT specimens. (b) The SEM image of tilted $\parallel$ CT specimen was captured under the SE mode to illustrate the effect of Nb deprived region on crack deflection. The black arrows are pointing toward bands of Nb deprived region. The discontinuous line traces the representative fracture surface in the fast fracture region.....	186
Figure 68 Representative tensile stress-strain response of horizontal tensile coupon extracted from large, small and solution treated large sample.....	189

List of Tables

Table 1 Brief summary on works relevant to in-situ alloying of Ti6Al4V based alloys with LPBF.....	34
Table 2 Brief summary on works relevant to Ti alloys with the addition of biocompatible β -stabilizer in-situ alloyed with LPBF.....	49
Table 3 Brief summary on works relevant to Ti alloys (not classified as Ti6Al4V based or Ti with β stabilizer) in-situ alloyed with LPBF.....	61
Table 4 Melting point, boiling point and density of biocompatible elements commonly utilized in the in-situ alloying process via LPBF [159].	66
Table 5 LPBF process parameters utilized for manufacturing the Ti-Ta alloy samples.	80
Table 6 Porosity and percentage unmelted Ta associated with each alloy composition.	83
Table 7 Percentage Ta content of matrix region, phase(s) and lath/acicular width associated with each alloy composition in-situ alloyed with LPBF. The phase(s) in majority are typed in bold.	84
Table 8 Lattice constant of α and α' martensite in Ti6Al4V.	86
Table 9 Different combinations of LPBF process parameters utilized for manufacturing the Ti-Nb alloy samples.....	108
Table 10 Summary of the defect characteristics and Archimedian density of the three LPBF printed samples. All values are quoted with a confidence interval of 99.7%..	116
Table 11 Dimensions and characteristics of the melt pool obtained from experiments and simulations.	134

Table 12 Different combinations of LPBF process parameters utilized for manufacturing the Ti41Nb alloy samples.	153
Table 13 Tensile properties of horizontal and vertical tensile coupon. All values are quoted with confidence interval of 99.7%.	166
Table 14 Summary of the FCG properties and fracture toughness of in-situ alloyed Ti41Nb in three orientations, based on the experiments conducted on CT specimens. The data in parenthesis indicates the value obtained from individual experiment.	171
Table 15 Tensile properties of horizontal tensile coupon extracted from large, small and solution treated large sample. All values are quoted with confidence interval of 99.7%.	189

List of Abbreviations

2D	Two Dimensional
3D	Three Dimensional
AM	Additive Manufacturing
ASLM	Anchorless Selective Laser Melting
BCC	Body Centered Cubic
BD	Build Direction
BSE	Backscatter Electron
CAD	Computer-Aided Design
CET	Columnar to Equiaxed Transition
CP	Commercially Pure
CT	Compact Tension
CTE	Coefficient of Thermal Expansion
DZ	Deposition Zone
EBSD	Electron Backscatter Diffraction
EDM	Electrical Discharge Machining
EDS	Energy Dispersive X-Ray Spectroscopy
FCG	Fatigue Crack Growth
FEM	Finite Element Method
FESEM	Field Emission Selective Electron Microscope
FIB	Focused Ion Beam
HAGB	High Angle Grain Boundary
HAZ	Heat-Affected Zone
HCP	Hexagonal Closed Packing

IPF	Inverse Pole Figure
KGT	Kurz-Giovanola-Trivedi
LAGB	Low Angle Grain Boundary
LPBF	Laser Powder Bed Fusion
MUD	Multiple of Uniform Density
OM	Optical Microscope
RPM	Rotation per Minute
RZ	Re-melting Zone
SAED	Selected Area Diffraction
SE	Secondary Electron
SEM	Scanning Electron Microscope
SIM	Stress Induced Martensite
SLM	Selective Laser Melting
SM	Stereo Microscope
TEM	Transmission Electron Microscope
US	Ultrasonic
UTM	Universal Testing Machine
UTS	Ultimate Tensile Strength
XCT	X-Ray Computed Tomography
XRD	X-Ray Diffraction
YS	Yield Strength
ZA	Zone Axis

List of Symbols

$\emptyset$	Porosity of the Packed Powder Bed
ΔH	Latent Heat of Fusion
ΔK	Stress Intensity Factor Range
ΔK_o	Threshold for Fatigue Crack Initiation
ΔT	Difference of Melt Pool Maximum Temperature & Material's Solidus Temperature
ΔT_c	Undercooling Temperature
ΔT_n	Nucleation Temperature
A	Absorptivity
b	Thickness of Compact Tension Specimen
Bo	Bond Order
C	Paris Constant
c_p	Specific Heat Capacity
D	Beam Diameter
d	Melt Pool Depth
D_{50}	Median Volume Equivalent Diameter
da/dN	Fatigue Crack Growth Rate
D_L	Solute Diffusivity in the Liquid
$d\gamma/dT$	Sensitivity of Surface Tension With Respect to Temperature
E	Elastic Modulus
E_d	Energy Density
f	Distribution Factor

G	Temperature Gradient Ahead of Solidification Front
h	Hatch Spacing
h_c	Convection Heat Transfer Coefficient
K	Heat Conductivity
K_{IC}	Mode I Fracture Toughness
L	Characteristic Length of Melt Pool
l	Length of Melt Pool
m	Paris Exponent
Ma	Marangoni Number
Md	Metal d-orbital Energy Level
Mo_{eq}	Molybdenum Equivalency
N_o	Density of Heterogeneous Nucleation Sites for Equiaxed Grains
P	Power of Energy Source/Laser
P_d	Power Density Distribution of Laser Source
Q	Heat Input
q_{conv}	Convective Heat Loss
q_{rad}	Radiative Heat Loss
R	Dendrite Growth Rate
R_{load}	Load Ratio
r	Radial Distance of Any Point From the Axis of the Heat Source
r_o	Radius of the Heat Source
S	Stripe Width
S_d	Laser Absorption Depth
t	Layer Thickness

T_{eq}	Equilibrium Solidification Range of the Alloy
T_o	Ambient Temperature
U_{Nb}	% Unmelted Nb (Relative to the Volume of Nb Addition)
U_p	% Volume Fraction of Porosity
V_L	Scanning Velocity
V_m	Melt Pool Velocity
w	Melt Pool Width
W	Width of Compact Tension Specimen
α	Thermal Conductivity
ε	Emissivity
ε_e	Engineering Strain
ε_f	Strain to Failure
θ	Volume Fraction of the Solid Phase
λ	Thickness of Simulated Volume
μ	Dynamic Viscosity
ρ	Density of Material
σ	Stefan-Boltzmann Constant
σ_e	Engineering Stress
Ψ	Sphericity of a Pore/Inclusion
Π	Surface Area of a Pore/Inclusion
Φ	Volume of a Pore/Inclusion

Table of Contents

List of Publications and Awards	VI
Abstract	VIII
Acknowledgement	XI
List of Figures	XV
List of Tables	XXIV
List of Abbreviations	XXVI
List of Symbols	XXVIII
Table of Contents	XXXI
Chapter 1 Introduction	1
1.1 Background	1
1.2 Motivations.....	10
1.3 Objectives.....	14
1.4 Research Methods	14
1.5 Organization of Report.....	17
Chapter 2 Literature Review	18
2.1 Introduction	18
2.2 Laser Powder Bed Fusion	20
2.3 In-situ Alloying of Titanium Alloys using Laser Powder Bed Fusion	28
2.3.1 Ti6Al4V Based	28
2.3.2 Ti with β Stabilizers	37

2.3.3	Other Ti Systems.....	56
2.4	Research Gaps - In-situ Alloying of β -Ti for Structural Implant Application via Laser Powder Bed Fusion.....	64
2.4.1	Effect of β Stabilizer Addition.....	64
2.4.2	Porosity-inclusion Dilemma	67
2.4.3	Material's Crack Responses.....	73
2.5	Summary	76
Chapter 3	Laser Powder Bed Fusion of Ti-Ta Alloys: Compositions and Designs for Biomedical Applications	78
3.1	Introduction	78
3.2	Experimental Details	79
3.2.1	Laser Powder Bed Fusion	79
3.2.2	Metallographic Characterization.....	80
3.2.3	Mechanical Characterization	81
3.3	Results and Discussion.....	82
3.3.1	Quality of Ti-Ta Parts	82
3.3.2	Microstructures of Ti-Ta Parts.....	84
3.3.3	Mechanical Properties of Ti-Ta Parts	97
3.4	Summary	100
Chapter 4	Resolving the Porosity-unmelted Inclusion Dilemma During <i>In-Situ</i> Alloying of Ti34Nb via Laser Powder Bed Fusion	102

4.1	Introduction	102
4.2	Experimental Details	106
4.2.1	Laser Powder Bed Fusion	106
4.2.2	Sample Evaluation	108
4.2.3	Metallographic Characterization.....	109
4.2.4	Finite Element Method Simulation.....	110
4.2.5	Mechanical Characterization	113
4.3	Results	114
4.3.1	Sample Quality.....	114
4.3.2	Phase Constituents and Microstructure.....	118
4.3.3	Melt Pool Morphology.....	125
4.3.4	Thermal Analysis of Melt Pool.....	129
4.3.5	Tensile Properties.....	134
4.4	Discussion	139
4.4.1	Mechanisms of Microstructure Formation.....	139
4.4.2	Melt Pool Size Control by Parameter Optimization	143
4.5	Summary	148
Chapter 5 Fracture Behavior of Laser Powder Bed Fusion Fabricated Ti41Nb via <i>In-situ</i> Alloying.....		150
5.1	Introduction	150
5.2	Experimental Details	152

5.2.1	Laser Powder Bed Fusion	152
5.2.2	Sample Evaluation	155
5.2.3	Metallographic Characterization.....	155
5.2.4	Mechanical Properties Characterization	156
5.3	Results	158
5.3.1	Parametric Study	158
5.3.2	Phase Constituents and Structural Characteristics	160
5.3.3	Tensile Behavior	165
5.3.4	Fatigue Crack Growth.....	169
5.3.5	Fracture Toughness	177
5.4	Discussions.....	178
5.4.1	Composite Effect of <i>In-situ</i> Alloying	178
5.4.2	Build Size Effect	186
5.5	Summary	191
Chapter 6	Conclusions and Future Work	193
6.1	Conclusions	193
6.1.1	Laser Powder Bed Fusion of Ti-Ta Alloys: Compositions and Designs for Biomedical Applications.....	193
6.1.2	Resolving the Porosity-unmelted Inclusion Dilemma During <i>In-Situ</i> Alloying of Ti34Nb via Laser Powder Bed Fusion	194

6.1.3	Fracture Behavior of Laser Powder Bed Fusion Fabricated Ti41Nb via In-situ Alloying.....	195
6.2	Future Work	196
6.2.1	Compositional Design for <i>In-Situ</i> Alloying.....	196
6.2.2	Modelling of <i>In-situ</i> Alloying Process.....	197
6.2.3	Understanding Strengthening Mechanism of Heterogenous <i>In-situ</i> Alloyed Component.....	197
6.2.4	Develop Methodology to Obtain Elastic Modulus of Heterogenous <i>In-situ</i> Alloyed Component via Ultrasound Device	197
6.2.5	Explore and Understand Capabilities of Top-hat Laser.....	198
6.2.6	Leverage on the Nucleation Phenomena of Partially Melted Particles	198
6.2.7	Develop Post-fabrication Heat Treatment Procedure	198
6.2.8	Understand Fracture Behavior under Operating Condition	199
	Appendix A Thermophysical properties of Ti34Nb (wt.%)	200
	Appendix B Melt Pool Evolution of 350W Ti34Nb (wt.%) Sample	201
	Appendix C Melt Pool Evolution of 950W Ti34Nb (wt.%) Sample	202
	Appendix D Slip Plane Associated with 350W Ti34Nb (wt.%).....	203
	Appendix E Simulated Thermal Profiles of Melt Pools Formed with Different Profiles and Spot Diameters Associated with 950W Ti34Nb (wt.%) Sample.....	205
	References.....	206

Chapter 1 Introduction

1.1 Background

Biomedical implants play an important role to replace missing, damaged, or weakened biological structures. Their impact on life is paramount for their ability to improve people's quality of life and even extend a person's life span. Unfortunately, structural implants like the hip joint replacement cannot always outlast a human's life. For instances, a comprehensive review by Ridzwan et al. shows that almost 10% of hip joint replacements performed need to undergo revision surgery and the probability of this can increase depending on the patient's condition. More than half of these revision surgeries are due to the loosening of implant and can largely be attributed to the effect of "stress shielding" [1]. The "stress shielding" effect is in accordance to the Wolff's law, stating that the bone in a healthy person or animal will adapt to the loads in which it is placed [2]. Current common commercial structural implant materials like 316L stainless steel (SS316L), CoCr, and Ti6Al4V have elastic modulus (E) that is significantly higher than that of cortical bone as illustrated in Figure 1. This will lessen the load being bore by the bone, leading to bone resorption and ultimately implant loosening. Moreover, implant loosening can also be attributed to other causes like wear, high joint space fluid pressure, bacterial infection and genetics [3].

Implant revision surgeries are expensive and dangerous. For instances, implant removal poses risks for re-fracture, nerve damage and infection due to second surgical exposure in scarred tissue [4]. As a patient becomes older or weaker, the risk of complications during a revision surgery increases exponentially. Aseptic loosening

of implants can affect a patient in as short as 10-20 years after the joint replacement surgery, which can be the result of insufficient initial fixation, gradual mechanical loss of fixation, or biologic loss of fixation due to particle-induced osteolysis around the implant [5]. This limited lifespan of structural implant could not cater for the need of contemporary society as the human's life span improves due to advancement in life sciences. There is also a need for long term implant for those of younger age. Hence, these calls for an improvement in the long-term fixation of an implant.

Figure 1 E of various implant materials as compared to human cortical bone [6]

One of the many directions to improve the quality and longevity of an implant is through materials exploration. Most of the current commercial implant materials, e.g. SS316L, CoCr, and Ti6Al4V, were originally deployed for their high corrosion resistance [7]. Besides, Ti6Al4V specifically found its way from the aerospace industry into the implant industry owing to its excellent biocompatibility [8]. These implant materials were however not designed with long term side effects in mind, thereby causing potential problems to the receiving patients. These problems include, but not limited to, the issue of stress shielding. CoCr and SS316L have high E (>200 GPa) as compared to human cortical bone (17.6 – 28 GPa) [9], potentially leading to

detrimental problem of osteolysis. Despite having a lower E for Ti6Al4V (around 130 GPa), the E of Ti6Al4V is still many times higher than that of human cortical bone. In addition to stress shielding, the alloying elements in these implant materials have been associated with cytotoxicity (Ni in SS316L, Co and Cr in CoCr, as well as Al and V in Ti6Al4V). The potential harm brought about by these elements shall not be further discussed here but it is good to mention that a comprehensive review on the toxicity of these elements has been done by Wapner [10].

Therefore, new β -Ti alloys composed of “non-toxic” elements such as Nb, Ta, Zr, Mo and Sn were since designed to achieve lower E , greater strength and greater corrosion resistance [11]. Interestingly, these alloy compositions were initially arrived via theory guided bottom up design approach based on the molecular orbital calculation of electronic structure without experimental trial and error. The experimental mechanical properties of these new alloys are shown in Figure 2 and Figure 3. It is worth noting that E as low as ~50 GPa can be achieved in these β -Ti alloys. It is also worth mentioning that some of these alloys have since become commonly used biomaterials for implants (e.g. Ti13Nb13Zr and Ti29Nb13Ta4.6Zr) [9].

It should be noted however that the term “non-toxic” should not be taken at face value, as the biocompatibility of “non-toxic” elements was often demonstrated on relatively large specimens in a relatively short time frame of less than a year [12-14]. For instances, Ti particles trigger cell engulfment and led to inflammatory response when they are smaller than the human neutrophil cells ($< 3 \mu\text{m}$) [15]. Meanwhile, Sn in the form of nano-oxides were shown to be cytotoxic to human breast [16], lung [17], colorectal [17] and liver [18] cells. In short, the “non-toxic” elements can be cytotoxic

in different size and form (a product of the element). Overtime abrasion and corrosion of Ti-based implant can release fine particulates[15], which may then lead to bone loss and osseointegration failure due to inflammatory reactions [19]. Hence, research on long term toxic response of metal implants composed of “non-toxic” elements remains an important topic, but is out of the scope of this thesis. Nevertheless, as of now, these “non-toxic” elements are deemed safer than other metallic elements such as Al, V and Ni [11].

*ST signifies Solution Treated and STA signifies Solution Treated plus Aging

Figure 2 Strength and Elongation of Designed β -Ti Alloys [11]

*ST signifies Solution Treated and STA signifies Solution Treated plus Aging

Figure 3 Elastic Modulus of Designed β -Ti Alloys [11]

Generally, a long-lasting implant should mitigate all potential causes of implant failure that leads to the need of revision surgery. Some of the common causes for failure of implants that leads to revision surgery are summarized in Figure 4.

Figure 4 Various causes for failure of implants that leads to revision surgery [8]

Instead of getting into the race of new material development, an alternative way of implant's bone modulus matching can be realized via proper manufacturing route to introduce porosity, lattice structure or achieve topological optimization. With the free-form fabrication capability of additive manufacturing (AM) technologies, systematically induced lattice structure (similar to homogenous porous material) and near net-shape topologically optimized implant can be realized. Besides, AM can

potentially produce functionally graded implant to meet stiffness and strength criteria while achieving excellent osseointegration property at the same time. As opposed to the traditional subtractive and formative fabrication methods, AM fabricates part via the addition of materials and a quick description of the process can be seen in Figure 5. One of the AM technology suitable for such feat is the laser powder bed fusion (LPBF) process.

Figure 5 Basic workflow of AM process.

The LPBF technology is classified as one of the powder bed fusion (PBF) techniques according to the ISO/ASTM standard [20] and is able to produce near-full-density part superior to casted part while comparable to wrought part [21]. As the technological classification implies, LPBF fabricates parts layer upon layer via laser fusion of intended powder bed areas. During fabrication, the laser source is deflected by the XY deflection system onto the powder bed to selectively melt the area specified by the software/user. The platform supporting the powder bed then goes

down by a layer thickness (t) (typically between 30 μm and 50 μm) where a fresh new layer of powder is subsequently re-coated. The process then repeats itself to fabricate parts with three dimensional (3D) geometry. Figure 6 illustrates the LPBF machine as well as a schematic of the LPBF process.

Figure 6 (Left) LPBF machine with a human beside for size comparison, and (Right) Schematic of LPBF process.

As compared to the directed energy deposition and electron beam powder bed fusion process, LPBF process has better resolution due to the smaller powder size range used. LPBF process exhibits rapid cooling cycle similar to that of quenching process, leading to the strengthening of part due to the refined microstructure [22]. The quench-like process also allows the stabilization of metastable β phase in low modulus Ti alloys and enables the control of strength afterwards by suitable heat treatment process to precipitate the α phase [23].

LPBF offers multiple benefits that potentially improves implant's quality and lifetime. First of all, LPBF is able to produce fully functional intricate parts on a short notice, achieving mass customization of implant that can better fit patient's anatomy [24]. Off the shelf implant has been used with traditional manufacturing methods and they do not always fit a patient's anatomy. Moreover, LPBF is able to fabricate open

porous structures that promotes osteo-integration of bone [25]. The ability to build lattice structures with LPBF also allows matching of E with appropriate scarification of strength to mitigate “stress shielding” effect [26]. Specially designed negative Poisson’s ratio lattice structures can be built to mitigate the effect of bone resorption as well [27].. In short, LPBF has immense potential as a mean to fabricate metal structural implants.

1.2 Motivations

The need to reduce stress shielding in load-bearing implants has pushed for extensive research in different alloy systems especially the β -Ti [28]. The β -Ti group is one of the most popular choice of alloys due their low E and biocompatibility when alloyed with proper alloying element(s). β -Ti stabilizer like Nb and Ta are of high biocompatibility and are the primary choices of elements for consideration when it comes to biocompatible β -Ti alloys (Figure 7). Elements like Zr, Mo and Sn can be added to modify phases and microstructure of resultant alloy if needed.

Figure 7 Biocompatibility of metals: (a) cytotoxicity of pure metals and (b) relationship between polarization resistance and biocompatibility of pure metals, CoCr alloy and stainless steels. [11]

Low modulus β -Ti alloys are often metastable and requires high cooling rate to manufacture [29]. It is often difficult to achieve uniform cooling rate in a bulky part manufactured with conventional manufacturing techniques like casting and forging. The LPBF is naturally designed for this job due to its quench-like rapid laser melting and cooling cycle, aside from being able to manufacture a near-net shape β -Ti part straight from a computer-aided design (CAD) file. The LPBF's unique characteristic

of thermal history offers the opportunity to tailor the microstructure of an alloy, potentially achieving different materials properties as compared to those produce via conventional methods [30].

As mentioned in the introduction, metal implants of high geometrical freedom can be customized to different patients using the LPBF process. The issue of “stress shielding” can be further reduced by designing an implant with matching E via impartation of cellular scaffold structure [31]. Furthermore, existence of *in-situ* alloying via LPBF process further the potential to produce high quality implant by enabling functionally graded implant. With the many advantages LPBF has to offer, LPBF has been chosen as the primary choice to manufacture the implant material for this research.

Despite having promising benefits, LPBF still has the issues of limited materials library and lack of understanding on how LPBF produced materials behave. This research strives to further contribute in the field of implant’s material manufacturing with LPBF. However, the usage of LPBF in real world application is yet to be normalized and pre-alloyed powder with good printability is not always available off-the-shelf. Pre-alloyed powders of new material compositions are often expensive and the cost is based on the economy-of-scale. The unavailability of spherical pre-alloyed powder for new alloy systems is one of the major challenges faced by development and research of new material. In order to manufacture unconventional Ti-based biomaterial with LPBF, the *in-situ* alloying route using powder blends of elemental powders instead of pre-alloyed powder can be chosen. The usage of powder blend as raw material greatly lowers the powder cost by mitigating the need of developing new parameters for atomization process as well as cutting the fixed cost required to

run a new series of powder production. *In-situ* alloying also offers greater research flexibility as new material's composition can be mixed on the go, hence eliminating the lead time of powder procurement process. Although challenging, understandings on *in-situ* alloying via LPBF could open up potentials to achieve parts with compositional gradient, providing better flexibility to implant's design. It is good to note that promising results had been achieved by *in-situ* alloyed biocompatible β -Ti targeted at structural implant application, through the demonstration of high yield strength (YS), low E , high strain to failure (ϵ_f) and good biocompatibility [32].

There are certainly strong incentives to fabricate biomedical structural implant using *in-situ* alloyed β -Ti fabricated via the LPBF process. However, the advantages offered by *in-situ* alloying does not come without drawbacks. To name a few, the issue of excessive vaporization of powder or unmelted powder particles can occur when powders of different melting and vaporizing temperatures are used. Moreover, macro-segregation of elements can occur when insufficient time is given for their diffusion, which usually appears as partially molten particles, especially in the extremely fast thermal cycle of laser melting process. This could lead to potential galvanic corrosion and compromises the longevity of an implant. Deviation and variation of mechanical behavior from the planned alloy composition can also be an issue. In some cases, this will also lead to unwanted intermetallic formation that embrittles the alloy. Fortunately, Ti has near neutral enthalpy of formation with Ta and Nb [33]. Hence, Ti-Ta and Ti-Nb based implant alloys do not generally form intermetallic even with severe compositional macro-segregation. Besides, the unmelted particles due to large melting point differences can lead to weak interface between particles and matrix. In contrast, an increment in volumetric energy density

input (E_d) to eliminate the unmelted particles typically leads to the formation of keyhole porosity. These issues associated with *in-situ* alloying via LPBF brings upon extra complication to the resultant parts especially in terms of mechanical properties. The mechanical properties of a material are crucial for the safe and reliable deployment of biomedical structural implant, which extends beyond tensile properties into fatigue and fracture properties. The current lack of understanding on the subject will hinder the application of *in-situ* alloyed β -Ti implant in a real-world setting. Hence, there is a need to explore how the *in-situ* alloying process affects the manufactured β -Ti and its associated mechanical properties.

The mechanical properties of a material are largely affected by its composition, defects and structural characteristics. At present, the compositional design guideline of β -Ti manufactured through the *in-situ* alloying route is not well established. The compositional optimization process of *in-situ* alloyed β -Ti is also neither straight forward nor well understood. For instance, the addition of β stabilizer into a Ti system can improve the desired material properties, but at the same time increase the tendency to form a component with compositional macro-segregation due to partially molten and diffused particles. Moreover, the process optimization of *in-situ* alloyed β -Ti was not well executed in the past to minimize the content of defects. Consequently, the studies on *in-situ* alloyed β -Ti is largely limited to only tensile behaviors. Without achieving parts of sufficient quality, the progress towards the relatively complicated and expensive mechanical tests such as the fatigue crack growth (FCG) and fast fracture studies are limited. The lack of literature on fatigue and fracture behavior for biomedical β -Ti alloys manufactured via LPBF represents

a huge research gap in the area, despite its importance in achieving high quality implant.

1.3 Objectives

There is a lack of literature on compositional design guideline and optimized fabrication strategy for *in-situ* alloyed β -Ti via LPBF. Consequently, there is no FCG and fast fracture studies on *in-situ* alloyed β -Ti, which requires relatively complicated and expensive testing methods. Hence, the research aims to address these research gaps with the objectives as follow:

1. To establish a preliminary compositional design guideline for *in-situ* alloyed β -Ti based on the resultant part's quality and mechanical properties.
2. To develop a novel laser scanning strategy that improves the *in-situ* alloying capability of LPBF process.
3. To understand the tensile behaviors, FCG characteristics and fracture mechanisms of *in-situ* alloyed β -Ti alloy manufactured via LPBF.

The research overview of the thesis is summarized in Figure 8.

1.4 Research Methods

The methods of the research are as follow:

1. X-ray computed tomography (XCT) for 3D defects reconstruction.
2. Stereo microscopy (SM), optical microscopy (OM) and field emission scanning electron microscopy (FESEM) for surface imaging. FESEM is also often simply referred as scanning electron microscopy (SEM).

3. X-ray diffraction (XRD), electron backscatter diffraction (EBSD), and transmission electron microscopy (TEM) for phase identification based on diffraction analysis.
4. Energy dispersive x-ray spectroscopy (EDS) for composition analysis.
5. Universal testing machine (UTM) for tensile testing of the *in-situ* alloyed samples. UTM also utilized for fast fracture and FCG characterization on half compact tension (CT) specimens, based on ASTM E399-12 and ASTM 647-15 standards.
6. Thermal finite element method (FEM) simulations for the study of melt pool evolution.

Figure 8 Research overview.

1.5 Organization of Report

This thesis consists of six chapters.

The background, aim, objectives and scope of the research are first given in Chapter 1. Chapter 2 is dedicated to the reviewing of past theories, methods and findings related to *in-situ* alloying of Ti alloys via LPBF. The research gaps for *in-situ* alloyed β -Ti are identified and summarized based on the literature review.

The effect of increasing Ta addition in Ti-Ta alloys is investigated in Chapter 4. The process-structural-property correlation is established based on the increasing amount of Ta content. Building from the takeaway in Chapter 3, a composition of Ti34Nb (wt.%) is used in Chapter 4, with a focus on new processing strategy development for *in-situ* alloying via LPBF. The improvement of *in-situ* alloying capability is explained based on the melt pool evolution observed through thermal modelling and experimentation. The experimental details will be included in each chapter due to the differences in research equipment, methodologies and materials.

The scientific understanding from Chapter 4 leads to slight modification in composition and fabrication approach in Chapter 5, which focusses on the mechanical properties of Ti41Nb (wt.%) at different orientations. The effects of *in-situ* alloying on the anisotropic tensile, FCG and fast fracture properties are explained based on the resultant material's structural characteristics.

In Chapter 6, conclusions and possible future work of this research are presented.

Chapter 2 Literature Review

2.1 Introduction

LPBF, also commonly known as selective laser melting (SLM), is an AM technique [34, 35] that has shown promising potential when applied to alloys [36] and ceramics [37, 38]. It facilitates near-net-shape manufacturing as the process starts from the preparation of CAD data files which are subsequently aligned with processing parameters and meshed into two dimensional (2D) stacked layers by computer software. The production process includes a loop of depositing layers of powder onto a substrate plate or previously processed layers, selectively melting the powder with a high energy laser beam according to each layer profile, lowering the platform by one-layer thickness, and then recoating a new layer of powder. The process ends with the deposition and melting of the last sliced layer of the 3D components [39]. Figure 9 illustrates the schematic of LPBF process and principles. The white fonts indicate the machine parts and the black ones are controllable parameters.

Figure 9 Schematic of SLM build chamber and process. The white fonts illustrate the machine components while the black fonts illustrate the key processing parameters [40].

LPBF allows quick 3D printing of parts with complex geometries directly from powders without the time-consuming mold design process [41-44]. Near-net shape manufacturing makes them suitable for end applications or at least minimizes the extent of post-processing. However, polishing and heat treatment are sometimes essential for LPBF parts [45]. LPBF results in superior property in parts compared to counterparts produced by conventional methods due to the ultrafine and graded microstructure attributed to the rapid cooling and solidification cycles (with cooling rate of 10^3 to 10^6 °C/s) during the process [46-48]. While LPBF exhibits promising potential in the production of parts with unique structure and properties even with metallic glass and metal matrix composite at a fair cost [49-52], there is still limited applications of this process in the industry. One of the main challenges is the limitation of materials available for LPBF. As mentioned, there has been extensive work done on LPBF processed materials, most of these alloys were designed for conventional methods. The widely known established materials for LPBF are stainless steel, tool steel, Ti6Al4V, and AlSi10Mg. Hence, there is a need for new alloys designed specifically for LPBF. The capability of LPBF to process powder mixtures has opened new and exciting material research opportunities, especially for metal matrix composites which have been researched widely. “*In-situ* alloying” is a term coined for using LPBF to simultaneously fabricate functional parts and to create alloys via mixed powder feedstock. This strategy has the potential for rapid design and verification of new alloys. While there are great promises, defects and issues unique to LPBF remain a significant concern. Therefore, to achieve *in-situ* alloying by LPBF, a thorough understanding of both materials and LPBF processing parameters is necessary.

Several reviews that focused on the knowledge of the LPBF process of metals or alloys are available [53-56]. The usage of powder mixtures instead of pre-alloyed powder incur changes in the physical properties of materials, thus affecting the melt pool's thermal and rheological behavior, resulting in the shift of LPBF processing window. A comprehensive understanding of the fabrication process and its relationship with part's performance is necessary, and this work seeks to gain a thorough understanding of the associated scientific and technological knowledge.

This chapter focuses on the *in-situ* alloying approach within the perspectives of LPBF. Other AM techniques are not within the scope of this review. Physical phenomena in LPBF will first be introduced to offer a basic understanding of the scientific challenges of this approach. An in-depth review of the fabrication consideration related to *in-situ* alloying of Ti alloys, including the materials and related processing parameters, is then presented. Emphasis on parts' physical properties and powder preparation techniques for *in-situ* alloying are placed in this review. The final part of this review then outlines the current research gaps for the *in-situ* alloying of β -Ti alloys for implant applications.

2.2 *Laser Powder Bed Fusion*

LPBF involves many physical phenomena such as absorption and reflection of laser irradiation, heat transfers, phases transformation, fluid flow, vaporization, emission of materials, and chemical reactions. Concurrently, powder to liquid and liquid to solid transitions happens [57, 58]. It is crucial to understand these physical phenomena and their relations to the successful manufacturing of defect-free parts using LPBF.

Heat absorption occurs during the interactions between laser and powder. Photons from a laser beam are reflected numerous times, however, only a small fraction of its energy is absorbed by the surface of the powder particles [59]. As such, the laser and powder characteristics are both critical in affecting the LPBF melt pool formation and geometry [60]. The power density distribution of laser source which often follows axisymmetric Gaussian profile is given by:

$$P_d = \frac{fP}{\pi r_o^2} \exp\left(-f \frac{r^2}{r_o^2}\right), \quad (1)$$

where f is the distribution factor, P is the power of the heat source/laser, r_o is the radius of the heat source and r is the radial distance of any point from the axis of the heat source. From Equation (1), the laser type and laser diameter, also known as spot size, are accounted for by f and r_o , respectively. These have been reviewed elsewhere [55]. As the laser characteristics are often not as easily varied as powder characteristics, due to them being machine-specific, emphasis in this discussion would only be placed on the controlled laser parameters such as P and scanning velocity (V_L). It is interesting to note that the laser beam can penetrate deeper into a powder bed than into a bulk material of the same composition due to the multiple photons reflections and absorptions [61]. Laser and powder interactions for *in-situ* alloying during LPBF will be further discussed as part of the research gaps.

Heat transfers including heat conduction, convection, and radiation, occurs simultaneously with fluid flow. Fluid flow can be explained using gravity, buoyancy, Marangoni flow, and vaporization. In LPBF, Marangoni flow and vaporization are more significant than gravity and buoyancy, hence, the latter are less discussed [62].

Marangoni flow is surface tension driven [63-65] and happens due to the pulling of liquid with low surface tension towards liquid with higher surface tension. In the melt pool, temperature or composition gradients may generate surface tension difference which results in Marangoni flow [66]. As lasers with Gaussian profiles are typically used in LPBF, the center of the melt pools has the highest temperature. Thus, the fluid flow within the melt pools tends to be radially outward [54]. Marangoni number Ma , which is used to measure the strength of the convective flow, is given below:

$$Ma = -\frac{d\gamma}{dT} \frac{L\Delta T}{\mu\alpha}, \quad (2)$$

where μ is the dynamic viscosity, α is the thermal conductivity of the material, L is the characteristics length of the melt pool, ΔT is the difference between the maximum temperature inside the pool and the solidus temperature of the material, and $\frac{d\gamma}{dT}$ is the sensitivity of the surface tension with respect to temperature.

The material vaporizes extensively when the temperature exceeds its boiling point, and the generated recoil pressures drive the fluid motion in return. High recoil pressure results in the removal of molten material by expulsion while low recoil pressure facilitates smoothing of the melt pool in LPBF [67-69]. Keyhole mode is formed when high recoil pressure is exerted on the melt pool with the laser beam penetrating the material up to a certain depth in LPBF. Additionally, selective evaporation of volatile elements changes the local and global material composition [58, 70]. This is especially important for *in-situ* alloying and will be discussed as a part of the research gaps.

It is important to understand the physical phenomena, hence, a thorough understanding of the variation in material properties due to the influence of processing parameters is important. The key processing parameters involved in LPBF include P , V_L , hatch spacing (h), t . Extensive research has been carried out on various alloys to study their effect on part microstructures and properties [26, 71, 72]. The relationship between densification and processing parameters for *in-situ* alloying resembles the one in typical processing of pre-alloyed powders, except there are additional complications for the emerging systems. Such complications that are dependent on the processing parameters would be detailed in the section on research gaps.

The individual parameters P , V_L , h , and t can be combined into one equation:

$$E_d = \frac{P}{V_L \cdot h \cdot t}, \quad (3)$$

where E_d represents volumetric energy density [73]. Since each material has specific laser absorbance and thermal properties, extensive experimental work must be carried out to obtain a processing window for new material systems that can lead to the production of parts with desired properties. Due to the specific nature of these processing windows, performance degradation can occur if they are applied to other materials [74, 75].

Energy input determines the heat transition modes during LPBF. Keyhole mode and/or conduction mode (Figure 10), distinguished by whether the boiling point is exceeded in the melt pools can occur during LPBF. Also shown in Figure 10, a typical melt pool can be divided into three zones including deposition zone (DZ) on the top,

re-melting zone (RZ) on the nether part, and heat-affected zone (HAZ) in the peripheral area of the melt pool. The length of RZ in keyhole mode is larger compared to conduction ones, penetrating deeper into the previous layers.

Figure 10 Macro-morphology of (a) keyhole and (b) conduction melt pools [76].

These two heat transition modes are related to the densification behavior in a LPBF process. Yang et al. plotted a parameters map for high relative density parts and revealed a limited region for keyhole mode whilst a wide region for conduction mode [76]. Significant vaporization of materials and resultant keyhole pores lead to relatively high porosity for parts formed from keyhole mode. Stable melt tracks with fewer defects are more attainable in conduction mode. Yadroitsev et al. asserted that the maximum temperature of melt pools significantly increases with P and only slightly decreases with V_L [77]. However, Yang et al. investigated the threshold for keyhole mode and highlighted the importance of laser E_d associated with V_L , P , and t , among which V_L is the most significant factor, followed by P and t [76]. Lower V_L indicates longer interactions between laser and materials with higher energy input

which may facilitate keyhole mode. Higher P , which results in higher energy input per second, and thinner t , which results in lesser materials, show a similar tendency to facilitate keyhole mode [78]. Extremely low V_L , high P , and thin t result in instability of the scanning tracks. In such cases, LPBF is accompanied by an increase of the melt volume but a decrease in the melt viscosity. Irregularity appears as the Marangoni effect becomes more significant. The vapor recoil pressure also results in distortion of the melt tracks. The irregularity of the melt tracks, which leads to poor powder depositions, and keyhole pores lead to low relative density. Overlapping hatches are expected to eliminate defects upon repeated re-melting of the part during subsequent laser scanning. h , which is the distance between the laser passes, is a significant variable in determining the E_d . Hence, the porosity and pore morphology vary due to different overlapping conditions of laser scanning tracks in LPBF. Likewise, the t is an essential parameter for layer fusion and hence, relative density. When a thicker t is used, more input energy is needed in melting the powder particles and less heat is left for re-melting of the previous layer. This results in poorer interlayer bonding and more residual pores. Qiu et al. simulated melt pool behavior and asserted that the interaction between the laser beam and melt pool is particularly violent when thick powder layers were processed. This is characterized by significant melt splashing and the increased velocity of melt flow within the melt pools. The increase in porosity and surface roughness as a result of the increase in t is also validated by experiments [79].

Mishra et al. showed that there exists a simple linear relation of h or t to the overlapping cross-sections of the melt pools and thus to the relative density [80].

Many research reported a direct increase in relative density with the h or t [81-83].

However, in some research, there exists a threshold for h [84, 85] and t [86, 87] respectively. Below this threshold, decreasing them would lower the relative density of the parts. Tang et al. established that sufficient overlap of melt pools to avoid incomplete melting is obtained if the following geometric criterion is fulfilled [88-90]:

$$\left(\frac{h}{w}\right)^2 + \left(\frac{t}{d}\right)^2 \leq 1, \quad (4)$$

where w is the melt pool width, and d is the melt pool depth.

As concluded in research done by Yang et al., high densification is more achievable in conduction mode as a wider region for parameter selection is available [76]. Nevertheless, careful optimization is necessary to avoid defects and imperfection.

The melt pool dimensions become too small when the wetting ability is not enough, the contact area between the melt pool and the substrate then becomes considerably limited. This leads to unfavorable wetting, flowing, and spreading characteristics. Melt pools with greater circumference-to-length ratios are supposed to show a more stable behavior [57, 91]. Therefore, balling occurs due to the longer melt pools which tend to become discontinuous with necking. This transition is also associated with P and t as they also affect the E_d . Lower P leads to lower energy input and resembles higher V_L . Although larger t enables a bigger melt pool [79, 86, 92], the melt pool is far away from the substrate, leading to a relatively smaller contact area between the melt pool and substrate that results in the balling effect.

Meanwhile, the laser beam profile plays an important role in deciding the LPBF part's quality. The earliest study that shows the differences between the most commonly

available gaussian profiled laser and the top-hat profiled laser can be back traced to a study by Loh et al. [93]. The gaussian laser was shown to create higher aspect ratio melt pool as compared to the top-hat laser in AlSi10Mg. In the conquest to reduce the cost of LPBF built part, Tenbrock et al. investigated the potential process efficiency of top-hat laser system [94]. They found that as long as the threshold intensity can be overcome, top-hat laser can be robust and efficient in building SS316L parts. Furthermore, Sow et al. found that the top-hat laser provides additional advantage through the improvement of process efficiency, suppression of spatters and the achievement of near full dense parts [95]. Aljaž et al. took advantage of top-hat laser to achieve melt pool with low cooling rate in an attempt to suppress solidification cracking in Hastelloy X [96]. Sun et al. uses top-hat laser to achieve (110) preferred texture in SS316L and simultaneously enhanced the strength and ductility of the parts [30]. While there are many benefits offered by top-hat laser, the available studies are limited. Possible shortcomings of top-hat laser are the poor side surface accuracy and roughness of parts produced due to the broad power distribution, hence it is best used alongside the gaussian laser.

Morphology of powder feedstock also affects the quality of LPBF produced part. Flowability of powder is one of the key powder properties that is affected by powder morphology, which will eventually affect the powder packing density [97]. Spherical powder with limited amount of satellites is typically ideal for powder flowability, in which the flowability deteriorates as the powder deviates from the as-mentioned criteria [98]. Previous studies on powder with angular morphology such as hydride-dehydride produced Ti6Al4V powder [99] and chemically reduced W powder [100] had shown that their poor packing ability can lead to higher tendency

of lack-of-fusion defect. Nevertheless, non-spherical powder typically offers cost advantage and the study on their usage feasibility remains important. In fact, Sing et al. had shown that a mixture of spherical and irregular powder can improve the resultant flowability of powder [32].

Detailed discussions about the formation of different regions within the process window of a material have been addressed elsewhere [55]. The determination of processing parameters for different alloys during *in-situ* alloying remains a challenge and would be discussed in later section.

2.3 *In-situ Alloying of Titanium Alloys using Laser Powder Bed Fusion*

In this section, previous works related to *in-situ* alloying of Ti alloys via LPBF will be reviewed. Despite the focus of the thesis on β -Ti, *in-situ* alloying of other Ti systems will also be covered. The review will be separated into Ti6Al4V based alloys, Ti alloys with β stabilizers and other Ti systems. It is good to mention that *in-situ* alloying is not exclusive to LPBF and is commonly used in other metal AM processes such as the directed energy deposition and electron beam melting.

2.3.1 Ti6Al4V Based

Using Ti6Al4V in original composition, the effect of precursor powder types (mixed powder for *in-situ* alloying or pre-alloyed powder) on microstructures and properties have been studied for LPBF [101]. In the study, pre-alloyed Ti6Al4V powder was used as a benchmark. Three different elemental powder mixtures were then prepared for study, namely: (1) simply mixing powders of similar size, (2) mixing large Ti powder with smaller V and Al powder, and (3) satellite smaller V and Al particles on larger Ti powder. It was found that the usage of (2) and (3) powder mixtures for LPBF

gave better density, homogeneity, and hardness as compared to the usage of (1). However, the powder mixture (3) did not fare as well as the powder mixture (2), mainly because the technique was not optimized in which the elemental V powder used in this study is not small enough to adhere to the Ti powder. Nevertheless, the key finding is that proper mixing and dispersing of small alloying particles with parental elements can produce parts comparable to that of pre-alloyed powder feedstock.

Using a similar technique as Simonelli et al. [101], the same group attempts to suppress the highly columnar prior- β formation of Ti6Al4V through the addition of Fe, which promotes columnar to equiaxed transition (CET) [102]. The choice of element addition was based on the growth restriction factor (GRF) in which high GRF favors constitutional supercooling that can lead to CET. Fe is a viable choice as it demonstrates relatively high GRF value, exhibits unfavorable kinetics to form unwanted intermetallic compounds with Ti, and exhibits similar thermo-physical properties as Ti. Upon investigating the microstructure on the cross section perpendicular to build direction (BD), it was found that the Fe addition of up to 3 wt.% leads to significant grain refinement with little increase in benefits at 4 wt.% (Figure 11). The Fe rejection during solidification inhibits side growth of columnar grain which reduces the competitive growth mechanism. Consequently, more columnar grains persist, leading to grain refinement and less prominent texture as compared to LPBF built Ti6Al4V. The addition of 3 wt.% Fe leads to retention of metastable β grains and forms desirable laminar $\alpha + \beta$ microstructure (while maintaining fine prior- β) upon suitable heat treatment.

To extend the existing LPBF materials library, an attempt to manufacture Ti6Al4V+10Mo (wt.%) had been done [103]. Without the addition of Mo, epitaxial growth from partial re-melting accompanied by stable planar solidification leads to large columnar β grains in Ti6Al4V. However, no columnar β grain was formed after Mo addition as it leads to instability of the planar solidification front and induces cellular solidification. As a result, the growth of β grains is toward the melt pool center. The as-built Ti6Al4V+10Mo (wt.%) was found to be fully β phase. Incompletely diffused Mo particles smaller than 10 μm were found to be randomly distributed throughout the matrix but are too minute to be picked up by XRD. The incomplete diffused Mo can lead to Mo-rich zones in which the β phase is fully stabilized. Depending on the temperature of heat treatment followed by quenching, the microstructure can consist of either $\alpha+\beta$ or fully β phase. With the heat treatment process, the homogeneity of Ti6Al4V+10Mo (wt.%) can be improved, and it gets better with higher temperatures. Similar work was also done by mixing Mo and Fe (which are both β -Ti stabilizer) into Ti6Al4V to form Ti10V2Fe5.5Al (wt.%) [104]. With different heat treatment processes, it was shown that the degree of α and β phases can be tailored to achieve a wide variety of mechanical properties.

Figure 11 Optical micrographs of as-built samples revealing the microstructure: (a) Ti6Al4V, (b) (Ti6Al4V)-2Fe, (c) (Ti6Al4V)-3Fe, and (d) (Ti6Al4V)-4Fe. The BD is indicated by the white arrows [102].

Functionalization of implants through the improvement of anti-microbial properties had been done via *in-situ* alloying of Ti6Al4V+1Cu (at.%) [105]. The ultimate tensile strength (UTS) of Ti6Al4V improved from 1243 to 1550 MPa after the minor addition of Cu. Cu addition also resulted in decreased *E. coli* growth by an order of magnitude and decreased *S. aureus* growth by two orders of magnitude. A similar study was also done by Maxpherson *et.al* using Ti6Al4V+5Cu (wt.%) [106]. It was found that Cu addition leads to a microstructural change from α' to extremely fine $\alpha+\beta$ Widmanstätten structure. Traces of Ti_2Cu were also detected in the matrix that leads to strength improvement. In addition, Ti_2Cu also serves to promote antibacterial

properties. *In-situ* alloyed Ti6Al4V+5Cu (wt.%) shows moderate anti-bacterial property which is inferior to that of casted counterpart, which can be caused by the high cooling rate of LPBF that leads to lesser Ti₂Cu. Maxpherson et al. also did studies on *in-situ* alloyed Ti6Al4V+0.5Ag (wt.%). The resultant alloy shows minimal changes in microstructure but leads to three times increased ductility while retaining the same strength as Ti6Al4V. The Ag addition did show anti-bacterial property but is inferior to the *in-situ* alloyed Ti6Al4V+ 5Cu (wt.%) parts.

To improve corrosion resistance, nano-sized Pd was added into pre-alloyed Ti6Al4V powder [107]. A novel dual centrifugal mixer was used in this study to avoid the possibility of powder agglomeration (low energy blender) and particle morphology change (when a planetary ball mill is used). The bending of one batch of powder can be done in just several minutes with nano-sized Pd being “doped” evenly on the surface of Ti6Al4V particles (Figure 12). *In-situ* alloying of Ti6Al4V+Pd powder mixture resulted in homogenous Pd distribution with occasional Pd rich areas in the form of lines (Figure 13). Pd addition does not affect the mechanical properties significantly but leads to improvement in corrosion properties. It can eliminate the active anodic region by shifting the corrosion potential into the passive region for Ti6Al4V, achieving improved corrosion resistance.

Figure 12 Backscattered electron SEM images showing the Pd powder (bright region) “doped” on Ti6Al4V powder [107]

Figure 13 Back scattered electron SEM images showing (a) microstructure and (b) magnified region of as-LPBF fabricated Ti6Al4V-0.2Pd where Pd rich region can be seen as bright region [107]

In short, *in-situ* alloying of Ti6Al4V with elements like Mo, Fe, Ag, Cu, and Pd have been done to develop new materials that improve biomedical related properties and to reduce the texture strength. Moreover, the pre-alloyed Ti6Al4V system had been chosen as a benchmark to study the effect of precursor powder on the quality of products made via *in-situ* alloying. A table to summarize notable works relevant to *in-situ* alloying of Ti6Al4V derived alloys with LPBF can be found in Table 1.

Table 1 Brief summary on works relevant to *in-situ* alloying of Ti6Al4V based alloys with LPBF.

Purpose	Alloy System	Powder Mix	Blending Method	Blending Parameters	Highest Relative Density	Reference Parameter	Scanning Strategy	Remarks	REF.
Investigation on <i>in-situ</i> alloyed Ti6Al4V-10Mo (wt.%) properties and its response to heat treatment.	Ti6Al4V-10Mo (wt.%)	Pre-alloyed Ti6Al4V (spherical, $D_{50} = 34 \mu\text{m}$) and Mo (irregular, mean 5 to 10 μm)				$P = 250 \text{ W}$ $V_L = 1600 \text{ mm/s}$ $t = 60 \mu\text{m}$ $h = 30 \mu\text{m}$	Zigzag with 90 ° rotation between layers	With heat treatment, the homogeneity of <i>in-situ</i> alloyed Ti6Al4V+10wt.%Mo improved and it got better with higher temperature.	[103]
Expend limited availability of pre-alloyed powder for aerospace industry and investigate the effect of heat treatment on <i>in-situ</i> alloyed Ti10V2Fe5.5Al (wt.%),	Ti10V2Fe5.5Al (wt.%)	Pre-alloyed Ti6Al4V (Spherical, 15 to 45 μm), V (angular, <45 μm) and Fe (irregular, <45 μm)	Tumbling mixer	2 hr	>99.9 %	1064 nm CW $P = 100 \text{ W}$ $V_L = 600 \text{ mm/s}$ $t = 30 \mu\text{m}$ $h = 60 \mu\text{m}$		Degree of α and β phase can be tailored with heat treatment and achieve a wide variety of mechanical properties.	[104]
Enhance anti-microbial property of Ti6Al4V via Cu addition.	Ti6Al4V-1Cu (at.%)	Pre-alloyed Ti6Al4V (spherical, $D_{50} = 22.9 \mu\text{m}$) and Cu (spherical, $D_{50} = 21.9 \mu\text{m}$)		1 hr		1075 nm CW $P = 170 \text{ W}$ $V_L = 700 \text{ to } 1300 \text{ mm/s}$ $t = 30 \mu\text{m}$ $h = 70 \text{ to } 100 \mu\text{m}$ Laser re-melting at each layer.		No unmelted Cu particles found but incompletely diffused Cu causes Cu rich regions of up to 35 wt.%.	[105]

Enhance anti-microbial property of Ti6Al4V via Cu addition.	Ti6Al4V-5Cu (wt.%)	Pre-alloyed Ti6Al4V (spherical, 53 μm) and Cu (rounded, 44 μm)	Tumbling mixer	1.5 hr	98.5 %	1064 nm CW $P = 200 \text{ W}$ $V_L = 1000 \text{ mm/s}$ $t = 50 \mu\text{m}$ $h = 120 \mu\text{m}$ Preheat 200°C .	xy	Shows moderate anti-bacterial property that is inferior to casted part.	[106]
Enhance anti-microbial property of Ti6Al4V via Ag addition.	Ti6Al4V-0.5Ag (wt.%)	Pre-alloyed Ti6Al4V (spherical, 53 μm) and Ag (angular, 1-5 μm)	Tumbling mixer	1.5 hr	98.7 %	1064 nm CW $P = 200 \text{ W}$ $V_L = 1000 \text{ mm/s}$ $t = 50 \mu\text{m}$ $h = 120 \mu\text{m}$ Preheat 200°C .	xy	Ag addition had no effect on microstructure but achieved 3 times better ε_f with similar strength. Showed anti-bacterial property but inferior to part with Cu addition.	[106]
To improve corrosion resistance of Ti6Al4V for biomedical applications.	Ti6Al4V-0.2Pd (wt.%)	Pre-alloyed Ti6Al4V (spherical, 45 to 75 μm) and Pd (Nanoparticles)	Novel dual centrifugal mixer	2500-3500 RPM for several minutes	~100 %	1075 nm CW $P = 400 \text{ W}$ $V_L = 2300 \text{ mm/s}$	Island strategy	<i>In-situ</i> alloying of Ti6Al4V with nanosized palladium powder resulted in homogenous palladium distribution with occasional palladium rich areas in the form of lines.	[107]
To investigate on powder mixture feedstock types on <i>in-situ</i> alloyed part's quality manufactured with L-PBF.	Ti6Al4V	Pre-alloyed Ti6Al4V (spherical, $D_{50} = 33.5 \mu\text{m}$)			99.7 %	1064 nm CW $P = 82 \text{ W}$ $V_L = 500 \text{ mm/s}$ $t = 40 \mu\text{m}$ $h = 90 \mu\text{m}$ Preheat 200°C .		Simply mixing with alloying components of relatively smaller size achieved properties compatible to that produced with pre-alloyed feedstock.	[101]
		Ti (spherical, $D_{50} = 57 \mu\text{m}$), Al (irregular, 45 to 60 μm) and V (irregular, $D_{50} = 21.2 \mu\text{m}$)	Tumbling mixer	20 min	98.2 %				

		Ti (spherical, 40 to 65 μm), Al(irregular, $D_{50} = 6.2 \mu\text{m}$) and V (irregular, $D_{50} = 21.2 \mu\text{m}$)	Tumbling mixer	20 min	99.2 %				
		Ti (spherical, 40 to 65 μm), Al (irregular, $D_{50} = 6.2 \mu\text{m}$) and V (irregular, $D_{50} = 21.2 \mu\text{m}$)	Satelliting via wet mixing with tumbling mixing followed by drying.		99.1 %				
To study the influence of Fe on Ti6Al4V alloy to achieve grain structure refinement and texture suppression.	(Ti6Al4V)-xFe x = 2 to 4 (wt.%)	Ti (spherical, $D_{50} = 33.5 \mu\text{m}$) and Fe ($D_{50} = 5.7 \mu\text{m}$)	Satelliting via wet mixing with tumbling mixing followed by drying.		> 99.8 %	1070 nm (Modulated) $P = 300 \text{ W}$ $V_L = 750 \text{ mm/s}$ $t = 50 \mu\text{m}$ $h = 70 \mu\text{m}$ <0.09% O_2	90° rotation	Fe addition led to grain refinement and weaker texture. The addition of 3 wt.% Fe led to retention of metastable β grains and formed desirable laminar $\alpha + \beta$ microstructure upon suitable heat treatment (while retaining refined prior- β grains).	[102]

2.3.2 Ti with β Stabilizers

In-situ alloying of Ti alloys with β stabilizer via LPBF is mainly for the making of biomedical implants. Biomedical Ti alloys with β stabilizer are the largest group of alloys to undergo *in-situ* alloying. As mentioned in the introduction, biomedical implant plays important role to replace missing, damaged or weakened biological structures [108]. However, most of the current commercial implant materials, e.g. SS316L, CoCrMo, and Ti6Al4V were intended for other industries like the aerospace and marine industries. They are not specifically designed as implant materials, thereby potentially causing problems to the receiving patients. CoCrMo and SS316L have high E of more than 200 GPa while that of human cortical bone range from 17.6 to 28 GPa [109], potentially leading to a detrimental problem of osteolysis. Despite having a lower E for Ti6Al4V, around 130 GPa [6], it is still many times higher than that of human cortical bone. This will lessen the load being borne by the bone, leading to bone resorption and ultimately implant loosening. Moreover, implant loosening can also be attributed to other causes like wear, high joint space fluid pressure, bacterial infection, and genetics [3]. In addition to implant loosening, the alloying elements in these commonly used implant materials have been associated with cytotoxicity, for example, Ni in SS316L, Co and Cr in CoCrMo, as well as Al and V in Ti6Al4V.

To improve the quality and longevity of implants, one of the directions is the development of new materials. Therefore, new β -Ti alloys composed of non-toxic elements such as Nb, Ta, Zn, Mo, and Sn were since designed to achieve lower E , greater strength and better corrosion resistance [11]. β -Ti stabilizers like Nb and Ta have high biocompatibility and are the primary choices of elements for consideration

when it comes to biocompatible β -Ti alloys. Elements like Zn, Mo, and Sn can be added to modify phases and microstructures of resultant alloys if needed.

An alternative way of implant's bone modulus matching can be realized via proper manufacturing route to introduce porosity [110], lattice structure [26, 111, 112], or achieve topological optimization [113]. With the free-form fabrication capability of AM, systematically induced lattice structures (like homogenous porous material) and near-net-shape topologically optimized implants can be realized. When paired with suitable alloy systems (such as low modulus β -Ti), AM can potentially produce functionally graded implants to meet stiffness and strength criteria while achieving excellent osseointegration property at the same time. LPBF is one of the AM techniques that is suitable.

Low modulus β -Ti is often metastable and requires a high cooling rate during the manufacturing process to retain the β phase [29]. It is often difficult to achieve a uniform cooling rate in a bulk part manufactured with conventional manufacturing techniques like casting and forging. LPBF is inherently designed for this due to its quench-like rapid laser melting and cooling cycle, aside from being able to manufacture a near-net-shape β -Ti part straight from a CAD design. LPBF's unique thermal characteristics and history offer the opportunity to tailor the microstructure of an alloy, potentially achieving different material properties as compared to those produce via conventional methods [30].

In-situ alloying using LPBF has been popular to achieve β -Ti using powder mixtures. This is due to the following reasons: (1) as opposed to using pre-alloyed powder, *in-situ* alloying of powder mixture allows for flexible and rapid adjustment of alloy

compositions. Different alloy compositions can be designed and manufactured within a short time frame for a quick study on the link between compositional variation and material properties. Optimal compositions for many alloys have not yet been found for LPBF which allows more research opportunities using *in-situ* alloying, (2) pre-alloyed β -Ti powder containing refractory β stabilizers such as Nb, Ta, and Mo is not easily available due to the huge differences in melting point and density between the stabilizers and Ti. The differences in material properties lead to challenges during the typical gas atomization process that manufacturing the pre-alloyed powder feedstock. Moreover, small batch production of pre-alloyed powder can be expensive. When purchased in small batches (< 15 kg), TiTa and TiNb alloys have significant cost advantage when they are physically mixed (as opposed to their pre-alloyed form). For instances, Ti30Ta (wt%) would cost around 1956 SGD/kg in its pre-alloyed form and 826.70 SGD/kg in its mixed powder form. As for Ti41Nb (wt%), the pre-alloyed form costs around 1818 SGD/kg and the mixed powder form costs around 504.89 SGD/kg. The mixed powder costs can be calculated based on the prices of raw powder, which are respectively 329 SGD/kg, 1988 SGD/kg, 758 SGD/kg for Ti, Ta and Nb. The prices were quoted for powder with spherical morphology and size distribution of 20 – 63 μm in the month of October 2021, and the price is similar for different vendors. Hence, in-situ alloying is currently an important technique for cost reduction from the research perspective and can be useful for small scale special production in a service bureau. That being said, the price gap between the two powder types will certainly decrease overtime with the arrival of new technologies (e.g. lab scale ultrasonic powder atomizer) and service providers. Whenever the cost allows, pre-alloyed powder is still undeniably the go-to choice when a chemically homogenous LPBF part

is required. Nevertheless, in-situ alloying remains future relevant for its ability to produce alloys with compositional gradient [114] or heterogenous microstructure with unique mechanical behaviour [115, 116].

Past studies showed that promising properties can be obtained for β -Ti alloys produced via *in-situ* alloying. *In-situ* alloying of β -Ti typically focused on the reduction of E to reduce the stress shielding effect. The reduction of E had been done with several approaches which include (1) optimization of β -stabilizer addition into Ti, (2) addition of other element(s) into binary Ti alloys with existing β -stabilizer and (3) porosity induction in β -Ti alloys. Despite the lack of pre-alloyed powder, the study on alloys of different compositions as a mission to search for optimal biomedical materials is possible due to the flexibility of *in-situ* alloying. The approaches for E reduction were done via *in-situ* alloying with LPBF and the key findings of each research are as follow:

(1) Optimization of β -stabilizer addition into Ti

Low E with sufficient YS can be, in principle, obtained when full β -phase is retained with minimal alloying components [38]. Past studies had shown that this minimal point can be obtained at 25.5 at.% or 40 wt.% Nb addition for binary Ti-Nb alloys upon quenching. Below the stated minimum Nb addition, undesired α'' and ω phases will be formed, decreasing YS and increasing the E . Above the stated minimum Nb addition, full β -phase can be retained, and the E will increase slowly with additional Nb. As such, most of the past studies on LPBF uses minimal Nb addition of 40 wt.% to retain single β -phase. Experimentally, the minimum E was found to be at the composition of Ti₄₂Nb (wt.%) [23]. Parameters optimization issues aside, most

research done on LPBF of Ti-Nb are on completely metastable β instead of near β compositions. In a typical binary low modulus Ti alloy with non-intermetallic forming β stabilizing element, it is known that two instances of E minima can be typically seen with varying amount of β stabilizer (Figure 14). The second minimum of near 42 wt.% Nb is of greater interest in the community for its lower modulus as compared to that of the first minimum. Depending on the thermal history, Ti alloy can exhibit phases like α , α' , α'' , metastable β , stable β , and ω through the addition of beta stabilizer [117-119]. The α and α' phases can be associated with as-quenched alloys with the minor addition of Nb while α'' , β , and ω phases can be associated with that when Nb addition is near that of fully β stabilized composition [29]. The metastable α' and α'' martensites, as well as the metastable ω phase, are formed when the alloy is rapidly quenched in which their formations are highly dependent on the amount of β -stabilizer added [120].

Figure 14 E variation of as-quenched Ti-based alloy with the addition of β stabilizer [23].

In-situ alloyed Ti-xNb using LPBF where $x = 0, 15, 25, 45$ at.% were studied by Wang *et.al* [121]. It was found that Ti25Nb has the lowest E among other compositions

tested due to its correspondence to full β retention with minimal Nb addition. This composition also demonstrated the best *in-vitro* appetite forming capability, possibly due to it having the highest volume fraction of β -Ti phase, which is associated with appetite nucleation. The addition of more Nb leads to more unmelted Nb volume and decreases the volume fraction of the β -Ti phase. Nevertheless, the *in-situ* alloyed Ti40.5Nb (wt.%) does achieve a comparatively low average E of 77 GPa despite the existence of unmelted Nb particles [122]. Meanwhile, a study by Zhao et al. investigated *in-situ* alloyed Ti-xTa of different compositions ($x = 6, 12, 18, 25$ wt.%) [123]. The composition for E minimization was found to be at Ti25Ta. The Ti25Ta alloy is α' phase dominated, which is the same as that reported by Brodie et al. [124]. Despite being far from β -stabilized compositions, *in-situ* alloyed Ti25Ta shows a low E of 89 GPa with a high YS of 1029 MPa. It was also found that Ti25Ta has the best corrosion resistance in ringer's solution among all other compositions tested due to the formation of stable Ta_2O_3 passive film. The Cl^- anion in ringer's solution can intensify the anodic dissolution of TiO_2 passivating film. The addition of Ta causes a rise in Ta_2O_5 passive layer, leading to better promising candidate for biomedical implants application. Despite having the unmelted Ta, in the study done by Sing et al., Ta dissolution has been proven to be sufficient for the retention of low modulus β -phase. The *in-situ* alloyed Ti50Ta successfully achieved a low E of 75.77 GPa with a high YS of 882.77 MPa [32].

With laser re-melting, the texture strength of Ti42Nb is reduced where prior- β grains close to that of equiaxed grains can be observed. Re-melting-induced texture weakening leads to an improvement of YS from 426 to 545 MPa while maintaining an E of 65 GPa. The strength improvement comes with a reduction of ϵ_f property from 42

25 % to 11 %. These mechanical properties were achieved despite the alloy consisting of mostly α' phase [125]. Another notable finding in this study is on the better choice of E_d in the range of 362 J/mm³ for the *in-situ* alloyed Ti-Ta system, a much higher value as compared to a previous study by Sing et al. (144 J/mm³) [32]. Laser re-melting strategy certainly shows promising potential to advance the *in-situ* alloying using LPBF. The main drawback of the strategy is the significantly increased build time, primarily due to the additional time needed for laser scanning.

The study on near β Ti-Nb system is limited and only two studies were done via *in-situ* alloying with LPBF. One research team had printed parts with the composition of Ti35Nb (wt.%) as an effort to study the effect of inhomogeneity on mechanical and corrosion properties [126]. The as-fabricated and solution-treated (1000 °C at 24 hrs followed by air cooling) samples were compared in the study. XRD analysis shows that the as-printed part is of majority β phase with unmelted Nb particles, achieving an E of 84.7 GPa. It is speculated that the concentrated laser energy source is the cause of incomplete melting/diffusion of Nb particles. Meanwhile, the solution-treated sample shows similar XRD analysis result but without the XRD peaks from Nb, indicating that better homogeneity was achieved. Large unmelted Nb particles act as arrest zones for shear bands and eventually act as stress concentrators for grain bound sliding, leading to poor ductility of as-printed parts as compared to heat-treated parts (38.5 to 47.3 %). A slight decrease in YS was detected after the heat treatment. The heat-treated part also shows better corrosion resistance due to its better chemical homogeneity. Unfortunately, no information on the change in E was shown after heat treatment. In another study, near β Ti20Nb (at.%) was manufactured and traces of α'' martensite were seen in XRD [127]. It was found that the martensite traces decrease

with increased E_d , which is caused by better dissolution of Nb into the matrix. No further studies were done on the alloy system in that research, possibly due to the presence of unmelted Nb. There is a general lack of study on as-fabricated near β binary Ti alloy systems and their mechanical behavior are not well understood.

Although not explicitly stated as an alloy designed for low modulus biocompatible implant, the work on the *in-situ* alloyed Ti-Re system has laid the groundworks for the future LPBF research on the system. Re has almost twice the melting point of Ti (3185 °C and 1668 °C), which leads to incompletely melting of Re particles that can be reduced with increasing E_d [128]. The addition of 5.66 wt.% Re in Ti greatly increases the YS (461 to 1038 MPa) while also reduces the E (119 to 103 GPa). However, the ε_f of the alloy is largely sacrificed down to a value of only 2 %. The phase constituent after Re addition is mainly of α' phase as the Re addition in the study is insufficient to retain the β phase. Further studies on Ti-Re alloys were made on 2 and 4 wt.% Re addition into Ti [129]. It was found that Re addition can lead to the refinement of lath phase α/α' microstructure which can be one of the factors behind the strength improvement. The nature of Re as β -Ti stabilizer leads to β phase retention around the incompletely diffused Re particles with the formation of the brittle ω phase. The ω phase, coupled with refined microstructure and enhanced O_2 level from Re addition eventually leads to brittle fracture characteristic. The brittle characteristic deteriorates FCG resistance of Ti-Re when compared to Ti. For the alloy system to be useful in structural application, further studies are required to ensure its safe use with predictable failure from fatigue loading.

In some cases, *in-situ* alloying technique serves as a quick tool to screen through the effect of element(s) addition on a part's biocompatibility. Using *in-situ* alloying, Wang et al. found that the addition of Nb into Ti leads to better *in-vitro* apatite forming capability as compared to its pure Ti counterpart [121]. A similar study shows that seeding of MC3T3-E1 osteoblast precursor cell line on *in-situ* alloyed Ti25Nb (wt.%) leads to better cell spread and proliferation when benchmarked with Ti parts, in addition to a superior *in-vitro* appetite forming capability [130]. Furthermore, *in-situ* alloyed Ti25Nb (wt.%) scaffold demonstrated impressive immunomodulatory properties [131]. The scaffold was also implanted into rabbit's tibia and shown to better promote bone regeneration and osseointegration as compared to the pure Ti counterpart. As for Ti50Ta (wt.%), Huang et al. found that using the same lattice structures, Ti50Ta possesses similar biological responses to Ti and Ti6Al4V based on the cell proliferation tendency of osteosarcoma cell line SAOS-2 [132]. Meanwhile, Yan et al. demonstrated that Ti15Ta10.5Zr does not induce infection and osteomyelitis in the surrounding of rat's tibia after five weeks of implantation in rat tibia's fracture [12]. All of these observations point toward the promising potential of *in-situ* alloyed Ti-based alloys as a biocompatible material for implant applications.

Pre-alloyed Ti with β -stabilizer is still not widely available and has very limited attempts to study on them. Despite that, a study on Ti45Nb (wt.%) where pre-alloyed powder feedstock was used has been made [133]. XRD patterns on the LPBF part show β -Ti peaks with broadening characteristics possibly due to residual stress in the part. The part showed a compressive strength of 723 MPa. Unfortunately, no E was reported in the study. Another study was done on Ti42Nb (wt.%) processed by LPBF using pre-alloyed powder [134]. Parts built were more homogenous (contains no

unmelted Nb) than those manufactured via *in-situ* alloying and they have a relative density of more than 99.5 %. Figure 15 shows the polished surface of Ti42Nb and occasional microstructural inhomogeneity can be seen in Figure 15c. This feat can be achieved with a relatively low E_d of 40 J/mm³ as compared to those done via *in-situ* alloying (214 J/mm³ when optimized [122]). Full- β matrix was obtained and the alloy also shows better compressive YS as compared to tensile YS (674.08 MPa to 831.58 MPa).

Figure 15 SEM-EDS image of polished Ti-42Nb tensile test specimen (a) 10x SE mode (b) 50x SE mode (c) 1000x BSE mode and (d) EDS mapping of region shown in (c).

(2) Addition of other element(s) into binary Ti alloy with existing β -stabilizer

The addition of Sn to near β Ti-Nb composition (forming Ti37Nb6Sn (wt.%)) has been experimented with to achieve parts with low E [135]. The Sn addition suppresses

hard and brittle ω precipitation in Ti-Nb of near β composition, in which the precipitation can lead to an increase in E . The study also found that increased Sn leads to more preferential [100] grain growth towards the BD. The optimal E_d value was found to be at 125 J/mm³ where the lowest E (66 GPa) and high YS (~775 MPa) were obtained. It is interesting to take note that, unmelted Nb particles with an average size of more than 30 μm were found to initiate secondary crack at the boundary, hence compromising the ductility. It was further suggested that the low modulus of this alloy can be attributed to the uniform α'' -colony within the β -matrix. Another study utilizes *in-situ* alloying to develop new material for biomedical application by the addition of Zr into Ti-Ta alloy [12]. Ti5Ta-xZr ($x = 1.5, 5.5, 10.5, 15.5$ wt.%) were studied and it was found that Zr can stabilize the β phase in these alloys. The phase constituent of Ti15Ta10.5Zr is almost pure β , exhibiting an impressively low E value of 42.93 GPa. A high YS of 768.61 MPa is also obtained, demonstrating the vast potential of TiTaZr alloys system as a candidate for biomedical implant material. Despite the outstanding properties, there are limited studies on the *in-situ* alloying process involving Zr. The speculated reason is due to the tendency of Zr powder to undergo autoignition in the atmosphere, hence needing proper facilities and intensive care to handle.

(3) Induced porosity in β -Ti alloy

Macro-porous Ti40Nb (40 wt.%) bulk LPBF samples were produced via *in-situ* alloying of mechanically alloyed (MA) powder [110]. A relatively slow V_L of 35 $\mu\text{m/s}$ was used in the study. Traces of α and α'' phases are found to be embedded in a β matrix based on transmission electron microscopy (TEM) observation. No macro-segregation of Nb particles were reported due to the powder preparation technique.

Owing to the porous structure (~17%), E as low as 33 GPa was achieved. Nevertheless, there is no information reported on tensile mechanical strength. Sing et al. also used *in-situ* alloying to fabricate Ti-Ta porous structures and concluded that the LPBF parameters can affect the physical and mechanical properties of these structures [26]. In another study of *in-situ* alloyed porous Ti-Mo, it was discussed that the porosity level of the manufactured part has a significant influence on corrosive properties [136]. The part's corrosion resistance was found to be higher in parts with lower porosity. Nevertheless, the parts with lower porosity values were also found to be more homogenous with lesser unmelted Mo particles. It is hence difficult to conclude that porosity value alone had caused the change in corrosion resistance, as compositional segregation can also play a part in such corrosion resistance properties.

To summarize, most low modulus biocompatible Ti alloys manufactured by LPBF were done using *in-situ* alloying. However, all β -Ti stabilizers used are refractory and the issue of unmelted particles remains an uncharted area to be explored. More research on *in-situ* alloyed β -Ti is needed in order to understand the suitability of *in-situ* alloyed biocompatible Ti alloys as implant candidates. A table to summarize notable previous works relevant to LPBF Ti alloys with biocompatible β -stabilizer (mostly *in-situ* alloyed) can be seen in Table 2.

Table 2 Brief summary on works relevant to Ti alloys with the addition of biocompatible β -stabilizer *in-situ* alloyed with LPBF.

Purpose	Alloy System	Powder Mix	Blending Method	Blending Parameters	Highest Relative Density	E	YS	Reference Parameter	Scanning Strategy	Remarks	REF.
To develop <i>in-situ</i> alloying of Ti-Nb alloy via L-PBF.	Ti40.5Nb (wt.%)	Ti (irregular, $D_{50} = 62 \mu\text{m}$) and Nb (irregular, $D_{50} = 25 \mu\text{m}$)			> 99 %	77 GPa (Ultrasonic)		1070 nm Discontinuous scan mode $P = 220 \text{ W}$ $t = 30 \mu\text{m}$ Point distance = $65 \mu\text{m}$ Dwell time = $50 \mu\text{s}$ $\varepsilon = 214 \text{ J/mm}^3$, Ar atmosphere < 0.5 % O_2 .	xy	ε increment reduced unmelted Nb but induced keyhole porosity.	[122]
To investigate the relationship between processing parameters, microstructure and tensile behaviour of <i>in-situ</i> alloyed Ti7.5Mo.	Ti7.5Mo (wt.%)	Ti (spherical), Mo (irregular, $\sim 10 \mu\text{m}$), Mo (Porous aggregate, $\sim 20 \mu\text{m}$)	Planetary ball mill	2 hr Ball ratio of 1/5	99.7 %	70 GPa (Tensile)	540 MPa (Tensile)	1073nm CW $P = 200 \text{ W}$ $V_L = 100 \text{ mm/s}$ $t = 50 \mu\text{m}$ $h = 100 \mu\text{m}$ <0.02% O_2 .	Zigzag, 67° rotation	Increasing ε reduced the amount of unmelted Mo and changed the type of porosity from lack-of-fusion to keyhole.	[137]
To investigate the relationship between processing parameters, relative density, microhardness and	Ti50Ta (wt.%)	Ti (spherical, mean $43.5 \mu\text{m}$) and Ta (irregular	Tumbling mixer	12 hr 60 RPM	99.85 %	75.77 GPa (Tensile)	882.77 MPa (Tensile)	1064nm CW $P = 360 \text{ W}$ $V_L = 400 \text{ mm/s}$ $t = 50 \mu\text{m}$ $h = 125 \mu\text{m}$	Island scanning strategy	Increasing ε reduced the amount of unmelted Ta and improved the relative density. Low modulus β -Ti can be retained	[32, 111]

surface roughness of <i>in-situ</i> alloyed Ti50Ta. Tensile properties of optimized part were identified.		, mean 44 μm)								with sufficient dissolution of Ta particles.	
To address porosity-inclusion dilemma with laser remelting strategy.	Ti42Nb (wt.%)	Ti (spherical, 20 to 63 μm) and Nb (spherical, 20 to 63 μm)	Tumbling mixer	6 hr 75 RPM	> 99.9 %			1064nm CW $P = 250 \text{ W}$ $V_L = 100 \text{ mm/s}$ $t = 50 \mu\text{m}$ $h = 100 \mu\text{m}$	Stripe scanning strategy with remelting.	The remelting strategy showed its potential to reduce macro-segregation without deteriorating the specimen's density.	[125]
To address porosity-inclusion dilemma with laser remelting strategy and to investigate the effect of remelting strategy on microstructure and mechanical properties.	Ti25Ta (wt.%)	Ti (spherical, 20 to 45 μm) and Ta (spherical, 15 to 45 μm)	Tumbling mixer	12 hr 15 RPM	> 99.99 % (Pore free)	65 GPa (Ultrasonic)	545 MPa (Tensile)	1070nm CW $P = 95 \text{ W}$ $V_L = 300 \text{ mm/s}$ $t = 25 \mu\text{m}$ $h = 35 \mu\text{m}$	Zigzag 90° rotation, with remelting.	The remelting strategy showed its potential to reduce macro-segregation while maintaining pore-free matrix. Remelting leads to reduction of texture strength, improves the YS but sacrifices ϵ_f property.	[124]
To investigate the low cycle fatigue behaviour of Ti25Ta manufactured via LPBF using conventional strategy and laser remelting strategy.	Ti25Ta (wt.%)	Ti (spherical, 20 to 45 μm) and Ta (spherical, 15 to 45 μm)	Tumbling mixer	N/A	99.85 %	65.4 GPa (Tensile)	545 MPa (Tensile)	1070nm CW $P = 95 \text{ W}$ $V_L = 300 \text{ mm/s}$ $t = 25 \mu\text{m}$ $h = 35 \mu\text{m}$	Zigzag 90° rotation, with and without remelting	Process induced defects were identified as dominant fatigue crack initiation sites, in which keyhole induced porosity is the main culprit. No evidence has been	[138]

										found on unmelted Ta particles to be responsible for fatigue crack initiation.	
To study on microstructure, mechanical properties and <i>in-vitro</i> appetite forming capability of Ti-xNb.	Ti-xNb x= 0 to 45 (at.%)	Ti (spherical, mean 30.3 μm) and Nb (irregular, mean 25.9 μm)	Ball grinder	2 hr	> 98.5 %	18.7 GPa (Possibility of error due to absence of extensometer) (Tensile)	516 MPa (Tensile)	1064 nm CW $P = 330 \text{ W}$ $V_L = 1000 \text{ mm/s}$ $t = 30 \mu\text{m}$ $h = 100 \mu\text{m}$ Ar atmosphere < 0.1 % O_2 .	Bi-direction with 90° rotation.	Ti25Nb exhibited densest appetite layer and showed lowest E among other parts.	[121]
To investigate the effect of Ta addition in Ti on mechanical properties and biocompatibility.	Ti-xTa x = 0 to 50 (wt.%)	Ti (spherical, $D_{50} = 43.5 \mu\text{m}$) and Ta (irregular, $D_{50} = 44 \mu\text{m}$)	Tumbling mixer	12 hr 60 RPM	99.8 %	71 GPa (Tensile)	920 MPa (Tensile)	< 0.05% O_2		Ti30Ta showed optimal mechanical properties of low modulus and high YS. Ti50Ta lattice structure exhibits similar SAOS-2 cell proliferation capability as Ti and Ti6Al4V lattice structure.	[132]
To investigate the effect of Ta addition in Ti on mechanical properties and corrosion resistance capability.	Ti-xTa x = 0-25 (wt.%)	Ti (spherical, mean 30.3 μm) and Ta (irregular, mean 3.66 μm)	Planetary ball mill	3 hr 180 RPM Ball Ratio of 1/4	95 %	89 GPa (Tensile)	1029 MPa (Tensile)	1064nm CW $P = 340 \text{ W}$ $V_L = 1200 \text{ mm/s}$ $t = 50 \mu\text{m}$ $h = 70 \mu\text{m}$	67° rotation.	Ti25Ta showed α' dominant microstructure with high strength and low modulus among all samples. It also exhibited the best	[123]

										corrosion resistance in Ringer's solution.	
To study the microstructure and mechanical properties of Ti37Nb6Sn with various scanning strategies.	Ti37Nb6Sn (wt.%)	Ti (spherical, mean 21.7 μm), Nb (irregular, mean 30.5 μm) and Sn (spherical, mean 8 μm)	Tumbling mixer 50RPM	20 hr	> 99 %	66 GPa (Tensile)	~775 MPa (Tensile)	$P = 225 \text{ W}$ $V_L = 1200 \text{ mm/s}$ $t = 30 \mu\text{m}$ $h = 50 \mu\text{m}$	Zigzag with 67 ° rotation	Increasing ϵ reduced unmelted Nb but compromised relative density. Exist critical size of Nb that compromised strength.	[135]
To develop new biocompatible Ti15Ta-xZr alloy <i>in-situ</i> fabricated with L-PBF.	Ti15Ta-xZr x = 1.5 to 15.5 (wt.%)	Ti (spherical, mean 41.5 μm), Ta (irregular) and Zr (mean 38 μm)	Tumbling mixer	15 hr 80 RPM		42.93 GPa (Tensile)	768.61 MPa (Tensile)	1064nm CW $P = 350 \text{ to } 400 \text{ W}$ $V_L = 205 \text{ mm/s}$ $t = 25 \mu\text{m}$ $h = 115 \mu\text{m}$ 65% Ar + 35% N ₂ environment. Followed by homogenization at 850 °C for 2 hr and atmosphere. Then annealed at 600 °C for 3 hr and air cooled.		Achieved excellent combination of strength and E at 10.5 wt.% Zr addition. No sign of infection or osteomyelitis in the surrounding of rat's tibia after 5 weeks of implantation in rat tibia's fracture.	[12]

To attempt <i>in-situ</i> alloying of porous Ti40Nb with L-PBF through the usage of mechanical alloyed powder.	Ti40Nb (wt.%)	Mechanical alloyed Ti40Nb (20 to 44 μm)	High energy ball mill	40 hr 250 RPM 15 min cool down period every 15 min of mechanical alloying.	83 %	33 GPa (Compressive)	968 MPa (Ultimate Compressive Strength)	1054 nm CW, $P = 200 \text{ W}$ $V_L = 0.35 \text{ mm/s}$ $t = 100 \mu\text{m}$ $h = 200 \mu\text{m}$ Ar atmosphere < 0.01 % O_2	hatch 74 ° rotation	As-built samples showed good biocompatibility. Induced porosity brings modulus down to 33 GPa.	[110]
To understand the effect of heterogeneity caused by undissolved Nb on the mechanical and corrosion properties.	Ti35Nb (wt.%)	Ti (spherical, 40 to 65 μm) and Nb (angled, 60 to 95 μm)	Tumbling mixer	60 min	98.1 %	84.7 MPa (Compressive)	660 MPa (Compressive)	1064 nm CW $P = 200 \text{ W}$ $V_L = 500 \text{ mm/s}$ $h = 100 \mu\text{m}$ Ar atmosphere < 0.1 % O_2 .		Substantial amount of unmelted Nb was detected in the study.	[126]
To attempt <i>in-situ</i> alloying of Ti with beta stabilizing elements.	Ti20Nb (at.%)	Ti (spherical, $D_{50} = 23.1 \mu\text{m}$) and Nb (spherical, $D_{50} = 13.3 \mu\text{m}$)						1060-1100 nm CW $V_L = 1000 \text{ mm/s}$ $h = 100 \mu\text{m}$ $\varepsilon = 3.0 \text{ J/mm}^2$	Zigzag with 90° rotation	Ti-Nb formed more volume fraction of β phase with increased ε . α'' martensite traces found in this composition.	[139]
To lay groundwork for the development of TiRe alloys mainly used in applications requiring improved	Ti-xRe $x = 1.95$ to 5.66 (wt.%)	Ti (spherical, 20 to 60 μm) and Re (irregular			> 99.95 %	103 GPa (Tensile)	1038 MPa (Tensile)	1070nm, $P = 100 \text{ W}$ $V_L = 24 \text{ mm/s}$ $t = 75 \mu\text{m}$ $h = 100 \mu\text{m}$	Zigzag 90 ° rotation	The addition of Re into Ti led to E reduction and significant strengthening.	[128]

low and high temperature properties, wear and corrosion resistance, “ α case” formation resistance and biocompatibility.		, < 40 μm)								However, it also led to deterioration of ε_f .	
To study the microstructure, mechanical properties and FCG resistance of Re enhanced Ti.	Ti-xRe x = 2 to 4 (wt.%)	Ti (spherical, 20 to 60 μm) and Re (irregular, < 40 μm)	Ball mill	Mechanical alloying of Ti-Re powder mix at 1:1 wt.% ratio followed by blending with Ti at 200 RPM.	> 99.59 %		1197 MPa (Tensile)	1070nm $P = 400 \text{ W}$ $V_L = 1000 \text{ mm/s}$ $t = 50 \mu\text{m}$ $h = 100 \mu\text{m}$	Zigzag 90° rotation	Re addition refined the α/α' lath which leads to strengthening. However, it induced brittle fracture and deteriorated FCG resistance.	[129]
To investigate the effect of volumetric E_d on printability, phase transformation, microstructure and mechanical properties of <i>in-situ</i> alloyed Ti25Nb.	Ti25Nb (wt.%)	Ti (spherical) and Nb (irregular) Mixed powder have $D_{50} = 31.4 \mu\text{m}$	Planetary ball mill	2 hr 300 RPM Ball ratio of 1/5	97.5 %	83.5 GPa (Tensile)	645 MPa (Tensile)	$P = 330 \text{ W}$ $V_L = 1000 \text{ mm/s}$ $t = 30 \mu\text{m}$ $h = 100 \mu\text{m}$	Zig zag 90° rotation	The matrix of optimized parameter consist of α' and β phase. The alloy had better cell spread and proliferation as well as superior appetite-forming capability when benchmarked against Ti parts.	[140]

To acquire comprehensive insight into the bioactive mechanism of <i>in-situ</i> alloyed Ti-xNb porous scaffold structure and to investigate the <i>in-vivo</i> bone regeneration ability of Ti25Nb porous scaffold structure.	Ti-xNb x = 0 to 45 (at.%)	Ti (spherical, mean 30.3 μm) and Nb (irregular, mean 25.9 μm)						$P = 330 \text{ W}$ $V_L = 1000 \text{ mm/s}$ $t = 40 \mu\text{m}$ $h = 100 \mu\text{m}$ Ar atmosphere < 0.05 % O_2 .	N/A	<i>In-situ</i> alloyed Ti25Nb exhibited superior immunomodulatory properties, allowed better bone regeneration and osseointegration as compared to pure Ti.	[131]
To attempt mechanical characterization of SLM parts manufactured with pre-alloyed Ti45Nb powder.	Ti45Nb (wt.%)	Pre-alloyed Ti-45Nb (spherical, 20 to 100 μm)			99.5 %			1054 nm CW $P = 250 \text{ W}$ $V_L = 35 \text{ mm/s}$ $t = 100 \mu\text{m}$ $h = 50 \%$	Hatch with 74° rotation to avoid interconnected pores	Phase formation is independent of scanning parameters.	[133]
To attempt mechanical characterization of SLM parts manufactured with pre-alloyed Ti42Nb powder.	Ti42Nb (wt.%)	Pre-alloyed Ti42Nb (spherical, $D_{50} = 44.8 \mu\text{m}$)			> 99.5 %	60.51 GPa (Tensile)	674.08 MPa (Tensile)	1070 nm CW $P = 50 \text{ W}$ $V_L = 400 \text{ mm/s}$ $t = 50 \mu\text{m}$ $h = 100 \mu\text{m}$	Square scanning pattern	Compressive strength is higher than tensile strength in fabricated parts.	[134]

2.3.3 Other Ti Systems

Aside from the widely used Ti6Al4V alloy and trending biomedical Ti alloys with β stabilizer, other Ti alloys were also explored for *in-situ* alloying using LPBF. The Ti-185 alloy is a high strength and economical Ti alloy but the formation of β -flecks (macro-segregation of Fe) via ingot casting restricted its commercial use. As such, an attempt to produce Ti-185 with LPBF has been made due to its rapid cooling rate that can potentially suppress the macro-segregation of elements [141]. As the composition is relatively new for LPBF, a ball-milled powder mixture was used in the study. It was found that the LPBF of Ti-185 resulted in good mechanical properties (1890 MPa compressive strength and 11 % ϵ_f) due to the absence of β -flecks, fine-grained structure, high dislocation density, distribution of nano-sized α -phase within β -matrix and high O₂ content. Heat treatment on the samples was also conducted and it leads to homogenous spreading of α -phase that further improves the mechanical properties (2380 MPa compressive strength and 26 % ϵ_f).

Although scarce, research on *in-situ* alloying of Ni-Ti, has also been explored as a cost-effective alternative to pre-alloyed Ni-Ti powder. Work has been done by Wang et al. to study the feasibility of making Ni-Ti parts via *in-situ* alloying with different AM techniques [142]. The rapid solidification of melt pools inherent to LPBF promotes the formation of TiNi, which is responsible for the shape memory effect in Ni-Ti shape memory alloys. However, this also led to the formation of unwanted brittle phases as well as metastable phases. On the other hand, a study by Zhang et al. shows that *in-situ* alloying of Ni-Ti is feasible when the V_L is slow enough for densification (more than 99.5 % relative density) and homogenization to form TiNi

phase [143]. With increasing V_L , an unwanted Ti_2Ni phase can form. No further study on recovery strain has been made, prompting the need for more research on the topic.

Furthermore, compositionally modified Ni-Ti alloy was done through the addition of Nb, mainly as an attempt to improve the alloy's toughness and biocompatibility [144]. Alloy with the composition of $Ni_{43.8}Ti_{44.0}Nb_{12.2}$ (at.%) was achieved via the mixture of prealloyed Ni-Ti powder and Nb powder. Samples were then built via LPBF and annealed at a temperature of 850°C for 0.5h. The retained Nb particles causes Nb diffusion that accelerates the formation of eutectic phase and β -Nb phase. The ultra-fine eutectic phase and nanoscaled β -Nb phase formation eventually leads to excellent compression properties of 1640 MPa (YS) and 39% (compressive ϵ_f), a significantly improvement as compared to the as-cast counterpart (YS of 960 MPa). A recovered strain of 8.2% was recorded from compressive unloading, up from a compressive strain of 21%. The elastic strain recovery is of 5.6% and the hyperelastic strain recovery is of 2.6%. Preliminary studies by Grigoriev et al. [145] and Polozov et al. [146] manufactured Ti_2AlNb -based (O phase) intermetallic part via *in-situ* alloying with LPBF. To achieve optimization of such an intermetallic part, *in-situ* alloying was first done with Ti_5Al (wt.%), followed by Ti_6Al_7Nb (wt.%) and finally $Ti_{22}Al_{25}Nb$ (at.%). Two types of laser were utilized for these studies: the Gaussian profile laser (400 W, 80 μm spot diameter) and the top-hat profile laser (1000 W, 700 μm spot diameter). Grigoriev et al. found that at constant volumetric E_d , high powered top-hat laser (950 W) can achieve *in-situ* alloyed Ti_5Al with better homogeneity but it is also more prone to cracking. However, Polozov et al. found that the usage of Gaussian profile laser at 275 W with constant E_d can achieve alloy composition nearer to the

designed composition due to milder Al evaporation. They then studied the *in-situ* alloying of Ti6Al7Nb and found the presence of partially molten Nb which can be reduced with heat treatment at 1350 °C (or more than 1200 °C [147]). The resultant Ti6Al7Nb exhibited an UTS of 850 MPa which is similar to that made by metal injection molding with sintering. Unfortunately, the LPBF Ti6Al7Nb exhibits poor ϵ_f of only 2% which might be caused by the large pores formed. A large amount of partially melted Nb is found in *in-situ* alloyed Ti22Al25Nb by Grigoriev *et.al*. Further heat treatments were done to manipulate the volume fraction of O phase where the hardness value increases with O phase fraction from 338.6 HV (as built) to 353.3 HV (1250 °C homogenized) towards 358.3 HV (1250 °C homogenized, 950 °C aged). Further study by Polozov et al. shows that the heat treatment time can influence the extent of Nb dissolution and O phase volume fraction (Figure 16). Nevertheless, the Ti22Al25Nb built here is not usable for engineering applications due to the significant number of cracks present in the bulk samples.

To reduce the anisotropy of LPBF parts, Barriobero-Vila et al. approached the problem through the addition of a rare earth element, La [148]. *In-situ* alloying of Ti2La (wt.%) exhibits less pronounced texture with a combination of equiaxed α grains and elongated tortuous α grains. Instead of the typical columnar β to α transformation, the reduced texture strength of Ti2La due to the formation of α nucleation at the solidification front. Further heat treatment of T2La leads to new α phase formation and extensive globularization, along with microstructural refinement that can be controlled by adjusting the cooling rate as seen in Figure 17. The main microstructure forming mechanism of Ti2La begins with the poor solubility of La in Ti α/β , which leads to La rejection to L_1/β interface that causes constitutional

58

supercooling where α nucleation happens via a peritectic path. A similar effect of La addition on the microstructure was demonstrated with *in-situ* alloying of Ti1.4Fe1La (wt.%). This shows the potential in avoiding epitaxial growth during LPBF.

Figure 16 The microstructure of the Ti-22Al-25Nb specimens after undergoing different heat treatment conditions: (a) 1250 °C, 2.5 hrs; (b) 1250 °C, 4 hrs; (c) 1350 °C, 2.5 hrs; (d) 1350 °C, 3.5 hrs [146].

Figure 17 Electron backscatter diffraction (EBSD) mapping showing the effect of heat treatment on SLM as-built parts from 950 °C ($L_1 + \beta$ field) down to room temperature, forming finer α grains with increasing cooling rate: (a) cooling with a 5 °C min⁻¹, (b) cooling with a 100 °C min⁻¹. The scale bars indicate a length of 50 μm. Black lines in EBSD mapping indicate HAGBs (>10°) [148].

The compilation of other Ti alloys not classified as Ti6Al4V based or Ti with β stabilizer manufactured via *in-situ* alloying can be seen in Table 3.

Table 3 Brief summary on works relevant to Ti alloys (not classified as Ti6Al4V based or Ti with β stabilizer) in-situ alloyed with LPBF.

Purpose	Alloy System	Powder Mix	Blending Method	Blending Parameters	Highest Relative Density	Reference Parameter	Scanning Strategy	Remarks	REF.
To produce Ti-185 alloy which is otherwise not feasible to be made via ingot casting.	Ti-185	Ti, Fe and pre-alloyed V-Al (flat cumulative powder, cumulative $D_{50} = 51 \mu\text{m}$)	Ball milling		99.38 %	1060 - 1100 nm CW $P = 370 \text{ W}$ $V_L = 1035 \text{ mm/s}$ $t = 60 \mu\text{m}$ $h = 120 \mu\text{m}$	Stripes with 67° rotation counter-clockwise	Unlike casted part, there are no β -flecks found in as built parts by L-PBF.	[141]
To study the feasibility of producing NiTi via <i>in-situ</i> alloying with different AM technologies.	Ni45Ti (wt.%) (Equiatomic)	Ti (spherical, 45 to 63 μm) and Ni (spherical, 20 to 63 μm)	Tumbling mixer with 1 L container (50 % filling ratio)	2 hr 30 RPM		1054 nm CW $P = 150 \text{ W}$ $V_L = 200 \text{ to } 1000 \text{ mm/s}$ $t = 50 \mu\text{m}$ $h = 100 \mu\text{m}$ Ar atmosphere, $< 0.05 \% \text{ O}_2$.	Stripe	Almost equal volume of TiNi and Ti_2Ni phase formed. Heat treatment led to more Ti_3Ni formed, which is detrimental to SMA.	[142]
To study the feasibility of producing NiTi via <i>in-situ</i> alloying with L-PBF.	Ni-45Ti (wt.%) (Equiatomic)	Ti (spherical, $D_{50} = 35 \mu\text{m}$) and Ni (Spherical, $D_{50} = 30 \mu\text{m}$)	Tumbling mixer	45 min	$> 99.5 \%$	1064 nm CW $P = 100 \text{ W}$ $V_L = 50 \text{ to } 200 \text{ mm/s}$ $t = 100 \mu\text{m}$ Focus offset = $50 \mu\text{m}$	Alternate xy	Low V_L led to TiNi phase formation but fast V_L led to brittle Ti_2Ni phase formation.	[143]

To understand the microstructure evolution and deformation mechanism of LPBF-produced NiTi–Nb shape memory alloys.	Ni _{43.8} Ti _{44.0} Nb _{12.2} (at.%)	NiTi (spherical, 10 to 50 µm) and Nb (irregular, 5 to 30 µm)	Ball mill	1 hr	N/A	$P = 200 \text{ W}$ $V_L = 600 \text{ mm/s}$ $t = 30 \text{ µm}$ $h = 120 \text{ µm}$ Preheat 160°C. Followed by annealing at 850 °C for 0.5 hr	67° rotation	The ultra-fine eutectic phase and nano-scaled β-Nb phase formation eventually leads to excellent compression properties of 1640 MPa (YS) and 39% (compressive strain), a significantly improvement as compared to the as-cast counterpart (YS of 960 MPa).	[144]
Investigation and evaluation on the possibility of synthesizing different types of Ti alloys from elemental powders via <i>in-situ</i> alloying by L-PBF.	Ti-5Al (wt.%)	Ti (spherical, $D_{50} = 44.6 \text{ µm}$), and Al (spherical, $D_{50} = 21.2 \text{ µm}$)	Tumbling mixer	12 hr	98.97 %	1064 nm CW $P = 275 \text{ W}$ $V_L = 760 \text{ mm/s}$ $t = 50 \text{ µm}$ $h = 120 \text{ µm}$ 1064 nm CW $P = 950 \text{ W}$ $V_L = 350 \text{ mm/s}$ $t = 100 \text{ µm}$ $h = 400 \text{ µm}$		High powered top-hat laser with large spot size produced more homogenous parts that had lesser cracks. Low powered Gaussian laser with small spot size created part closer to the intended composition.	[145, 146]
Investigation and evaluation on the possibility of synthesizing different types of Ti alloys from elemental powders via <i>in-situ</i> alloying by L-PBF.	Ti6Al7Nb (wt.%)	Ti (spherical, $D_{50} = 44.6 \text{ µm}$), Al (spherical, $D_{50} = 21.2 \text{ µm}$) and Nb (spherical, $D_{50} = 32.9 \text{ µm}$)	Tumbling mixer	12 hr	99.4 %	1064 nm CW $P = 950 \text{ W}$ $V_L = 350 \text{ mm/s}$ $t = 100 \text{ µm}$ $h = 450 \text{ µm}$		Strength similar to metal injection moulding with sintering part. However, poor ϵ_f of only 2 % which may be due to large porosity formation.	[146]
Preliminary study on L-PBF manufactured	Ti22Al25Nb (at.%)	Ti (spherical,	Tumbling mixer	12 hr	97.3 %	1064 nm CW $P = 950 \text{ W}$		Heat treatment can affect the extent of partially melted Nb	[145, 146]

Ti2AlNb-based (O phase) intermetallic part.		D ₅₀ = 44.6 μm), Al (spherical, D ₅₀ = 21.2 μm) and Nb (spherical, D ₅₀ = 32.9 μm)				V _L = 350 mm/s t = 100 μm h = 450 μm		dissolution and O phase formation. Significant cracks found in bulk material.	
To break through the lack of coordinating microstructure of Ti-based system which leads to close YS and UTS values for its lack of work hardening.	Ti6Al4V + Ti5553 (Equal mass)	Ti6Al4V (spherical, D ₅₀ = 35 μm), and Ti5553 (spherical, D ₅₀ = 35 μm)	Blender not specified	3 hr 300 RPM	> 99.5 %	1064 nm Discontinuous scan mode P = 200 W t = 30 μm h = 105 μm Point distance = 55 μm, Dwell time = 80 μs < 0.01% O ₂	Stripes (5 mm stripe size) with 67° rotation	<i>In-situ</i> alloying of Ti6Al4V and Ti5553 to achieve non-homogenous part (retention of composition of raw material) can simultaneously improve UTS and ductility. Further heat treatments can alter the mechanical properties to requirements.	[149]
To achieve property enhancement through generation of sophisticated microstructure that covers all possibility phases/structures in the Ti systems.	Ti + Ti6Al4V + Ti5553 (Equal mass)	Ti6Al4V (spherical, D ₅₀ = 35 μm), and Ti5553 (spherical, D ₅₀ = 35 μm)	Blender not specified	300 RPM	> 99.4 %	1064 nm Discontinuous scan mode P = 200 W t = 30 μm h = 105 μm Point distance = 45 μm, Dwell time = 50 μs, < 0.01 % O ₂	Stripes (5 mm stripe size) with 67° rotation	The ternary HYTA possesses complex microstructure with each phase having subtle differences in strength, thus eliminating double yielding phenomena in binary HYTA. A high YS of ~1000 MPa (UTS ~1100 MPa) and good ε _f (~20%) were achieved.	[115]

2.4 Research Gaps - *In-situ Alloying of β -Ti for Structural Implant Application via Laser Powder Bed Fusion*

The study on *in-situ* alloying of β -Ti via LPBF is still in its early stage. Though efforts have been made to develop the *in-situ* alloying strategy for β -Ti, many research gaps still exist. For example, the effect of β stabilizing element addition into Ti was not well studied. Moreover, there is a lack of novel fabrication strategy to obtain high quality part as characterized by the porosity and incompletely molten particles. Such conundrum to achieve high quality part can also be known as the porosity-inclusion dilemma. Finally, there is no understanding on the influence of mesostructure induced by *in-situ* alloying process on the resultant crack response of the material. In the remaining parts of this section, each of these research gaps will be elaborated in more details.

2.4.1 Effect of β Stabilizer Addition

The effect of β stabilizer addition into Ti has been well studied in the past. With the addition of β stabilizing elements into Ti, the alloy will undergo phase evolution in the sequence of $\alpha \rightarrow \alpha' \rightarrow \alpha'' \rightarrow \alpha'' + \beta \rightarrow \beta$ upon water quenching [117, 150]. As the α' , α'' and β phase is typically retained after fast cooling cycle, they are metastable phases and will undergo further phase transformation with heat treatment. The lattice structure of α and α' are both hexagonal close packed (HCP), α'' is orthorhombic and β is body centered cubic (BCC) [151]. The metastable β phase possesses the ideal E and YS when the amount of β stabilizing element is minimized [28]. However, if there are too little β stabilizer, the α'' martensitic start temperature will approach room temperature. Subsequently, β to α'' stress induced martensite (SIM) transformation will occur, leading to lowered YS of the material [152]. Upon low temperature aging

of the metastable β -Ti, isothermal ω_{iso} phase will precipitate and strengthen the resultant alloy. With ω_{iso} phase however, the E of the resultant alloy will be increased while the ε_f will be substantially reduced, hence the trade-off associated with ω_{iso} phase needs to be carefully balanced [153]. Depending on the recipe of low temperature aging, the ω_{iso} phase can be partially or fully collapsed, with the ω_{iso} phase increasingly collapsed with longer aging duration. The partially and fully collapsed ω_{iso} phase possesses trigonal and hexagonal lattice structure respectively [154], with the latter influencing the resultant mechanical properties to a greater extent [153].

Nevertheless, the understanding on β stabilizer addition are mostly based on materials fabricated via the casting and quenching route. A study on dislocation introduction and grain refinement via cold roll plus annealing showed that the β phase can be further stabilized and mitigate α'' SIM formation [152]. The study highlighted the importance of stress history experienced by a material under a certain fabrication process, in addition to the thermal history. Given LPBF as a process with drastically different thermal and stress history experience by the material, the resulting effect of β stabilizer addition could be different and requires further exploration.

Moreover, *in-situ* alloying adds to another complication to the LPBF process due to the usage of mixed powder. Selective vaporization of specific element with relatively higher vaporization pressure has been observed in LPBF. In a study to *in-situ* alloy Al50Si (wt.%), the resultant part shows higher Si content due to Al evaporation [155]. It was observed that the extent of Al evaporation increases with the input E_d . During LPBF for Al 7075, evaporation of Zn and Mg can occur and reduces the overall strength, however, the problem of volatile elements evaporation can be compensated

via adjustment for the raw material used [156]. If E_d was to be increased further to promote melting and mixing, the recoil pressure from vaporized metal can lead to the formation of keyhole porosities. During the *in-situ* alloying of Ni-Ti, an exothermic reaction between Ti and Ni can lead to turbulent melt pools and it was hypothesized that selective ejection of particles might have occurred during LPBF, leading to depletion of Ti in the manufactured part [142]. In another study done using a Mg-Al alloys system, it is found that with high energy input, the powder was evaporated due to the low boiling point of Mg [157]. Like welding process, the change in composition during LPBF depends on the vaporization rate and the volume of the melt pools. Although the rate of vaporization increases with P , the change in composition is most pronounced at low P because of the small size and, consequently, the high surface-to-volume ratio of the melt pools. The high V_L ensures a shorter time span of the melt pools and reduces vaporization [158]. Biocompatible β -Ti stabilizers are mainly comprised of refractory elements, hence Ti depletion during the *in-situ* alloying process via LPBF is possible and the possibility was not investigated. The comparison of melting point, boiling point and density of Ti, Nb and Ta can be seen in Table 4.

Table 4 Melting point, boiling point and density of biocompatible elements commonly utilized in the in-situ alloying process via LPBF [159].

Element	Melting Point (°C)	Boiling Point (°C)	Density (g/cm ³)
Ti	1675	3260	4.51
Nb	2468	4930	8.57
Ta	2997	5425	16.6

Furthermore, the addition of β -Ti stabilizer could influence the melt pool forming dynamics and lead to different defects or microstructural formation. The possibility

of changes brought by β -Ti stabilizer addition is inexhaustible. Despite previous studies on the effect of β -Ti stabilizer addition on *in-situ* alloyed Ti-xNb [130] and Ti-xTa [123] via LPBF, the former has abnormal ε_f and E results and the latter has study on only a narrow range of Ta addition. Hence, a systematic study of such is required to develop an insight on the direction to develop *in-situ* alloying strategy via LPBF for biocompatible β -Ti alloys.

2.4.2 Porosity-inclusion Dilemma

Porosity is commonly encountered in *in-situ* alloying with LPBF and is shown in a study by Fischer et al. [122]. Ti40.5Nb (wt.%) was studied and a laser with discontinuous scan mode was used. As the volumetric E_d increases, the cause of porosity transits from lack of fusion to having a minimum amount of porosity and finally to keyhole formation. The increment in E_d changes the melt pool formation mechanism from conduction mode to keyhole melting, subsequently causing an increased aspect ratio of the melt pool and lead to a higher probability of keyhole porosity formation. An illustration of the effect of melt pool aspect ratio on keyhole porosity is shown in Figure 18.

Figure 18 The effect of melt pool depth-to-width ratio on pore formation [160] The effect of melt pool depth-to-width ratio on pore formation [160].

It is found that for mixed powders, each component powders must be melted to enable chemical mixing in a liquid state as compared to using pre-alloyed powder [161]. For the case of Al-Si alloys system, Si has a higher melting point which makes it more difficult to create sufficient melt pools when the Si fraction increases. Higher P is necessary to melt the Si powder which can cause melt pool instability and results in the keyhole induced porosity (Figure 19). Melt pool instability is due to fluid forces

that leads to effect such as Reyleigh instability, causing discontinued melt tracks. For the fabrication of Ti37Nb6Sn (wt.%) alloy via *in-situ* alloying, the increased E_d leads to improved homogeneity but induces higher porosity due to more Sn evaporation [135].

Figure 19 Micrograph of AlSi25 sample produced at 400W and 2000 mm/s, some melt pools are marked by dotted lines, and keyhole porosity is indicated by red arrows, BD is building direction [161].

During the *in-situ* alloying of Ti26Nb (at.%), the amount of unmelted Nb decreases as the E_d increases which led to the formation of parts with better compositional homogeneity [122]. The trend of porosity and unmelted Nb with increasing E_d are illustrated in Figure 20. When a certain minimum E_d threshold is crossed, E_d increment generally leads to a better dissolution of Nb particles but induces more keyhole porosity. It is of interest to note that the issue with *in-situ* alloying of Ti-Nb via LPBF is that, the minimum porosity parameters do not necessarily lead to a homogenous part (Figure 21). The narrow melt pool produced by LPBF only encircles

a few powders and can contribute to macro-segregation due to localized inhomogeneity of the powder mixture [142]. This leads to a seemingly limited process window in which the part's quality can only be partially optimized. It is also hard to decide on the optimal combination of keyhole porosity percentage and the amount of unmelted Nb in the LPBF parts. Such a dilemma between the need for unmelted particles reduction and keyhole porosity reduction remains a challenge, leading to a porosity-inclusion dilemma that needs to be addressed.

Figure 20 Typical defects of in-situ alloyed Ti-Nb binary alloy with increasing E_d (a) porosity (b) unmelted Nb [122].

Figure 21 SEM of Ti40.5Nb at different E_d (a) 39 J/mm^3 (b) 214 J/mm^3 [122].

Similarly, the *in-situ* alloyed Ti7.5Mo (wt.%) system studied by Kang et al. shows a similar influence of E_d on the number of unmelted Mo particles and porosity [137]. The E_d increment improved part's densification to a maximum of 99.7 % while minimizes the amount of unmelted Mo particles. However, the porosity type shown in the optimized part contains keyhole porosity, indicating that further reduction of unmelted Mo particles with increased E_d will only lead to more keyhole porosity formation. This observation reinforces the need to address the porosity-inclusion dilemma. A study on *in-situ* alloyed Ti50Ta (wt.%) by Sing et al. also points towards a similar trend of density and unmelted Ta particles with increased E_d [111]. The optimized parts in the study contain unmelted particles which signify the possibility for improvement. It is difficult to eliminate the compositional segregation caused by unmelted Ta particles while obtaining parts with no porosity. The issue of unmelted particles and compositional segregation is commonly seen in the *in-situ* alloying technique. This issue, however, is especially prominent when it comes to the *in-situ* alloying of biocompatible β -Ti. As previously mentioned, the main reason behind such occurrence is that biocompatible β -Ti stabilizers are mostly composed of refractory elements, in which the β -Ti stabilizers' melting point is very different from that of Ti (Table 4).

There is a need to come up with creative unconventional strategies to deal with the issue of compositional segregation without compromising the part's density to propel the *in-situ* alloying technique via LPBF. To resolve this issue, a preliminary study by Huang et al. demonstrated the effectiveness of laser re-melting strategy to address the porosity-inclusion dilemma of *in-situ* alloyed binary alloys with elements of drastically different melting points [125]. The essence behind the laser re-melting

strategy is to have multiple laser passes on the same layer, effectively giving more opportunity for the dissolution of refractory alloying elements without resorting to excessive E_d that leads to keyhole porosity. Ti42Nb (wt.%) parts were built in the study and it was found that laser re-melting strategy could enhance the part's homogeneity while maintaining the amount of keyhole porosity. The laser re-melting strategy was also studied by Brodie et al. on *in-situ* alloyed Ti25Ta (wt.%) [124]. It was shown that the effectiveness of the re-melting strategy to approach the porosity-inclusion dilemma is highly dependent on the laser parameters choice. When the single scan parameters are optimized, pore-free parts can be achieved with a large amount of area percentage unmelted Ta (~0.75%). Utilization of laser re-melting further reduces the area percentage unmelted Ta to ~0.25% without inducing additional porosity. Besides having a higher melting point, Ta possesses higher thermal conductivity as compared to Ti. Ta particles essentially cool faster and have limited time for diffusion, in which the re-melting strategy provides a second chance for dissolution. However, laser re-melting leads to the need of more time and energy to build a part, which could translate to undesirable increment in cost to manufacture of a part.

Looking beyond β -Ti alloy system, *in-situ* alloying of Al-xCu leaves unmelted Cu particles which can deteriorate tensile properties by acting as crack nucleation sites. To mitigate this problem, Martinez et al. proceeded with the preheating of the powder bed [162]. A density of more than 99.1% can be achieved for *in-situ* alloyed Al-xCu manufactured from both preheated and non-preheated powder bed. At the same time, the preheated powder bed resulted in samples that are more chemically homogenous.

However, preheating might not be suitable for metastable β -Ti due to the possibility of *in-situ* aging that could lead to excessive formation of ω_{iso} phase.

In short, the existing laser re-melting technique and preheating of substrate can resolve the porosity-inclusion dilemma. However, these techniques have their shortcomings and requires further innovation of new fabrication technique. The new technique of *in-situ* alloying should encompass process efficiency improvement and at the same time resolve the porosity-inclusion dilemma.

2.4.3 Material's Crack Responses

There is a need to look beyond stress shielding effect to extend the life of an implant in service. For instance, fatigue and fracture can lead to the failure of an orthopedic implant due to a combination of design flaw, material's characteristic and fabrication defect [163]. As LPBF advances, implant mass customization will become more common. The flexibility to modify an implant's design is however a double edged sword. Without going through the test of time, frequent change in implant design could lead to more instances of design flaw that subsequently lead to premature failure of an implant due to fatigue and fracture. Hence, it is important to have better understanding on the material's crack responses to improve the implant design guideline. Furthermore, given the inclination of LPBF manufactured implant towards incorporation of lattice structure, stress concentration can occur and exposes the implant to the possibility of crack formation. Despite the immediate need to understand the fatigue and fracture behavior of LPBF manufactured biocompatible β -Ti, the study on the topic is almost non-existence.

The fatigue and fracture behavior of LPBF manufactured biocompatible β -Ti via *in-situ* alloying will be different from the conventionally manufactured ones. For example, compositional segregation is a commonly seen phenomena in LPBF processed part, and more so when the *in-situ* alloying technique is involved. Though the segregation can be minimized, it is hard to completely eliminate the issue. Hence, formation of part's mesostructure unique to *in-situ* alloying will be formed due to the segregation. The *in-situ* alloying induced structure will inevitably affect the resultant material's crack responses, e.g. FCG behavior and fracture toughness. A past study on Al12Si (wt.%) had demonstrated the effect of LPBF induced mesostructure on the material's crack responses [164]. The interaction of crack with Si decorated melt pool boundary led to tortuous crack growth and toughens the alloy. Based on this study, it is certainly interesting to study the crack interaction with structural characteristics formed within an *in-situ* alloyed biocompatible β -Ti.

Moreover, the effect of unmelted particles on crack responses is not well understood. A past study on *in-situ* alloyed Ti35Nb (wt.%) found shear localization at the interface between unmelted Nb particles and the matrix. This signifies that unmelted particles are potential sites for stress concentration and crack nucleation upon cyclic loading. Meanwhile, an investigation done by Brodie et al. on the low cycle fatigue behavior of LPBF manufactured Ti25Ta (wt.%) shows that keyhole induced porosity is the dominant fatigue crack initiation site, with no evidence found on unmelted Ta particles to initiate fatigue crack [138]. Aside from low cycle fatigue study, there is no attempt to study the effect of unmelted β stabilizing particles on the FCG and fracture toughness of *in-situ* alloyed β -Ti.

Despite not directly related to crack responses, it is good to take note of one innovative approach by Zafari & Xia to leverage the inherent inhomogeneity issue of *in-situ* alloying to achieve hybrid Ti alloy (HYTA) with enhanced mechanical properties [149]. As opposed to having a homogenous material, Ti6Al4V (wt.%) and Ti5Al5V5Mo3Cr (wt.%) powder of equal mass were mixed and *in-situ* alloyed to intentionally achieve full dense parts with blocks of material portion retaining the composition of its raw materials. The approach leads to the retention of α' (Ti6Al4V) and β (Ti5Al5V5Mo3Cr) phases where each phase undergoes a series of work hardening mechanisms progressively that eventually improves the UTS to more than 1200 MPa and ϵ_f to more than 15%. The strain mismatch or stress concentration at α'/β interface is relieved by the activation of twinning at the interface as well as the smooth transfer of deformation from β to α' phase, hence achieving simultaneous strengthening and improvement in ductility. Additional study on HYTA has been done using equal mass of Ti (wt.%), Ti6Al4V (wt.%), and Ti5Al5V5Mo3Cr (wt.%) powder [115]. The ternary HYTA has microstructure which is much more complex but with each phase having subtle differences in strength, eventually eliminating double yielding phenomena in binary HYTA to achieve a high YS of ~1000 MPa (UTS ~1100 MPa). The formation of highly heterogeneous microstructure leads to a large variety of deformation mechanisms such as slip, twinning, strain induced martensitic transformation and grain rotation activated. Accompanied by smooth transfer of deformation between phases, enhanced ductility of ~20% ϵ_f was achieved. Further heat treatment on HYTA can achieve tailored strength and ductility as needed, making the HYTA system a promising material to be used despite the highly inhomogeneous compositional distribution. With the success of HYTA,

inhomogeneity induced by *in-situ* alloying could very well be beneficial and deserves a proper investigation on the *in-situ* alloyed material's crack responses.

All in all, the structural characteristics of parts manufactured via *in-situ* alloying is not well understood in terms of its crack responses, especially when it comes to the FCG behavior and fracture toughness. The effect of compositional segregation and unmelted particles on crack responses is not well understood at this point of time. As demonstrated by previous studies, compositional segregation in a material could be beneficial to the resultant mechanical properties. Therefore, it is certainly important and interesting to study the FCG behavior and fracture toughness of an *in-situ* alloyed β -Ti for implant application.

2.5 Summary

An analysis of the available literature on the *in-situ* alloying technique via LPBF has revealed its importance and explores the possibilities it offers in expanding LPBF applications. LPBF will be increasingly employed for fabricating high quality, low cost, repeatable, and reliable functional parts. With these new approaches, LPBF enhances manufacturing and engagement in the industry. *In-situ* alloying allows the expansion of the materials library that is available for processing by LPBF as it also allows rapid feasibility studies of different composition of alloys. It has also been highlighted that *in-situ* alloyed parts have comparable part properties compared to the same materials formed using pre-alloyed powder by LPBF. With new materials with comparable performance, it should encourage higher adaptation rate in the industry.

Biocompatible Ti with β stabilizer is in particular the most widely *in-situ* alloyed material group. The *in-situ* alloying technique imparts flexibility in the composition

of powder feedstock, which is otherwise difficult to achieve if prealloyed powder is to be used. The compositional flexibility also enables the potential of manufacturing functionally graded implant. Past studies have also shown promising mechanical properties and biocompatibility of *in-situ* alloyed β -Ti. However, the study on *in-situ* alloyed biocompatible Ti with β stabilizer is still in the early stage and presented several research gaps that need to be addressed in order to propel the field. It is identified that the effect of β stabilizer addition needs to be better understood. New scanning strategy to efficiently resolve the porosity-inclusion dilemma is also required. To establish implant design guideline for *in-situ* alloying via LPBF, the crack responses of *in-situ* alloyed biocompatible Ti with β stabilizer needs to be explored. By bridging these research gaps, advancement in *in-situ* alloying process for Ti alloys with β stabilizer can be ensured, but not without further challenges to be addressed before the process can be widely adopted for implant manufacturing.

Chapter 3 Laser Powder Bed Fusion of Ti-Ta Alloys:

Compositions and Designs for Biomedical Applications

3.1 *Introduction*

Due to the interest in using LPBF for biomedical applications, many studies have focused on LPBF of pure Ti and Ti-based alloys [165-167]. Ta is an excellent choice for alloying with Ti for biomedical applications due to its high biocompatibility, corrosion resistance and good mechanical properties. In addition, Ti-Ta alloys are promising materials for such applications due to high strength to density ratio [168]. Despite the advantages, Ti-Ta alloys are still not widely adopted in applications due to the difficulty in combining these two metals as they have great difference in density and melting point [169]. Density of Ti and Ta is 4.5 and 16.6 g/cm³, while melting point of Ti and Ta is 1670 °C and 3020 °C respectively. These large differences could lead to inhomogeneity during the alloy formation as the large difference in density can lead to segregation of elements in the alloys. The high melting point of Ta may risk the Ti being vaporized during conventional alloying processes that typically melt both materials. The boiling point of Ti is 3287 °C, which is very close to the melting point of Ta. Previous work has shown LPBF is capable of producing Ti-Ta alloys [111, 123, 170, 171], proving the potential for *in-situ* alloying and direct fabrication of functional parts. In addition, the Ti-Ta system was chosen in this study due to the group's past experience in manufacturing the alloy.

As LPBF produced Ti-Ta via *in-situ* alloying is new, little is known about the effect of Ta compositions on the defect formation, microstructure and mechanical properties of the alloys. In this chapter, the effect of Ta compositions is investigated by

characterizing the LPBF produced samples' defects, microstructure and mechanical properties. LPBF process was used to fabricate samples of Ti-Ta alloys with 0, 10, 30 and 50 wt.% of Ta using *in-situ* alloying. As-fabricated samples comprised of randomly dispersed pure Ta particles in a Ti-Ta matrix. Porosity and unmelted Ta particles of the samples were revealed using an OM. The microstructure of the alloys were determined by combination of FESEM, EBSD and XRD. The mechanical properties of the alloys were investigated with tensile test and Vickers hardness test. The study will provide direct intuition on effects associated with *in-situ* alloying of Ti alloys with increasing addition of β stabilizer.

3.2 *Experimental Details*

3.2.1 Laser Powder Bed Fusion

Samples were fabricated using in-house developed Ti-Ta powder blends (with 10, 30 and 50 wt.% Ta). The Ti-Ta powder blends were obtained from mixing gas atomized commercially pure Ti (CP Ti) and Ta powders. The CP Ti powder (Grade 2 ASTM B348, LPW Technology Ltd, United Kingdom) particles were spherical with median volume equivalent diameter (D_{50}) of 43.5 μm . The Ta powder (Singapore Demand Planner Ltd, Singapore) particles were irregular in shape with D_{50} of 44 μm . The two elemental powders were mixed and then spun for 12 h at a rate of 60 rpm using a tumbler mixer (Inversina 2 L, Bioengineering AG). The powder characteristics were previously characterized and can be found in the study by Sing et al. [32], which shows that the powder blend is well mixed.

The fabrication of the samples was carried out using a SLM 250 HL machine (SLM Solutions Group AG), equipped with a fibre laser with a Gaussian beam profile and focus diameter of 80 μm . The maximum P is 400 W. All processes were carried out

in an Ar environment with less than 0.05% O₂ to prevent oxidation and interstitial element contaminations such as H₂ and N₂ pick up during the LPBF process. All samples were prepared using the same process parameters as shown in Table 5. The choice of scanning strategy is the stripe scanning strategy. The set of process parameters is optimized for CP Ti and is given by the LPBF equipment manufacturer.

At the time of this study, there was no literature on the effect of β -stabilizer addition into *in-situ* alloyed Ti. As a preliminary study, it is most feasible to have a fixed and known parameter that serves as a baseline. Given the volumetric majority of Ti in the powder mix (79% vol.% of Ti in Ti50Ta), parameter optimized for CP Ti was used. That gives the benefit to have a preliminary comparative study from the process point of view, e.g. understanding the problem/effect associated with *in-situ* alloying upon Ta addition.

Table 5 LPBF process parameters utilized for manufacturing the Ti-Ta alloy samples.

Power, P (W)	Hatch, h (μm)	Stripe Width (mm)	Scanning Velocity, V_L (mm/s)	Layer Thickness, t (μm)	Rotation ($^\circ$)	Energy Density, E_d (J/mm ³)	Laser Profile
275	120	10	1100	30	33	69.4	Gaussian (80 μm)

3.2.2 Metallographic Characterization

The samples were sectioned to reveal the cross-sectional area perpendicular to the BD. The cross-sections were then ground with grit #320 SiC-paper followed by MD-Largo (DiaPro Largo 9 μm suspension). They were finish polished with MD-Chem (OPS 0.04 μm suspension + H₂O₂) to achieve mirror finish for further analysis.

The polished samples were observed with optical microscope (OM) to reveal the part's quality. Image analysis was done with ImageJ software to obtain the percentage porosity and area percentage of unmelted Ta.

To identify the constituent phases, the polished samples were analyzed with X-ray diffraction (XRD, PANalytical Empyrean, Netherlands) using Cu-K α radiation and a step size of 0.05°.

Microstructure analysis was done with a field emission scanning electron microscope (FESEM, JEOL 7600F, JEOL, Japan) equipped with backscatter electron (BSE) detector. Texture analysis was done with electron backscattering diffraction (EBSD) analysis using FESEM equipped with an AZtecHKL Oxford system, scanning with a step size of 0.5 μm .

3.2.3 Mechanical Characterization

Tensile coupons, based on ASTM E8 sub-size specimen, were produced using electrical discharge machining (EDM) from blocks fabricated by LPBF. An Instron Static Tester Series 5569, 50 kN machine with a loading rate of 1 mm/min was applied on all tensile samples. Tensile test loading direction was perpendicular to the BD (z-direction) of the samples. Five replications of tensile tests were conducted for each composition for repeatability study. Average values are derived from the mean of five specimens for each Ti-Ta alloy of a particular Ta content. Fracture surfaces were observed with FESEM under the secondary electron (SE) mode to obtain the fractography.

The microhardness test of the material was carried out using Vickers hardness tester (DuraScan, Struers, Denmark) on the xy- and yz- planes where a load of 100 g and a

loading time of 15 s were used. Average values are derived from the mean of 20 indentation on each plane, across five specimens, for each Ti-Ta alloy of a particular Ta content.

3.3 Results and Discussion

3.3.1 Quality of Ti-Ta Parts

Table 6 summarizes the percentage porosity and the area percentage of unmelted Ta associated with each LPBF built Ti-Ta alloys via *in-situ* alloying. The values were obtained from OM image analysis where the sampled surface area for each sample was 6 mm × 8 mm. With the addition of Ta, an increasing trend of porosity level and the amount of unmelted Ta particles were observed. Nevertheless, a dip of porosity level can be seen when 10 wt.% Ta was added into Ti. OM images of polished cross sections revealed possible reason behind such porosity trend (Figure 22). With the addition of Ta, the size of spherical keyhole porosity decreases while the amount of lack-of-fusion defect increases. With constant E_d input, the addition of Ta leads to higher vaporization point and suppressed the formation of keyholes. Meanwhile, the Ta particles can agglomerate and is commonly associated with lack-of-fusion defect (Figure 25d). The mechanism of which is however unclear at this point. Qualitatively speaking, Ti50Ta having more lack-of-fusion defect should have more Ta rich clusters than Ti30Ta. The constant E_d input also leads to increasing amount of unmelted Ta particles as Ta (3017 °C) has much higher melting point as compared to Ti (1668 °C). The data points in Table 6 gave insights on the process issues associated with Ta addition – the simultaneous increase in lack-of-fusion porosity and unmelted particles with constant process parameter.

Table 6 Porosity and percentage unmelted Ta associated with each alloy composition.

Alloy Composition	Porosity (%)	Unmelted Ta (%)
CP Ti	0.062	N/A
Ti10Ta	0.039	0.317
Ti30Ta	0.236	1.724
Ti50Ta	0.466	2.685

Figure 22 OM images revealing the quality of LPBF built Ti-Ta alloys via in-situ alloying: (a) CP Ti (b) Ti10Ta (c) Ti30Ta and (d) Ti50Ta.

3.3.2 Microstructures of Ti-Ta Parts

Table 7 summarizes the Ta content in matrix region, the available phase(s) and the mean lath/acicular width within the matrix region associated with each alloy composition in this study. The Ta Content in matrix regions (region away from unmelted Ta particles and Ta depleted area) were identified via EDS analysis. Meanwhile the phase(s) in majority are typed in bold and the phases formation are consistent with past studies on rapidly cooled Ti-Ta alloys [151, 172]. The conclusion of phase(s) formation is a combined evidence from the XRD analysis, BSE observation and EBSD analysis which will be discussed later in this section. With the BSE and EBSD analysis, the mean lath/acicular width associated with each part at the matrix region were measured and calculated.

Table 7 Percentage Ta content of matrix region, phase(s) and lath/acicular width associated with each alloy composition in-situ alloyed with LPBF. The phase(s) in majority are typed in bold.

Alloy Composition	Ta Content in Matrix Region (wt.%)	Available Phase(s)	Lath/Acicular Width (μm)
CP Ti	N/A	Lath α	4.637
Ti10Ta	9.8	Lath α' , Unmelted Ta	3.279
Ti30Ta	29.1	Acicular α'' , Lath α' , Unmelted Ta	0.079
Ti50Ta	47.6	Equiaxed β , Acicular α'' , Lath α' , Unmelted Ta	0.052

Figure 23 illustrates the XRD curves of LPBF as-built Ti(0, 10, 30, 50)Ta obtained from *in-situ* alloying.

Figure 23 XRD patterns of LPBF-built in-situ alloyed Ti-Ta alloys with different Ta contents.

The XRD curve of CP Ti shows the typical HCP α -Ti peaks. With slight addition of 10 wt.% Ta, peaks of HCP α' martensite can be observed which is a supersaturated solid solution of β stabilizing elements obtained from a quench-like process. Further addition of Ta in Ti30Ta leads to peak broadening without obvious peak splitting at the α' peaks. This signifies a mixed HCP α' martensite and orthorhombic α'' martensite formation. Further addition of Ta leads to the appearance of BCC peaks in addition to the α' and α'' martensite(s) peaks in Ti50Ta. The BCC peaks in Ti50Ta are jointly contributed by the unmelted Ta particles as well as the β -Ti phase. The co-existence of Ta particles and β -Ti phase in Ti50Ta are further confirmed with BSE observation (Figure 25d) and EBSD analysis (Figure 26d). It is good to take note that

short peaks that coincides with β -Ti peaks indicates the existence of unmelted Ta in all Ti-Ta alloys in this study.

LPBF is known to result in high cooling rates (between 10^4 and 10^6 K/s) that forms metastable phases [22, 40, 173, 174]. It was well agreed that metastable phases such as (α' , α'' , ω and metastable β) can exist in rapidly cooled Ti alloy systems [151]. The quench-like process of LPBF leads to the formation of full α' martensite due to fast cooling from the temperature range of β phase stability. The critical cooling rate necessary for the initiation of the martensitic shear process can be achieved in the LPBF process [175]. The α' phase is a supersaturated solid solution of β stabilizing elements in near α Ti composition and can lead to an increase in the α' unit cell volume [151]. Nevertheless, distinguishing XRD peaks between α and α' martensite can be difficult as there are only slight differences in their lattice constant. The differences can be shown in α phase [176] and α' martensite [177] of Ti6Al4V alloy, as shown in Table 8. To eliminate the possibility of *in-situ* α' martensitic decomposition into lamellar $\alpha + \beta$ structure [178], line EDS was conducted on Ti10Ta to confirm the retention of α' martensite based on the absence of solute diffusion (Figure 24a). The analysis shows that the lath phase does contains nearly 10 wt.% of Ta with no segregation at the lath boundaries, hence confirming it as the α' phase (Figure 24b).

Table 8 Lattice constant of α and α' martensite in Ti6Al4V.

Phase	α	α'
Lattice Structure	HCP	HCP
Space Group	P63/mmc	P63/mmc
Lattice Constants	a = 0.295 nm c = 0.469 nm	a = 0.293 nm c = 0.467 nm
Reference	[26]	[27]

Figure 24 Line EDS analysis on Ti10Ta part: (a) Line EDS analysis across lath- α_0 boundary (b) Result of line EDS analysis.

As the composition changes from Ti10Ta to Ti30Ta, the peak broadening effect without obvious peak splitting signifies a transition from α' martensite to α'' martensite. The absence of peak splitting in Ti30Ta is due to the slight changes in lattice structure from α' to α'' martensite(s). The transition of these two martensitic phases is continuous and is often considered as one martensitic phase $\alpha'(\alpha'')$ [179]. The extent of changes in such martensite's lattice structure is highly dependent on the amount of solid solution added [172, 180]. Similar XRD peak broadening effect on Ti-Ta alloys can be observed in past literature [172, 181].

For Ti50Ta, the addition of Ta lowers the martensitic finish temperature to below room temperature. Hence, partial martensitic transformation can be observed with the existence of retained prior- β phase. The XRD peaks of unmelted Ta coincides with the peaks of β phase in Ti50Ta, hence body centered cubic (BCC) XRD peaks can be observed in all *in-situ* alloyed parts with Ta addition [170].

The SEM images illustrated in Figure 25 were taken under the BSE (or SE when specified) mode to reveal parts' microstructure as well as compositional segregation.

Ta is a heavier element compared to Ti, which can lead to more back scattering of electrons, hence making BSE imaging mode an effective method to show the compositional contrast in such binary alloys. Figure 25a shows the microstructure of as-built CP Ti in this study which depicts the typical Widmanstätten lath- α microstructure ($\sim 4.637 \mu\text{m}$ width) in a LPBF produced CP Ti part [123, 148]. With slight Ta addition, Ti10Ta shows a finer lath- α ' microstructure ($\sim 3.279 \mu\text{m}$ width) transformed from prior- β phase with cellular dendritic sub-structure (Figure 25b). The prior- β grain boundaries in Ti10Ta cannot be easily observed from the BSE images and can be better seen from the EBSD mapping (Figure 26b). Both CP Ti (Figure 25a) and Ti10Ta (Figure 25b) parts show occasional microcracks in between the laths with CP Ti showing longer microcracks. The highly orientated microcracks from the fractography of CP Ti (Figure 31a) seems to be closely related to the microcracks as observed in BSE image of CP Ti (Figure 25a). Further addition of Ta as seen in Ti30Ta leads to substantial formation of Ta poor area (Figure 25c). High magnification BSE images at the matrix region (Figure 25e) of Ti30Ta shows the nanometer sized acicular- α'' structure ($\sim 0.079 \mu\text{m}$ width) while the Ta poor region (Figure 25f) shows the lath- α' structure. At Ti50Ta, β phase with cellular dendritic sub-structure was stabilized (Figure 25d) which is further confirmed in the EBSD analysis (Figure 26d). A higher magnification of Ti50Ta in the matrix region (Figure 25g) vaguely shows the existence of nanometer scale acicular- α'' structure ($\sim 0.052 \mu\text{m}$ width). Similar to Ti30Ta, Ta poor region in the Ti50Ta part shows the formation of lath- α' structure (Figure 25h). In all *in-situ* alloyed Ti-Ta parts, Ta-rich area

88

(indicated with red arrows in Figure 25) can be seen with some of them surrounded by Ta depleted area. The Ta-rich area is caused by incompletely diffused/melted Ta particles and the frequency of occurrence increases with more Ta addition due to the constant E_d input. In Ti50Ta, the BSE image shows a dark Ta-depleted area surrounding a cluster of agglomerated Ta particles (Figure 25d). The Ta depletion of the area leads to the formation of fine lath- α' martensite which is more obvious in the EBSD-mapping of Ti50Ta represented by overlaid band contrast mapping (Figure 26f). Moreover, the Ta depleted areas are seen to be commonly associated with the lack-of-fusion defect as seen in the overlaid SE image in Figure 25d.

Figure 26 EBSD mapping with IPF-Z coloring (BC showing minor phases): (a) CP Ti (IPF coloring for HCP), (b) Ti10Ta (IPF coloring for HCP and BC for unmelted Ta), (c) Ti30Ta (IPF coloring for orthorhombic and BC for unmelted Ta), (d) Ti50Ta (IPF coloring for BCC and BC for HCP), (e) Low magnification BSE image of CP Ti, (f) Higher magnification EBSD mapping for Ti50Ta to highlight lath- α phase. The white arrows highlight some of the Ta-rich areas/unmelted Ta.

The effect of rapid cooling cycles in LPBF process is clearly reflected in the microstructure of fabricated parts. The effect of such quench-like process can be seen in BSE images where non-equilibrium elongated phases such as lath- α' (Figure 25f) and acicular- α'' (Figure 25e) were formed. Meanwhile, the formation of cracks between laths might be due to the residual stress from the fast cooling cycle inherent to LPBF process. The α/α' colony size as well as the width of lath/acicular phase in all the printed parts can be closely associated to the addition of Ta. Ta exhibits slower diffusion rate in high temperature β -Ti as the concentration of Ta increases [182]. Such sluggish diffusion of Ta can become a limiting factor for the growth rate of lath/acicular phase which subsequently leads to finer microstructure [183]. The observed microstructure refinement is consistent with a similar Ti-Ta study previously done [123]. Lath refinement is often related to faster cooling rate in the past [184], but not as suitable as an explanation in this study for the same process parameter has been used for all the studied compositions. With smaller α/α' colonies, the effective slip length will be shorter. A smaller α/α' colony has more resistance towards micro-crack formation as the boundaries and martensitic plates are strong obstacles against microcrack propagation [185]. Rapid solidification can also lead to limited Ta diffusion, leaving some areas solidified before Ta has the chance to completely diffuse and homogenize the area. Hence, most of the Ta depleted areas can be seen accompanied with some unmelted/incompletely diffused Ta particles. Such compositional segregation can lead to formation of different phases in different areas, in which the effect is especially prominent in Ti50Ta. The compositional segregation of Ta leads to the formation of α' martensite due to insufficient β -stabilizing element to suppress such $\beta \rightarrow \alpha'$ transformation.

The formation of cellular dendritic substructure can be seen in parts with addition of Ta and can be related to the planar interface breakdown condition as shown in Equation (5).

$$\frac{G}{R} < \frac{T_{eq}}{D_L}, \quad (5)$$

where R is the dendrite growth rate, G is the temperature gradient ahead of solidification front, T_{eq} is the equilibrium solidification range of the alloy and D_L is the solute diffusivity in the liquid [186].

During the solidification process of Ti-Ta alloys, Ti rejection by the solid into the liquid ahead of solidification front occurs and the Ti needs to be transported away from the interface. This leads to a compositional gradient ahead of the solidification front which translates to a variation of liquidus temperature. Depending on the G/R ratio, substructure morphology can go from planar, cellular, cellular dendritic, columnar dendritic to equiaxed dendritic. If the $\frac{G}{R} > \frac{T_{eq}}{D_L}$, the cellular dendritic solidification front can be simply re-melted leading to stabilization of the planar interface. The formation of cellular dendritic substructure of Ti-Ta parts in this study can be ascribed to the satisfaction of $\frac{G}{R} < \frac{T_{eq}}{D_L}$ condition. This leads to the breakdown of a planar interface, resulting in constitutional supercooling and the formation of cellular dendritic substructure. In dilute Ti alloys (Figure 25a), there is subtle difference between the solidus and liquidus line and T_{eq} approaches 0. Furthermore, the temperature gradient is positive towards the BD in a LPBF process where $\frac{G}{R} > 0$ [72]. The stable planar interface can be formed in this case without existence of constitutional supercooling, hence the absence of cellular dendritic substructure.

Figure 26 elucidates the EBSD mapping of each samples in inverse pole figure (IPF) - Z coloring. Band contrast (BC) mappings are overlaid in some images to show minor phase(s) present in the mapping. Despite being a BSE image, Figure 26e is included to show columnar prior- β grain boundaries associated with Figure 26a.

CP Ti is IPF colored for HCP indexing (Figure 26a), Ti10Ta for HCP indexing (Figure 26b), Ti30Ta for orthorhombic (Figure 26c) and Ti50Ta for a BCC lattice indexing (Figure 26d). The band contrast was overlaid on the mapping to show unmelted Ta in as-built Ti10Ta and Ti30Ta while showing lath- α' in as-printed Ti50Ta. Large amounts of black colored unindexed area can be seen in the EBSD mapping of Ti30Ta (Figure 26c) and Ti50Ta (Figure 26d) due to the compositional segregation that causes phase differences as well as continuous changes in lattice constant. EBSD mapping of CP Ti (Figure 26a) clearly shows different variants of lath- α nucleated from prior- β grains. Unfortunately, the prior- β grain boundaries in CP Ti cannot be clearly observed in the EBSD mapping. With the aid of BSE image (Figure 26e), long and large columnar prior- β grains in which the lath- α nucleates from can be seen. Nevertheless Ti10Ta (Figure 26b) shows finer lath- α' transformed from columnar prior- β along with some stray prior- β grains. Meanwhile Ti30Ta (Figure 26c) shows orthorhombic phase with more randomly orientated elongated prior- β grains. Mapping of Ti50Ta shows equiaxed β phase (Figure 26d) as well as lath- α' phase (Figure 26f) surrounding areas with unmelted Ta due to insufficient Ta to retain the β phase. The speckles of unindexed area of Ti50Ta within the β phase might be caused by the embedded acicular- α'' phase which is difficult to be indexed (Figure 26f).

Pole figures were plotted to highlight the effect of Ta addition towards the overall parts' texture, as shown in Figure 27.

Figure 27 Pole figure with in-plane axis parallel to the BD (a) Ti (HCP) (b) Ti10Ta (HCP) (c) Ti30Ta (Orthorhombic) and (d) Ti50Ta (BCC).

Burger's orientation relationship of β phase with other phases are listed below to provide a better idea on texture of β grain prior to transformation to a stable/meta-stable phases at room temperature:

$$(0001)\alpha \parallel (011)\beta [176]$$

$$(001)\alpha' \parallel (011)\beta [177]$$

$$(001)\alpha'' \parallel (011)\beta [176]$$

The minimum and maximum value in the pole figures represent the “multiple of uniform density” (MUD) value which can be defined as the intensity of crystallographic orientation with relation to the normalized value in random orientation. The pole figure of CP Ti shows a highly columnar prior- β texture that has the axis of (001) plane strongly aligned with the BD. The pole figure obtained for the as-built Ti is similar to the Ti that undergoes unidirectional rolling above β transus temperature [185]. The maximum MUD value for Ti10Ta (9.81) becomes weaker compared to CP Ti (16.39) but still exhibits columnar prior- β characteristics. The pole figure for Ti30Ta shows a more randomly orientated prior- β texture compared to Ti10Ta. Nevertheless, preferential prior- β grain growth in the (001) direction can still be seen along the BD. As-built Ti50Ta shows the weakest texture among all the printed samples. The maximum MUD value is the lowest among all samples (5.44) with the β phase having slight preferential (001) growth in the BD. The general trend of texture with Ta addition can be clearly depicted with the MUD value associated with each part (Figure 27).

The crystal nucleation mechanism of an alloy can greatly influence the resultant texture. LPBF process typically possesses high G/R ratio that promotes epitaxial growth (heterogenous nucleation) from the previously formed crystal. Moreover, the general direction of heat flow is opposite to the BD and promotes competitive growth of crystals. Hence, LPBF processed Ti alloys typically possess long columnar prior- β grains with respect to the BD [187]. The addition of Ta can limit the columnar prior- β grain formation by acting as nucleation sites if the Ta particles do not melt completely before the part solidifies. The promotion of epitaxial growth of prior- β crystals from unmelted Ta particles can occur due to the low lattice mismatch between

the two phases. A BSE image of Ti50Ta in the matrix region (Figure 28) clearly shows nucleation of β grain from an unmelted Ta particle. With the unmelted Ta acting as a heat sink, β -Ti “stray” grain can nucleate and grow away from the Ta particles. With the existence of such “stray” grain, columnar β grain parallel to the Z direction will be fully/partially blocked. This results in more grains of different orientations to grow epitaxially from, leading to smaller prior- β grains. As more Ta were added while retaining the same E_d used during LPBF, more unmelted Ta particles are retained and disrupt the formation of columnar grains. Hence, the texture of β /prior- β phase becomes weaker as more Ta particles are added.

Figure 28 SEM BSE images revealing prior- β grain nucleated from unmelted Ta particle.

3.3.3 Mechanical Properties of Ti-Ta Parts

The tensile properties of LPBF produced Ti-Ta alloys are shown in Figure 29.

Figure 29 Mechanical properties of Ti-Ta alloys with different Ta wt.% (a) E (b) UTS (c) YS and (d) ϵ_f .

With the addition of Ta, the YS and UTS increases and peak at Ti30Ta which immediately followed by a slight drop at Ti50Ta. An inverse trend is observed for the E where Ti30Ta exhibits the lowest average value. Such trend is similar to the trend reported in a previous work [188]. The strengthening of the Ti-Ta alloy systems up to Ti30Ta can be caused by a combination of (a) Solid solution strengthening (b) Lattice transformation and (c) Grain boundary strengthening - Hall Petch effect. From the BSE and EBSD analysis, it can be observed that the average value of lath/acicular size decreases with the addition of Ta (Table 7). As the microstructure becomes finer, dislocation movement across the grain boundary can become difficult and thus increases the mechanical strength (Hall Petch effect). The slight drop of strength at Ti50Ta is caused by the formation of β (BCC) phase which exhibits more slip systems. Unlike other Ti-Ta compositions, Ti50Ta has large retained β grains as the majority phase according to the EBSD analysis (Figure 26d). As such, the strengthening effect

from lath/acicular refinement is not as effective for Ti50Ta as compared to those in CP Ti, Ti10Ta and Ti30Ta where the lath/acicular phase forms the phase majority. It can be seen that the trend of YS and UTS is closely followed by the trend of microhardness value tested in either the xy- and yz- planes (Figure 30). Moreover, the effect of Ta addition on hardness for both xy- and yz- planes is similar.

Figure 30 Vickers microhardness value of Ti-Ta alloys with different Ta wt.% (a) x-y plane (b) y-z plane.

The fractography of the Ti-Ta alloys are shown in Figure 31.

Figure 31 Fractography of (a) CP Ti (b) Ti10Ta (c) Ti30Ta (d) Ti50Ta.

All four groups of specimens show signs of ductility as the specimens showed necking before the specimen fractured. The fractographies obtained from SEM confirm that they exhibit both brittle and ductile fracture. The surfaces of the specimens show the presence of cleavage facets that indicates brittle failure, and ductile dimples and voids that indicates ductile fracture. From the fractography, preferential crack path behaviors can be observed in CP Ti (Figure 31a) which can be correlated with those in Figure 25a. Meanwhile, the fractographies (Figure 31a-d) show that the void occurrence on the fracture surfaces increase with Ta addition which is closely related to the porosity level and the amount of unmelted Ta (Table 6). As observed in the BSE images in Figure 25c and d, unmelted Ta is commonly surrounded by Ta poor region which is comprised of lath- α' phase. Strain incompatibility and stress concentration can be expected at the lath- α' (HCP)/Ta(BCC) boundary due to the lattice mismatch between the two phases [149]. Such mismatch possibly leads to interface rupture and subsequently contribute to void formation and coalescence. Hence, the addition of Ta showed decreasing trend of elongation due to the occurrence of defects such as porosity and unmelted Ta particles. Similar observation was indeed observed in a study on LPBF *in-situ* alloyed Ti-Nb-Sn [135]. Nevertheless, such claim of voids formation remains a sound hypothesis and the fractography only provides indirect evidence. Further investigation is still required to study and confirm such claim of void formation mechanism.

3.4 Summary

This study shows that the amount of Ta in Ti-Ta alloys fabricated using LPBF has effect on their defect formation, microstructure and mechanical properties.

Based on the results, the key findings can be summarised:

- 1) The addition of Ta leads to defects evolution from keyhole induced porosity to incomplete fusion of melt pool.
- 2) As the content of Ta increases in the Ti-Ta alloys, the phases present in the alloys change from $\alpha \rightarrow \alpha' \rightarrow \alpha'' + \alpha' \rightarrow \beta + \alpha'' + \alpha'$. Phases detected in the alloy matrix are in bold text.
- 3) Ti30Ta provides the optimal mechanical properties for orthopaedic applications due to its lowest modulus while having the highest UTS and YS. The addition of Ta refines the lath/acicular phase size which strengthens the Ti-Ta alloy up to Ti30Ta. Further Ta addition to Ti50Ta leads to coarse β phase retention.
- 4) The decrease in ε_f with Ta addition is due to the increased amount of porosity and unmelted Ta in the alloy matrix.

This study provides a preliminary understanding on the issues and details associated with the *in-situ* alloying of Ti-Ta alloys. The understandings can be suitably extended to other Ti alloys with refractory biocompatible β stabilizer addition. This will provide ideas for future planning that helps to expedite development in this area of studies.

Chapter 4 Resolving the Porosity-unmelted Inclusion Dilemma During *In-Situ* Alloying of Ti34Nb via Laser Powder Bed Fusion

4.1 *Introduction*

Based on the previous chapter on Ti-Ta alloy, the defects formation associated with Ta addition needs to be addressed. To further reduce the defects formation, Nb was utilized in place of Ta due to Nb's lower melting point as compared to Ta (Table 4). The lower melting point is useful to achieve *in-situ* alloyed part with better homogeneity. Moreover, a slightly lower than fully β meta-stabilized composition (range for α'' martensite formation) of Ti34Nb (wt.%) was chosen based on the previous chapter on Ti-Ta alloy, where it was shown that the slightly lower than fully β meta-stabilized composition range can have a combination of low E and high YS. The range of α'' martensite formation for Ti was shown to be between 23 [180] to 50 [189] wt% Ta addition or with 21.5 [190] to 40.6 [191] wt% Nb addition. The underlying assumption is that having similar phase stability will lead to similar deformation mechanism and effect of elastic modulus reduction. Phase stability of Ti with β stabilizer can be generalized with the average Bo ($\overline{Bo}$) and Md ($\overline{Md}$) value of the resultant alloy, where Bo is the bond order and Md is the metal d-orbital energy level [28]. The $\overline{Bo}$ and $\overline{Md}$ of a resultant Ti based alloy can be obtained by taking the compositional average of Bo and Md value associated with each element. Since Nb and Ta have similar Bo and Md value, their addition into Ti will yield similar effect.

As the defect minimization in an *in-situ* alloyed β -Ti component remains the biggest challenge, this chapter focusses on addressing the issue.

Similar to Ti-Ta alloys, Ti-Nb alloys are considered promising materials for making biological implants that support and strengthen broken bones in the human body. Ti-Nb alloys are appealing as their E ranges from 30 to 65 GPa, depending on the Nb concentration. An additional advantage of Ti-Nb alloys as an implant material is that the constituents are non-toxic, whereas Ni in SS316L, Co and Cr in CoCrMo and Al/V in Ti6Al4V are associated with cytotoxicity [10].

Although Ti-Nb alloys have low E , they can only be considered structurally viable for implant applications if they possess reasonable strength and toughness. The key requirements to satisfy these conditions are (a) a single phase β -Ti microstructure, which is the toughest phase in Ti alloys (b) a texture that ensures minimum E , and (c) a strengthening mechanism that ensures high yield strength. A recent study reported that a cold rolled and annealed Ti33Nb4Sn (wt.%) alloy has the ideal combination of low E ~36 GPa and high strength of 853 MPa due to a fine grained β -Ti microstructure with high dislocation density. Employing similar conventional processing techniques, implants manufactured from Ti13Nb13Zr and Ti29Nb13Ta4.6Zr are already commercially available [152, 192]. However, switching to AM technologies, such as LPBF, to develop these implants is a more attractive alternative as the process is significantly more cost effective, time efficient and recycling friendly [9]. The method offers customizability of design and the option of tuning process parameters such as, P , V_L , scanning patterns, etc. to develop specific microstructural features that suit a particular need [164, 193-198]. It is also specifically suited for making Ti-Nb implants,

as the fast cooling cycles, intrinsic to the LPBF process, is ideal for obtaining a fine microstructure and retaining metastable β -Ti phase at room temperatures.

Despite these benefits, LPBF fabrication of Ti-Nb alloy implants is limited by the unavailability of printable pre-alloyed powders of specific compositions, a problem similar to Ti-Ta alloys. As previously mentioned, although *in-situ* alloying is cost effective and conceptually trivial, it has the following drawback associated with it. Since the constituents are expected to have different melting points, it is unlikely that the two would melt uniformly when scanned with the same P . Typically, one of the constituents either vaporizes or segregates as an unmelted inclusion in the alloy. In Ti-Nb alloys the latter situation is often encountered. Some studies suggested that the content of unmelted Nb can be reduced by increasing the volumetric E_d [122, 135]. As discussed in literature review section, E_d is related P , V_L , h and t , by Equation (3). Based on Equation (3), P must be increased while all the other parameters must be decreased to increase E_d . However, it was observed that while a progressively higher E_d is effective in reducing the content of unmelted Nb, it leads to the formation of keyhole induced porosity in the alloy, which is also an undesirable defect. This conundrum, referred to as the porosity-inclusion dilemma, which is also observed in other Ti based alloys such as Ti-Ta, has not been resolved by optimization strategies that vary E_d , although a few have been tried [122, 124, 135]. It was also noted that while E_d is a good measure of the energy input during printing, it does not consider the subtle variations associated with material-laser interactions, and hence becomes an empirical method to predict build characteristics. To compensate for this, a normalized enthalpy optimization strategy, which involves material as well as printing parameters in LPBF, was developed [199]. However, the application of this strategy

in the case of *in-situ* alloying was unsuccessful as the formulation does not consider the effect of multiple constituent powders [124]. Moreover, the normalized enthalpy approach does not capture the re-melting effect of adjacent laser scans as the influence of h is not incorporated in the equation. Considering the limited success of this method in the context of *in-situ* alloying via LPBF, E_d has been the de-facto standard when it comes to process optimization for the *in-situ* alloying process. Some other studies partially resolved the porosity-inclusion dilemma and reduced the content of unmelted inclusion, at a fixed porosity content, by employing the laser re-scanning/re-melting technique, where at least twice the number of scans are performed on each layer to ensure better mixing of the constituents [124, 125]. However, this method significantly increases the printing time and energy consumption, which translates to a higher average cost per part.

This chapter demonstrated an alternate strategy of focusing on the melt pool characteristics and dynamics, instead of E_d optimization, is the real key to resolving the porosity-inclusion dilemma in LPBF printed Ti-Nb alloys. For this, samples were built with three different printing parameter sets, where P and V_L were varied while h and t were held constant. P and V_L were also varied in the same proportion, i.e. their ratios were the same in all parameter sets, to ensure invariance of E_d . In addition, the effect of two different laser profiles, namely the Gaussian and top-hat, and influence of the stripe scanning strategy were also considered. The quality of samples was examined via XCT, the microstructural characterization was performed with FESEM and EBSD and, the mechanical properties were assessed by conducting uniaxial tension tests. Results of these investigations show that a combination of highest P and V_L , short stripe width scanning strategy and a top-hat laser profile produces a fully

105

dense Ti-Nb alloy with a minimal volume fraction of unmelted Nb. Moreover, the microstructure of the sample printed with this parameter set has the optimum microstructure for superior mechanical performance -- β -Ti columnar grains and a dominant {100} texture along the BD. Using direct visualization of single tracks and single stripes, complemented by a simple thermal FEM simulation of the latter, it is arguable that optimizing the dynamics and dimensions of the melt pool, which is facilitated by appropriate parameter optimization -- is necessary for printing defect free, high quality Ti-Nb implants.

4.2 *Experimental Details*

4.2.1 Laser Powder Bed Fusion

Samples were fabricated using an in-house developed Ti-Nb elemental powder blends with 34 wt.% Nb. The Ti34Nb powder blend was obtained by mixing spherical gas atomized CP Ti and Nb powders (> 99.8%). The CP Ti powder (Grade 2 ASTM B348, LPW Technology Ltd, United Kingdom) particles have a median diameter of 43.5 μm while the Nb powder (Tecnisco Advance Material Pte Ltd, Singapore) has a particle size distribution that ranges between 20 to 63 μm . The two elemental powders were mixed and blended for 12 hours at a rate of 30 rpm using a tumbler mixer (Inversina 2 L, Bioengineering AG). The blending process was conducted under an Ar atmosphere. The primary reason to step down the rpm (as compared to Chapter 3) is to reduce the extent of heating and vibration of the blending machine. Nevertheless, the powder is found to be well mixed which can be seen in Figure 32.

Figure 32. *Ti₃₄Nb powder mix for in-situ alloying.*

The sample fabrication process was carried out using the SLM 250 HL machine (SLM Solutions Group AG). The machine was customized to be equipped with two fibre laser types, as shown in Figure 33a. One of the fibre lasers is conventionally available in many other LPBF machines, which is a Gaussian beam profile laser (1064 nm) with a focus diameter of 80 μm and a maximum P of 400 W. The second equipped fiber laser (1064 nm) has a top-hat profile with a focus diameter of 200 μm and a maximum P of 1000 W. All fabrication processes were carried out in an Ar environment of < 500 ppm O_2 to prevent oxidation and interstitial element contaminations. The samples were built on Ti base plates with area dimensions of $100 \times 100 \text{ mm}^2$. Also, all samples were prepared using the same E_d input and rotated stripe scanning strategy but with different P and V_L . The schematic of a single track and stripe pattern is shown in Figure 33b. While a single track involves laser scan movement along one direction, a stripe pattern consists of anti-parallel scan vectors, which raster and create a scanned patch that has a much larger width than a single track (blue dashed line in Figure 33b). Each layer is built by a series of parallel stripes that spans its entire length. A

schematic of the rotated stripe scanning strategy is shown in Figure 33c. In every subsequent new layer, the stripes rotate clockwise by $\sim 79^\circ$ with respect to the previous layer. The details of scanning parameters associated with each sample can be seen in Table 9. Note that the samples will hitherto be referred to by the corresponding applied P used for printing them, i.e. 350W, 650W and 950W. The laser profile of sample 350W is Gaussian, whereas those of the other two are top-hat.

Figure 33. Schematic representations of (a) Gaussian and top-hat laser profiles, (b) Schematic of single track and single stripe scanning and (c) The scanning strategy employed. The black arrow in (b) indicates the laser scan paths and directions associated with each scan type.

Table 9 Different combinations of LPBF process parameters utilized for manufacturing the Ti-Nb alloy samples.

Sample name	Power, P (W)	Hatch, h (μm)	Stripe Width (mm)	Scanning Velocity, V_L (mm/s)	Layer Thickness, t (μm)	Rotation ($^\circ$)	Energy Density, E_d (J/mm^3)	Laser Profile
350W	350	80	1	350	50	79	250	Gaussian (80 μm)
650W	650	80	1	650	50	79	250	Top-Hat (200 μm)
950W	950	80	1	950	50	79	250	Top-Hat (200 μm)

4.2.2 Sample Evaluation

The percentage porosity and percentage of unmelted Nb in fabricated samples were analysed via XCT (SKYSCAN 1173, Bruker, Germany). X-ray scanning was

performed at a voltage of 130 kV using a brass filter on the side surface of the sample, which is on the surface perpendicular to the BD. The 3D reconstructed volumes are made up of isotropic cube voxels with a side length of 5.7 μm . Only pores/inclusions with at least 9 voxels were considered to minimize the probability of false segmentation. 3 threshold values were taken during the analysis to account for the error [200] and the standard error was obtained. The sphericity, ψ of each pore/particle was determined from:

$$\psi = \frac{6 \cdot \pi^{\frac{1}{2}} \cdot \Phi}{\Pi^{\frac{3}{2}}}, \quad (6)$$

where Φ is the volume and Π is the surface area of a pore/inclusion. Archimedes principle was used to measure the density and the surface melt pool characteristics of the samples were examined using confocal microscopy (VK-X250, Keyence, Japan). The surface profile for as-printed samples was scanned using a height pitch of 0.1 μm .

4.2.3 Metallographic Characterization

The samples were sectioned to reveal the cross-sectional area parallel and perpendicular to the BD. Grit #320 SiC-paper were then used to grind the cross-sections followed by a fine grinding with MD-Largo (DiaPro Largo 9 μm suspension, Struers). Finally, the samples were polished to a mirror finish using MD-Chem (OPS 0.04 μm suspension + H_2O_2 , Struers). OM was employed to assess the quality of the surface finish after polishing. The identification of constituent phases in all samples were done by analysing each sample with XRD (PANalytical Empyrean, Netherlands) using Cu-K α radiation and a step size of 0.01°. Microstructural characterization was conducted with a FESEM (JEOL 7600F, JEOL, Japan) equipped with a BSE detector. EDS was done to ascertain the composition of phases. Texture analysis was done with

EBSA analysis using FESEM equipped with an AZtecHKL Oxford detector. The EBSA mapping was conducted with a scanning step size of 1.5 μm .

4.2.4 Finite Element Method Simulation

A simple thermal simulation was performed for a single stripe scan using the FEM function in COMSOL Multiphysics to model the melt pool geometry and its evolution as a function of the laser scanning parameters in the LPBF process. The solver analyses the laser-powder interaction at 350W and 950W to obtain the temperature history of the powder and substrate. The temperature evolution due to thermal conduction, convection and radiation were obtained by solving the following equations:

$$Q = \rho c_p \frac{\partial T}{\partial t} - \nabla \cdot (K \nabla T), \quad (7)$$

$$q_{conv} = h_c (T - T_0), \quad (8)$$

$$q_{rad} = \sigma \varepsilon (T^4 - T_0^4), \quad (9)$$

Where, Q is the heat input, q_{conv} is the convective heat lost due to Ar gas flow, q_{rad} is the radiative heat loss, ρ is the density, c_p is the specific heat capacity, K is the heat conductivity, h_c is the convection heat transfer coefficient (~ 0.25), σ is the Stefan-Boltzmann constant, ε (~ 0.45) is the emissivity and T_0 (~ 293.15 K) is the ambient temperature. Radiative and convective heat loss are considered on the top surface as the boundary conditions, whereas all the other surfaces are thermally insulated. The size of the model is chosen to be sufficiently large such that the effect of heat accumulation at the insulated model boundaries does not affect the melt pool formation. Meshing was performed with 12663 brick elements with maximum and

minimum feature size of 75 μm and 25 μm respectively. Mesh convergence analysis confirmed that further mesh refinement has insignificant effect on melt pool formation. The results were validated with the top views and cross sections of single stripe scans, based on the observed melt dimensions. Time step for 350W and 950W were set at 10 and 30 μs respectively. A schematic of this meshed model is shown in Figure 34.

Figure 34 Schematic of model to study melt pool evolution during laser scanning.

For the gaussian and top-hat distributions laser beam profiles, Q is estimated from a volumetric heat source that is based on the Beer Lambert's law [201]:

$$Q_{Gaussian} = \frac{2AP}{\pi r_0^2 S_d} \exp\left(-\frac{2(x^2 - y^2)}{r_0^2}\right) \exp\left(\frac{-|\lambda - z|}{S_d}\right), \quad (10)$$

$$Q_{Top\ Hat} = \frac{2AP}{\pi r_0^2 S_d} \exp\left(-\frac{2(x^2 - y^2)^5}{r_0^{10}}\right) \exp\left(\frac{-|\lambda - z|}{S_d}\right), \quad (11)$$

Where A is the absorptivity of laser (~ 0.17), r_0 is the laser beam radius, λ is the thickness of the simulated volume and S_d is the laser absorption depth. The lower absorptivity in comparison to emissivity is due to the assumption where energy loss

due to vaporization was not considered. The r_0 value used for gaussian and top-hat beam are 40 μm and 100 μm respectively. The S_d value in this study is limited to the thickness of powder bed ($\sim 50 \mu\text{m}$). The usage of volumetric heat source had been shown to provide better estimation of thermal history over surface heat source [202].

The thermophysical properties of Ti34Nb are obtained from commercially available thermodynamics software and are listed in Appendix A. To account for the Marangoni effect on heat transfer, the K above the liquidus temperature was artificially increased by a factor of two.

The modelling framework contains elements of the powder and substrate. Above the liquidus temperature, T_m of the powder, it is assumed that the powder and substrate have the same K and ρ . However, below the solidus temperature, T_s , The K and ρ of the powder and substrate have the following relationships.

$$K_{\text{powder}} = K_{\text{substrate}}(1 - \emptyset)^x, \quad (12)$$

$$\rho_{\text{powder}} = \rho_{\text{substrate}}(1 - \emptyset), \quad (13)$$

Where $\emptyset$ is the porosity of the packed powder bed, which is 0.4 and $x \sim 4$ is an empirically determined exponent [93, 203].

At a temperature intermediate of the solidus and liquidus temperature, K and ρ of the material is estimated as [203]:

$$K = \frac{K_{\text{substrate}}(T_m) - K_{\text{powder}}(T_s)}{T_m - T_s} (T - T_s) + K_{\text{powder}}(T_s), \quad (14)$$

$$T_s < T < T_m$$

$$\rho = \frac{\rho_{\text{substrate}}(T_m) - \rho_{\text{powder}}(T_s)}{T_m - T_s} (T - T_s) + \rho_{\text{powder}}(T_s), \quad (15)$$

$$T_s < T < T_m$$

As the powder melts, it undergoes a powder (porous solid) to liquid transformation. Upon cooling, the liquid transforms to solid, and is treated as a substrate (solid) material.

The latent heat of fusion, ΔH , is incorporated in the modified expression for determining c_p , which is,

$$c_p = \frac{1}{\rho} \left[\theta \rho_{\text{solid}} c_{p,\text{solid}} + (1 - \theta) \rho_{\text{liquid}} c_{p,\text{liquid}} + \Delta H \frac{\delta}{\delta T} \left(\frac{(1 - \theta) \rho_{\text{liquid}} - \theta \rho_{\text{solid}}}{2[\theta \rho_{\text{solid}} + (1 - \theta) \rho_{\text{liquid}}]} \right) \right], \quad (16)$$

Where θ is the volume fraction of the solid phase.

4.2.5 Mechanical Characterization

Two sets of custom designed mini tensile coupons were produced from the LPBF manufactured 350W and 950W Ti34Nb samples using EDM. The two samples and machined tensile coupons are shown in Figure 35a and b, respectively. Reference axes are also indicated in the figure. A schematic of the tensile coupon showing its dimensions is displayed in Figure 35c. Uniaxial tensile test were performed on a UTM (AG-X plus 10 kN, Shimadzu, Japan) with a loading rate of 0.024 mm/min. The tensile coupon is loaded perpendicular to the BD (y axis in Figure 35b) and the strain is measured with a video extensometer during test (TRview x55s, Shimadzu, Japan). While it is important to conduct tests along the BD, such samples could not be

fabricated due to build volume limitation stemming from the limited availability of powder.

A minimum of three tests were performed for each sample. Fractography was performed with a FESEM in the SE mode. Post facto EBSD and BSE analysis were performed on the side surfaces (y-z plane) of the coupon.

Figure 35 Images of (a) In-situ alloyed parts built via LPBF and (b) Machined customized tensile coupon. (c) Schematic representation of the customized tensile coupon.

4.3 Results

4.3.1 Sample Quality

In-situ alloyed samples printed by LPBF typically contain pores and unmelted metal particles as inclusions. Therefore, the print quality is benchmarked with respect to the porosity and inclusion content. The OM images and 3D reconstructed volumes (obtained from XCT) of the 350W, 650W and 950W Ti34Nb alloy samples are displayed in Figure 36. Pores and unmelted Nb inclusions were identified and color

coded with green and red, respectively, for visualization purposes. The same are also labelled in the corresponding OM images. 3D reconstructed volume from XCT of each sample was analysed with XCT analysis tool and the % volume fraction of porosity, U_P , was obtained. Similarly, the volume % of unmelted Nb inclusions and their D_{50} were also measured. Then, the % unmelted Nb, U_{Nb} , was calculated from the following equation:

$$U_{Nb}(\%) = \frac{\text{Volume \% of Nb particle detected by XCT in sample (\%)}}{\text{Volume \% of elemental Nb particles in powder mix (\%)}} \quad (17)$$

Where the volume % of elemental Nb particles in powder mix is 21.3%. Note that the XCT analysis can only resolve porosities and inclusions that are larger than a minimum volume equivalent diameter of 14.7 μm . Table 10 lists U_P , U_{Nb} , D_{50} and the density¹ of each sample. In the 350W sample, $U_{Nb} \sim 0.028\%$, but is 5 times lower in the 650W sample and further reduces to $\sim 0.002\%$ in the 950W sample. Variations in D_{50} also follows a similar trend i.e. it is 43.6 μm in the 350W sample but 37.8 μm and 35.8 μm in the 650W and 950W samples, respectively. Visual examination of OM images in Figure 36 also validates these observations. This indicates that higher P assists *in-situ* alloying by facilitating better melting and mixing of Nb particles, which in turn improves compositional homogeneity of the alloy. This trend in the reduction of the inclusion size is similar to that seen in a study on *in-situ* alloyed electron beam melted Ti-Nb where lower inclusion size was correlated to increased alloy homogeneity [204]. The Ψ distribution of Nb inclusions are shown in Figure 37. For

¹ The density should not be directly correlated with the volume fraction of porosity in this study as macro-segregation of unmelted Nb occurs

all samples Ψ is in the range of 0.8 - 0.9, which confirms that they are predominantly spherical.

Figure 36 XCT reconstruction showing the 3D porosity and unmelted Nb distribution in the 350W, 650W and 950W samples. Pores and unmelted Nb are marked in green and red, respectively. OM images of the corresponding samples show the 2D appearance of these defects.

Table 10 Summary of the defect characteristics and Archimedian density of the three LPBF printed samples. All values are quoted with a confidence interval of 99.7%..

Sample name	350W	650W	950W
Porosity volume fraction (%), U_P	0.12±0.1	N/A	N/A
Unmelted Nb (%), U_{Nb}	0.028±0.0024	0.006±0.0005	0.002±0.0002
Median size of unmelted Nb, D_{50} (μm)	43.6±0.9	37.8±0.4	35.8±0.6
Density (g mm ⁻³)	5.33±0.008	5.36±0.006	5.35±0.002

Similarly, while $U_P \sim 0.12\%$ for the 350W sample, no pores were observed in the 650W and 950W samples via XCT. The pores in the 350W sample (see Figure 38) have irregular shapes with well-defined rims and their appearance matches those of keyhole induced porosities [205]. Careful SEM imaging of 650W and 950W samples confirmed the absence of lack-of-fusion porosity and keyhole induced porosity. However, both samples contain negligible amounts of spherical gas porosities, which have a diameter $< 7 \mu\text{m}$. Less than 8 pores were detected over an area of 20 mm*15

mm for all samples. Representative SEM images of the different types of pores observed in this study are shown in Figure 38.

Figure 37 Sphericity distribution of Nb inclusions corresponding to 350W, 650W and 950W samples.

Figure 38 Representative SEM images of porosity defects: keyhole porosities corresponding to 350W sample and gas porosity corresponding to 350W, 650W and 950W samples.

Prior studies on LPBF printed Ti-Nb alloys, observed that builds with lower U_{Nb} have a higher content of keyhole porosities and vice versa [122, 135]. Therefore, the simultaneous reduction in inclusion content and porosity in 650W and 950W samples is a significant breakthrough in process optimization of in-situ alloying with LPBF. The negligible porosity level also implies that the practice of including an additional

remelting/rescanning step for porosity minimization can be discontinued, which will reduce the time and cost of manufacturing [124, 125]. From these results it is evident that printing a 950W laser with a top-hat profile and stripe scanning strategy is most preferable in terms of build quality, time efficiency and cost savings.

4.3.2 Phase Constituents and Microstructure

EDS and XRD data were examined to evaluate the phase compositions and their respective constituents in the 3 samples and the results are displayed in Figure 39a and b, respectively. In all samples, EDS was performed at locations away from the unmelted Nb inclusions. The Nb content in all samples are ~34% and are within $\pm 1\%$ of the target or expected composition. The deviation is reasonable considering the quantification error involved with samples with compositional macro-segregation. This is denoted by a dotted horizontal line in Figure 39a. A definitive trend in compositional variations cannot be identified as the scatter will be affected by the resolution limit of EDS. On indexing the XRD scans from each sample, only peaks corresponding to a BCC phase were detected, which indicates the presence of β -Ti in all of them. According to the phase diagram of Ti, the room temperature phase is the α phase that has a hcp crystal structure. Alternately, the β phase is stable above the β transus, which is 700 °C. However, if the composition of the alloy and cooling rate is suitably adjusted, β -Ti can also be stabilized at lower temperatures. For Ti-Nb alloys the ideal composition for ensuring β stability at ambient temperatures is determined from the Molybdenum equivalency (Mo_{eq}), which is defined as [103]:

$$Mo_{eq} (\%) = 1.0Mo + 0.67V + 0.44W + 0.28Nb + 0.22Ta + 1.0Al \text{ (wt.\%)}, \quad (18)$$

For alloys in the current study, $Mo_{eq} \sim 9.52\%$, which is very close to the prescribed critical value of 10% required for β stabilization [206]. The retention of β phase at room temperature is further facilitated by the inherent fast cooling rates associated with the LPBF process. A similar result was obtained in a previous study on *in-situ* alloying of Ti35Nb via LPBF [126], although the XRD peaks corresponding to the β phase in this study are comparatively sharper owing to better compositional homogeneity of the samples in this study.

Figure 39 (a) Composition of the three LPBF printed Ti-Nb samples analysed by EDS and (b) their XRD patterns. The error bars represent confidence interval of 99.7%.

Figure 40a displays the SEM images of top view (x-y cross-section) and side view (x-z cross-section) of 350W, 650W and 950W samples. Specific regions of interest in Figure 40a, which are enclosed by blue, red and yellow rectangles are magnified and shown in Figure 40b-d. In the side view of the 350W sample, the melt pools, traced by dashed blue lines, have a relatively high aspect ratio and contain pores within them.

The formation of pores within a melt pool of comparatively high aspect ratio provides further evidence that they are keyhole porosities.

The magnified view of a section from the top view of 350W sample (see Figure 40b) reveals that defects such as pores and unmelted Nb are located near the edge of a scan stripe boundary. Although it is relatively less obvious in 650W and 950W samples, the unmelted Nb inclusions in them are also located near the scan stripe boundary (see Figure 40a). The formation of keyhole pores at the scan stripe boundaries of all samples is the outcome of the deceleration or the shutting down of the laser beam at the end of the laser scan [207]. A rapid transition in the V_L causes vapor collapse followed by partial infill of liquid metal, thereby trapping gas, which in turn leads to pore formation. While this mechanism explains the formation of pores in the 350W sample, the negligible porosity level in the 650W and 950W samples appears to be an outcome of other factors, which will be addressed later.

Alternately, the formation of unmelted Nb inclusions at the stripe boundaries is an outcome of fast cooling rates, which limits Nb diffusion away from the stripe edge. Fast cooling rates in the vicinity of the scan stripe boundary is facilitated by the rapid heat dissipation to the adjacent solidified stripes and the cold unscanned powder, the two of which act as heat sinks. In addition, the extent of re-melting near the stripe boundaries is limited, which further contributes to the amount of unmelted Nb inclusions.

A magnified view of the stripe center region in 350W samples is shown in Figure 40c. This region has a coarser cellular dendritic substructure compared to that in the stripe boundary region, indicating that it experienced a relatively slower cooling rate [130].

Moreover, the grain growth direction in the stripe boundary region, near unmelted Nb, is relatively random (see Figure 40b and Figure 40d), unlike that in the stripe center region (Figure 40c), where grains grow along the BD.

Figure 40 (a) 3D representative microstructures of 350W, 650W and 950W samples imaged in the BSE mode. Microstructures of the 350W samples (b) near the end of laser scan track, and (c) middle of laser scan track. d) High magnification BSE image of unmelted Nb in the 650W that is enclosed within a yellow rectangle in (a). Dashed lines in (a) are used as guides to show the melt pool boundary.

The (100) pole figures, which are the graphical representation of the textures, of 350W, 650W and 950W samples are displayed in Figure 41a-c, respectively. All samples have the {100} fiber texture, which implies that the {100} direction of most grains are oriented along BD. Fiber texture is typically associated with directional grain growth, which leads to the formation of columnar grains. The MUD value, which is also referred to as the ‘texture strength’ and describes the relative strength of a particular orientation in the sample w.r.t. other orientations, is calculated for {100}

and is presented in each pole figure. MUD for 350W is 19.51 but is 42.38 and 52.02 for 650W and 950W samples, respectively.

Figure 42a-c shows the grain orientation maps of 350W, 650W and 950W samples, respectively, on the y-z cross section with inverse pole figure Z (IPF-Z) coloring. In all samples, the majority of the β -Ti grains are elongated and colored in red, confirming that the microstructures predominantly consist of columnar grains with their $\{100\}$ crystallographic directions oriented parallel to the BD. However, the 350W sample also contains a significant fraction of randomly oriented smaller grains. Such randomly oriented grains are much lesser in 650W and 950W samples. This is consistent with the above-mentioned trend in the strength of fiber texture for the three samples. The observed $\{100\}$ fiber texture is also consistent with the XRD results (see Figure 39), where all samples show weak signals on their 211 and 321 peaks. In addition, the planes with $\langle 100 \rangle$ common zone axis were predominantly detected with XRD, which is possible if the $\{100\}$ direction of most grains are aligned with the BD.

Next, the grain widths in each sample is measured and its distribution is shown in Figure 43. The average grain width of the 350W sample is 71 μm , whereas that of the 650W sample is 160 μm . 950W sample has the largest average grain width of 243 μm , which suggests that grain coarsening occurs with progressive increase in the P . Then, the proportions of HAGBs and low angle grain boundaries (LAGBs), which are defined for grain boundary misorientations, $\kappa > 15^\circ$ and $2^\circ < \kappa < 15^\circ$, respectively, were also measured. The percentage of LAGBs in the 350W sample is only 25% whereas in the 950W sample it is almost 60%.

On analyzing the grain orientation map of 950W sample (see Figure 42c) further, it was noted that almost all stray grains contain an unmelted Nb inclusion at the bottom, which are marked by white arrows. Similar observations were made in 650W and 350W samples as well (not marked in the images to preserve clarity). This suggests that stray grains prefer to nucleate near unmelted Nb inclusions and since 350W samples have high U_{Nb} , a relatively higher proportion of stray grains are present in them. Alternately, samples 950W and 650W, which have lower U_{Nb} , exhibit greater grain widening.

From these results, it is evident that a predominantly columnar microstructure with a strong $\{100\}$ fiber texture and high average grain width can be obtained by implementing the printing parameters corresponding to the 650W and 950W sample.

Figure 41 Texture distribution represented by the (100) pole figure for (a) 350W (b) 650W and (c) 950W samples.

Figure 42 Representative grain orientation maps (IPF-Z coloring), obtained using EBSD for (a) 350W (b) 650W and, (c) 950W samples. (d) Pole figure for 350W. LAGB ($2^{\circ} - 15^{\circ}$) are depicted with gray while HAGB ($> 15^{\circ}$) with black lines. The white arrows in (c) indicate the presence of unmelted Nb inclusions.

Figure 43 Grain width (short axis of columnar grain) distribution of the as-printed samples.

4.3.3 Melt Pool Morphology

To further analyze the dynamics of porosity and Nb inclusions, single tracks, printed with the scanning parameters corresponding to 350W, 650W and 950W samples, are examined with SEM. The cross-sections of these single tracks are displayed in Figure 44a-c, where the insets display their top views. Single tracks of the 350W sample (with a gaussian beam profile) have a relatively deep melt pool (see Figure 44a) compared to those of 650W (see Figure 44b) and 950W samples (see Figure 44c). The melt pool penetration depth, d , scales as [208]:

$$d \propto \frac{P}{DV_L} \quad (19)$$

where, D is beam diameter. By applying E_d relation in Eq. (3), the scaling law becomes:

$$d \propto \frac{E_d h t}{D} \quad (20)$$

Since E_d , h and t are constants in this study:

$$d \propto \frac{1}{D} \quad (21)$$

For the 650W and 950W samples, $D \sim 200 \mu\text{m}$, whereas that of 350W $\sim 80 \mu\text{m}$, which suggests that the former should have smaller d , or shallower melt pools. The top views of these single tracks indicate that only the single track of 350W sample (Figure 44a) is continuous and uniform whereas those of 650W (Figure 44b) and 950W (Figure

44c) samples are irregular and contain humps. It is well-known that high V_L , high P scanning in LPBF creates long and thin melt pools, which is susceptible to the Plateau-Rayleigh instability. Under high recoil pressure, the material in the melt pool flows backward and creates humps on the tracks, much like those seen on the single tracks of 650W and 950W samples [209, 210]. While such humps on single tracks have been cited as the main cause for keyhole porosity in builds, the 650W and 950W samples do not exhibit any porosity.

Next, the melt pools formed in single stripes are compared with those in single tracks for the three samples. Figure 44d-f are SEM images of the cross-sections of single stripe of 350W, 650W and 950W samples, respectively, which are perpendicular to the direction of single track scans at the top layer. Variations in d in single stripe are unlike what was seen in the case of single tracks. The single stripe of the 350W sample has the shallowest melt pool with $d \sim 122 \mu\text{m}$, while $d \sim 200 \mu\text{m}$ and $181 \mu\text{m}$ for those of 650W and 950W samples, respectively (see Figure 44d-f). Although this observation appears to contradict the scaling relation in Eq. (21), it is not clear whether the relation itself is applicable to melt pool in single stripe. This is because Fabbro [208] developed this equation for single track scans and did not consider the evolution of the melt pools in a single stripe scan.

Interestingly, the maximum slope of melt pool boundary, θ , which is measured at the intersection between the melt track profile and re-melt layer (shown in Figure 44d-f), is smaller for deeper melt pools. The slope of the melt pool boundary, θ , in the 350W sample is 28° , whereas it is 15° and 16° for the 650W and 950W samples, respectively.

Figure 44 Representative SEM images of the single tracks (top and cross section view) corresponding to (a) 350W (b) 650W and (c) 950W samples and that of single stripe (top layer, cross section view) corresponding to (d) 350W, (e) 650W, and (f) 950W samples. The maximum angle of melt pool boundaries are measured as the angle tangential to the melt track profile at the intersection between melt track profile and the re-melt layer.

The top surfaces of the single stripes are further examined to determine other features of the corresponding melt pools. Figure 45 shows the surface topology of the single stripe scans corresponding to 350W, 650W and 950W samples. The laser scanning directions are indicated by black arrows and superimposed on the scans. Several curved lines, appear on top of all the as-built parts, which are identified as solidified traces of ripples that form on the melt pool during laser scanning [211]. These ripples, marked with black lines on the images, are analogous to those formed on water surfaces from an external disturbance [209]. They travel radially outward from the source of disturbance, which is the laser heat source, and terminate at the edge of the melt pool boundary. At the edge of the melt pool boundary, the ripples conform to the

melt pool boundary curvature and solidify when they reach the melt pool boundary. Consequently their shape and widths can be approximately equated with that of the melt pool boundary. In the 350W sample, the ripples have two distinct portions with different curvatures, one perpendicular to the laser scanning path and the other parallel to it. The portion perpendicular to the scanning path has a smaller span ($\sim 200 \mu\text{m}$) and radius of curvature compared to that of the latter, which implies that the melt pool boundary is elongated along the direction of the laser scanning path. In contrast, the ripples in 650W and 950W samples span $> 1 \text{ mm}$ and have a large but uniform radius of curvature along its length. This implies that the melt pool in these samples are significantly larger with roughly semi-circular boundaries. Moreover, these ripples' characteristics also hinted the direction of melt pool velocity, which is along the laser scanning direction for 350W but perpendicular to the laser scanning direction for 650W and 950W. Equating the ripple span with that of the melt pool width, w , it is determined that 350W samples have the melt pool aspect ratio, $d/w \sim 0.61$, whereas those of 650W and 950W samples is 0.2 and 0.18 respectively.

Figure 45 A confocal microscopy scan showing the topology of the top surfaces for (a) 350W (b) 650W and (c) 950W samples. The red arrows illustrate the stripe scanning path of laser (not to be scaled and meant for illustration purposes only). The black lines highlights several frozen ripples within a single stripe scan.

4.3.4 Thermal Analysis of Melt Pool

To understand differences in the evolution of single stripe melt pools in 350W and 950W samples, their corresponding thermal profiles were simulated by thermal FEM. As the melt pool formation in 650W is highly similar to 950W, the resources had been allocated to focus on 350W and 950W (the 2 extreme cases) only. The simulated melt pool morphologies of the 350W and 950W samples, after the stripe scans achieve a steady state, are shown in Figure 46a and b. Based on the color coding of thermal intensity, the positions of the laser source and the melt pool were identified. For the 350W sample, a small melt pool can be seen growing along the direction of the laser scan (see snapshots of simulation in Appendix B). This melt pool solidifies shortly after the laser scan moves ahead and since it does not interact with the adjacent linear

laser scan, the melt pool velocity, $V_{m,350}$, can be approximated to be the same as the laser scanning velocity, $V_{L,350}$. The melt pool velocity is the net displacement per second of the melt pool.

In contrast, a huge melt pool, whose span is a multiple of the h , forms in the 950W sample (see Figure 46b). Such a melt pool is the manifestation of interactions between multiple laser passes of constant h . Simulations also indicate that due to the high V_L and P of the laser employed, the melt pool induced by the first scan is unable to solidify completely and interacts with the melt pool created by the adjacent scan (see snapshots of simulation in Appendix C). Besides creating an additional melt pool in its location, the adjacent scan provides energy input to the existing melt pool and prevents its solidification. This leads to the merger of several melt pools, resulting in a single large melt pool that spans multiple h . Moreover, the large melt pool grows and traverses perpendicular to the linear laser scan direction (see Figure 46b and snapshots of simulation in Appendix C). Hence, the melt pool velocity of the 950W sample, $V_{m,950}$, can be rewritten as:

$$V_{m,950} = V_{L,950} \cdot \frac{h}{S}, \quad (22)$$

Where S is the stripe width. The experimental observation of ripples formation (Figure 45) well agrees with the simulated melt pool traverse direction. This unique type of melt pool dynamics, which results from the interaction between adjacent scan tracks, was also observed by Sun et al. in SS316L when they used an appropriate combination of high P and V_L and scanning strategy [30].

From Equation (22), the ratio of melt pool velocities, V_m of the 950W and 350W samples is expressed as:

$$V_{m,950}/V_{m,350} = V_{L,950}/V_{m,350} \cdot \frac{h}{S}, \quad (23)$$

In this study, $\frac{V_{m,950}}{V_{m,350}} = 0.217$, which implies that the V_m using the parameter set corresponding to 950W is 4.6 times slower than that of 350W. Figure 46c and 12d are x-z cross sections of melt pools associated with the 350W and 950W samples. These cross sections are taken from Figure 46a and 12b at the locations corresponding to that observed in experiments and displayed in Figure 44a and c. The y-z cross-sections of the same are displayed in Figure 46e and f. In

Table 11, the dimensions and characteristics of the melt pool obtained from experiments (measured from Figure 44 and Figure 45) and simulations are listed and compared. The simulated values of d for the 350W and 950W samples are 119 μm and 180 μm respectively, which is very close to that observed in experiments. Moreover, a close match is obtained between the experimental and simulated values of w and d/w . Note that w is measured in the direction perpendicular to the melt pool motion (see Figure 46a and 12b). However, there is a significant difference in the experimentally measured and simulated values of θ in the 350W sample, which are $\sim 49^\circ$ and $\sim 28^\circ$, respectively. This difference is attributed to the underestimation of absorptivity in the simulations of the 350W sample. Since significant overlap of melt pools smears out the variance in absorptivity, a similar divergence in the values of θ in the 950W sample is not observed. Nevertheless, the trend in the variations of all parameters in experiments and simulations are consistent for the two samples. The good conformance of dimensional aspects evaluated from simulations and experiments suggests that the V_m determined via simulations are reliable. Based on this premise, it is reasonable to state that the approximate melt pool volumes, determined via simulations and henceforth referred to as $d \times w \times l$, of 350W and 950W samples would correspond to the actual melt pool volumes. The latter has a $d \times w \times l$ of 0.15 mm^3 , which is an order of magnitude higher than that of the former.

Figure 46 Simulated temperature profile snapshots, which represents the melt pool evolution in a single stripe during laser scanning with printing parameters corresponding to (a) 350W and (b) 950W samples. The x-z cross section of the simulated profiles at the locations corresponding to that observed in experiments for parameters corresponding to (c) 350W and (d) 950W samples. y-z cross sections of the same location for (e) 350W and (f) 950W samples. The 200 μm scale bar is applicable for c-f.

Table 11 Dimensions and characteristics of the melt pool obtained from experiments and simulations.

Melt Pool Characteristics	350W		950W	
	Experiment	Simulation	Experiment	Simulation
d (μm)	122	119	181	180
w (μm)	~200	214	~1000	1167
l (μm)	N/A	600	N/A	706
d/w	0.61	0.56	0.18	0.15
θ ($^\circ$)	28	49	16	15
$d \times w \times l$ (mm^3)	N/A	0.015	N/A	0.15

*experimental melt pool width estimated from ripple observation

4.3.5 Tensile Properties

To assess which microstructure vis-à-vis the printing parameters, leads to superior mechanical properties, tensile tests were performed on the coupons obtained from 350W and 950W samples.

Their representative engineering stress, σ_e , vs. engineering strain, ϵ_e , responses are shown in Figure 47. In the inset, the change of normalized strain hardening rate with true strain and the measured values of E , YS, UTS, and ϵ_f , for the two samples are also displayed. The 350W sample has E which is 14% higher than that of 950W sample. This difference is expected because although the two samples have similar textures, the former has a higher proportion of stray grains, whose E are expected to be slightly higher [212]. The 350W has higher YS due to its comparatively finer grain structure, which leads to greater Hall-Petch strengthening. However, beyond the yield point, the two samples undergo strain softening and exhibit nearly perfectly plastic stress-strain response until failure. Also, the ϵ_f of the 350W and 950W samples are comparatively

lower than those of conventionally manufactured Ti-Nb alloys, which have $\epsilon_f > 8\%$ [191].

To understand the lack of strain hardening and origin of low ductility of these alloys, post facto microstructural analysis and fractography were conducted on the tensile-tested samples. The side surfaces of the samples were polished and examined under the SEM. Figure 48a and b display the EBSD band contrast images of these side surfaces for the 350W and 950W samples, respectively. Some of these twins and slip bands are also identified in BSE image of the unetched 950W sample, as indicated in Figure 48c. While traces of slip bands were observed within all grains (marked with yellow arrows in Figure 48a-c), a few twins were also observed in some grains, which was mapped by EBSD and superimposed over the band contrast images of the two samples. In the EBSD analysis software (Channel 5), twin boundaries can be identified based on the known misorientation angle and rotational axis, where $\{332\}\langle 113 \rangle$ twin boundary corresponds to misorientation of 50.57° around $\langle 110 \rangle$ and $\{112\}\langle 111 \rangle$ twin boundary corresponds to misorientation 60° around $\langle 111 \rangle$ [213]. Figure 48d displays the relative fraction of misorientation angles of the twins present in 350W and 950W samples. In the 350W sample, only the $\{332\}\langle 113 \rangle$ twin system was indexed whereas the two $\{332\}\langle 113 \rangle$ and $\{112\}\langle 111 \rangle$ twin systems were indexed in the 950W sample. Since the EBSD mapping was done on highly deformed and distorted areas near the fracture surface, some twin boundaries were not captured. Despite the segment of detected $\{112\}\langle 111 \rangle$ boundaries by Channel 5 software being only 2 to 3 pixels long, the detection of such twinning system is not an artifact for the following reasons: (1) Well defined $\{112\}\langle 111 \rangle$ twin boundaries can

be observed, (2) The $\{112\}\langle 111 \rangle$ twin boundary region is highly unindexed and is difficult to be detected by Channel 5 software. Manual examination however found consistent misorientation angle between the $\{112\}\langle 111 \rangle$ twins and their neighbouring grains, (3) The same twin systems ($\{332\}\langle 113 \rangle$ and $\{112\}\langle 111 \rangle$) had been observed previously in metastable β -Ti alloy [8]. Nevertheless, the two samples are expected to contain the same twin systems as they are compositionally alike. In Figure 48e and f, the fracture surfaces of the tensile-tested 350W and 950W samples are displayed. The two samples exhibit a mix of intergranular and transgranular brittle fracture features. Fracture along the keyhole induced porosity can be also be observed on the fracture surface of 350W. In contrast, the fracture surface of the 950W sample shows stepped cleavage facets with self-similar cleavage angles, which is characteristic of failure occurring in columnar grains. Based on these results, the following is a description of the deformation mechanisms in the LPBF manufactured Ti-Nb samples:

On yielding, deformation occurs via planar slip of dislocations on either of $\{110\}$, $\{112\}$ or $\{123\}$ planes, which leads to the formation of several slip bands. The identification of slip planes corresponding to 350W is in Appendix D. Negligible interactions between dislocations during planar slip leads to localization, which manifests as strain softening in the stress-strain curve. A similar lack of strain hardening was also observed in other metastable β -Ti alloys undergoing planar slip during plastic deformation [214, 215]. At a later stage of deformation, twins form in the two samples, which could reorient the crystal to potentially facilitate slip on multiple planes and lead to interaction between dislocations. However, since no change in the strain softening behavior of the two samples is observed with continued

straining, these twins appear to have insufficient contribution towards strain hardening. One reason for this could be that the volume fraction of twins is lesser than that required for sufficient interference with slip in the material. This argument is supported by the fact that even at the point of failure, only few twins were observed in isolated grains, whereas almost all grains contained a dense array of slip bands. Despite similar deformation mechanisms, the 950W sample has higher ϵ_f than the 350W sample. This could be attributed to the presence of keyhole pores in the latter that serve as stress concentrators and lead to premature failure. Overall, while the 950W sample is superior than 350W sample in terms of E and ϵ_f , the latter is marginally stronger. Nevertheless, the two alloys exhibit strain softening and undergo strain localization during plastic deformation.

Figure 47 Tensile stress-strain response and the change in normalized strain hardening rate with true strain of 350W and 950W samples. All values are quoted with confidence interval of 99.7%.

Figure 48 Post facto EBSD mapping of the side surfaces of tensile-tested (a) 350W and (b) 950W samples showing twin boundaries overlaid on band contrast. (c) Post facto BSE micrograph of the side surface of tensile-tested 950W sample. (d) Misorientation angle distribution from EBSD analysis in (a) and (b). The representative fracture surface of (e) 350W and (f) 950W sample. The yellow arrows are used to indicate the slip band traces. The BD and tensile direction (TD) are indicated wherever applicable.

4.4 Discussion

4.4.1 Mechanisms of Microstructure Formation

Melt pool solidification in all samples initiates by columnar grain growth along the BD, as it coincides with the direction of the maximum thermal gradient. In the 350W sample, although the microstructure is predominantly composed of columnar grains, the formation of several stray grains is also observed. The other two samples also contain similar stray grains, albeit in significantly lower proportions. The formation mechanism of these stray grains has been a topic of debate in studies where *in-situ* alloyed β -Ti with Nb or Ta were produced via LPBF. Some studies on Ti37Nb6Sn (wt.%) and Ti26Nb (at.%) correlate the stronger {100} texture in the BD with increasing E_d input but do not explain how the texture evolved [122, 135]. Sing et al. observed that the stray grains in their Ti-50Ta are an outcome of the CET in the alloy, which depends on the relative magnitudes of the thermal gradient and dendritic growth rate at a location [32]. In contrast, Brodie et al. [124] and Huang et al. [216] suggest that heterogeneous nucleation of grains from unmelted Ta particles or processes involving constitutive undercooling of the melt near the Ta particle lead to the formation of stray grains in Ti-Ta alloys. Although the observation that unmelted Nb inclusions exist beneath a stray grain supports the arguments of Brodie et al. and Huang et al., examination of variations in thermal gradient, G and dendrite growth rate, R , for the 950W and 350W samples to assess if CET can occur in the absence of inoculants was nevertheless conducted. For this, the primary assumption is that the alloy system is assumed to be homogenous and that grain nucleation does not occur on unmelted Nb particles. Thereafter, the Kurz-Giovanola-Trivedi (KGT) model [217] was used to obtain the relationship between the undercooling temperature, ΔT_c and R .

Then, the Hunt's criterion for growth of equiaxed grain is applied to obtain a relationship between G and ΔT_c [218]:

$$G = 0.6N_o^{\frac{1}{3}}\Delta T_c \left(1 - \frac{\Delta T_n^3}{\Delta T_c^3}\right), \quad (24)$$

Where G is the thermal gradient, N_o is the density of heterogeneous nucleation sites for equiaxed grains and ΔT_n is the nucleation temperature.

ΔT_c was replaced with R in Equation (24) and the parameters used for applying the KGT model and Hunt's criteria were obtained from Ref. [219], which were suitably modified for the current alloy composition. Figure 49 shows the plot of R as a function of G , which is referred to as the CET curve, and is utilized for identifying specific regimes corresponding to columnar and equiaxed growth. The region to the left of the curve corresponds to the equiaxed grain growth regime. Using the thermal history data from FEM, the values of G and R in the melt pool within the mushy zone is evaluated and superimposed on the plot (see Figure 49), to examine the grain growth behaviour of 350W and 950W samples. Data points corresponding to the two samples lie in the columnar grain growth regime, which rules out the formation of equiaxed grains at any stage of solidification. The alternate mechanism of stray grain growth is schematically illustrated in Figure 50. As the laser beam scans the powder bed, a melt pool forms and then solidifies to form columnar grains, which grow epitaxially over the previously printed layer. It is also easy to visualize that epitaxial growth of $\{100\}$ grains in the BD would be favored when θ is gentler, as seen in 950W samples. If the melt-pool contains unmelted Nb, grain growth can occur in its vicinity via either of the following mechanisms. The first mechanism suggests that during solidification,

Nb diffuses into the melt and creates conditions of constitutional supercooling in its vicinity, which leads to the spontaneous formation of several nuclei. These nuclei grow into grains with random orientations. If this were the operative mechanism, the 950W sample, which facilitates maximum diffusion of Nb in its melt pool, would exhibit a greater extent of constitutional supercooling and should contain a larger number of stray grains than the 350W sample. The alternate mechanism suggests that Nb is an inoculant and acts as a heterogeneous nucleation site for the formation of short columnar grains, along directions that satisfy the appropriate orientation relationship. In this scenario, there would only be a few stray grains in the vicinity of a Nb inclusion. Since the experimental results show that 950W samples have only one or two such grains near a Nb inclusions (see Figure 42c), the second mechanism, involving heterogeneous nucleation, is more likely to facilitate stray grain formation.

The solidification mechanism also affects the relative proportions of LAGBs and HAGBs in the Ti-Nb samples. The rapid cooling and thermal gradient in the melt during LPBF generate residual stresses in the solidified material. Repeated heat input from multiple laser scans relieves this residual stress and triggers polygonization, which in turn results in the formation of several LAGBs in the material [220-223]. This mechanism has also been seen for several other Ti alloys where epitaxial growth of columnar grains was observed [122, 224]. However, since stray grains form rapidly from a heterogeneous nucleation source, polygonization does not occur, which leads to the formation of HAGBs around them. Therefore, the 950W sample, which have a lower proportion of stray grains, has a relatively higher proportion of LAGBs whereas the converse is true in the 350W sample.

Figure 49 Plot of dendritic growth, R , and the thermal gradient, G , for Ti34Nb. The range of values of G and R in the melt pools of 350W and 950W samples are superimposed on the plot to assess the possibility of CET.

Figure 50 Schematic of stray grain formation due to unmelted Nb particles.

4.4.2 Melt Pool Size Control by Parameter Optimization

From the analysis of the melt pool characteristics, it is evident that $d \times w \times l$, V_m , d/w and θ , all influence the quantity of unmelted Nb, keyhole porosity and microstructure in LPBF built Ti-Nb alloys. A combination of large $d \times w \times l$ and low V_m such as that seen in 950W sample, promotes homogenization by preventing localized melting, lowers the rate of cooling in the melt pool and provides enough time for the heat to distribute evenly. Therefore, all the constituents, specifically Nb, has sufficient time for diffusing and mixing before the melt pool solidifies, resulting in lower content of unmelted Nb in the alloy. The slower cooling rate in the melt pool, due to large $d \times w \times l$ and low V_m , is also the primary cause for grain coarsening in the 950W samples. Alternately, lower d/w and V_m of the melt pool ensure that 650W and 950W samples have vanishing keyhole induced porosity, although the exact mechanism for this is still not well understood. Nevertheless, it is reasonable to expect that a low aspect ratio (d/w) melt pool would be less prone to collapsing and forming shut pores [207].

Lower θ aligns the thermal gradient along the BD, which in turn increases the strength of $\{100\}$ fiber texture of the columnar β -Ti grains along the BD. The formation of columnar grains with a dominant $\{100\}$ texture is also promoted by a large $d \times w \times l$ and low V_m as they suppress unmelted Nb content, which in turn decreases the possibility of strain grain formation. Note that, in terms of lower E requirements of implants, the $\{100\}$ fiber texture is highly preferred. This is because the Young's modulus along the $\langle 100 \rangle$, $E_{100} \sim 39.5$ GPa, which is at least 1/2 and 1/3rd of that along $\langle 110 \rangle$ and $\langle 111 \rangle$, respectively [212]. A dominant $\{100\}$ texture will ensure that the polycrystalline alloy has the lowest value of E . Note that the preference for obtaining a columnar grain structure in this study is exclusively relevant for

developing components such as in hip implants and jet engine turbine blades, which are directionally loaded. Otherwise, in the absence of these application specific requirements, an equiaxed grain structure is more sought after for its refined grain size and isotropic properties.

From these observations it is evident that a melt pool with a combination of low V_m , low d/w , low θ and large $d \times w \times l$, is ideal for printing pore free Ti-Nb implants that have {100} textured β -Ti columnar grains and minimum unmelted Nb inclusions. As indicated by simulations in section 4.3.4, a melt pool with these characteristics can be developed by printing with high values of P and V_L . Note that this particular printing recipe is successful only when a sufficiently small S , such as the one mentioned in this work, is employed. If the stripe width is significantly high or approaches the length of a single track, an existing melt pool would solidify before the laser returns to scan the adjacent regions. This would limit interactions between multiple smaller melt pools, which is necessary for obtaining the above-mentioned combination of V_m , d/w , θ and $d \times w \times l$.

Besides these factors, the influence of the laser profile on the melt pool dimensions is also worth examining. For this purpose, the single-track melt pool dimensions of the 350W and 950W samples can be referred, which were printed with Gaussian and top-hat profile lasers, respectively (Figure 44a and c). As can be seen in these images, the melt pool of the former is much deeper and narrower than that of the latter, which suggests that the top-hat laser profile typically leads to a lower d/w . This is expected because a Gaussian profile has a conical shape and concentrates the laser energy at its apex (see Figure 33a), thus favoring the formation of a melt pool with a high d/w . In

contrast, the cylindrical shape of the top-hat laser profile distributes the laser energy over the scanned area and facilitates the formation of a melt pool with low d/w . On the basis of the above-mentioned discussions, which suggests that an optimum melt pool should have a lower d/w , the top-hat laser profile appears to be more favorable than the Gaussian profile.

However, it may be inappropriate to equate the characteristics of melt pools obtained from single tracks and single stripes as their formation mechanisms are distinctly different. Extending this premise further, it may also be argued that it is possible to obtain the desired melt pool attributes by simply employing the ideal combination of P , V_L and stripe width, regardless of the laser profile. Moreover, there is a possibility that the relatively larger spot size of the top-hat laser, compared to that of the Gaussian laser in this study, may be a more relevant parameter to consider. To address these arguments, the thermal profiles of single stripes were simulated for (a) a Gaussian profile laser and a spot size of 80 μm , (b) a Gaussian profile laser and a spot size of 200 μm profiles and (c) a top-hat profile and a spot size of 80 μm , with all other parameters corresponding to that used for printing the 950W sample. The simulated melt pool geometries of the above-mentioned conditions are shown in Appendix E. For lasers with spot sizes of 80 μm and 200 μm , the top-hat profile laser yields melt pools with identical V_m , d/w , θ and $d \times w \times l$. Similarly, simulated thermal profiles of melt pools generated by a laser with Gaussian profile, but with different spot sizes, are also identical, which implies that the spot size has no significant influence on melt pool characteristics or dynamics. The different melt pool formation seems to be more dependent on the laser profile rather than the beam cross-sectional area/diameter, at least in the range of 80 to 200 μm diameter, based on the FEM results. Too small of a

145

diameter however could lead to laser ablation, hence deteriorating the processibility of an alloy. Moreover, the simulated melt pool formed by a laser with a top-hat profile is superior to that formed with a Gaussian profile as it possesses the ideal combination of V_m , d/w , θ and $d \times w \times l$ (see also Appendix B and Appendix C for snap shots of the simulation videos). This confirms that besides P , V_L and stripe width, the choice of a laser profile is also critical for obtaining the ideal melt pool attributes. The improvement of *in-situ* alloyed component's quality associated with ideal melt pool formation is generally applicable to all powder mix regardless of the material's composition.

While prescribing this particular parameter optimization strategy, it is recognized that three critical questions could be raised. First, is it also possible to eliminate unmelted Nb completely by further increasing P and V_L ? Although the limitations of current printing setup prevented the testing of this hypothesis, it is reasonable to expect that further increasing P and V_L , would produce a larger melt pool with a reduced cooling rate. Such a melt pool would promote complete melting of Nb particles but will also promote grain coarsening, due to a slower cooling rate, and this is undesirable from the mechanical property perspective as coarse-grained materials have lower strengths. Also, the formation of a large melt pool limits the smallest feature size and compromises the dimensional precision of the build. This is because the size of the melt pool is limited by the external dimensions of the build and if the melt pool forms at the latter's edge, the molten material may accidentally overflow or lose shape, which will alter the final dimensions of the build. However, this caveat can be resolved by altering the single stripe width to limit the dimensions of the melt pool according to the feature size.

Second, is the prescribed strategy uniquely applicable for *in-situ* alloying of Ti-Nb using LPBF or can it be adopted for pre-alloyed powder to print highly dense parts of any material? The answer to this question is not yet known as the strategy was not yet applied on different types of pre-alloyed powder. Nevertheless, if the processing parameters required for forming a single stripe melt pool with the optimum dimensions are determined, the possibility to print any material with negligible porosity can be hypothesised. The single stripe melt pool formation can definitely be manifested upon the usage of pre-alloyed powder with top-hat laser, and had been demonstrated by Sun et al. on pre-alloyed SS316L for the purpose of texture modulation [14]. In the broader context, this implies that the next technological advancement towards porosity minimisation in LPBF manufactured materials requires dedicated efforts towards determining the processing window, which optimizes the dimensions of the melt pool in single stripe than that in a single track. The FEM can serve as a tool for the preliminary estimation of single stripe melt pool processing window. Thereafter, more computationally heavy simulation that includes melt flow physics and vaporization phenomena can be used to verify the window to a greater accuracy. In fact, since the method inherently promotes epitaxial crystal growth along the thermal gradient, it is ideal for manufacturing single crystal or columnar grained Ni-based superalloys [225, 226].

Finally, will a defect free Ti-Nb sample built by LPBF be better than that prepared by conventional manufacturing methods in all aspects? From the point of view of cost savings, time savings and customizability, the LPBF built Ti-Nb samples are much better than those manufactured by other conventional means. However, as was noted earlier, there is a large scope to improve the ductility of the material by tailoring the

microstructure in a way that mitigates localization from planar slip. One way to achieve that is to develop an equiaxed and fine grained microstructure by tweaking the printing strategy. An alternate way to improve strain hardening, without modifying the columnar microstructure, is to destabilize the β phase further so that profuse twinning occurs, which in turn promotes increased interactions between dislocations. Also, it is not clear whether alloys manufactured by this strategy will have better structural integrity than that of the conventionally manufactured ones, as their fracture toughness and fatigue strengths have not yet been evaluated or compared.

4.5 *Summary*

With the objective of minimizing the porosity and unmelted Nb inclusions in LPBF built Ti34Nb, three sets of processing parameters, in which P , V_L and laser profile were varied, were used to print samples. After detailed microstructural investigations followed by simulations and mechanical property evaluation of these samples, the following are the key conclusions drawn from this study. The combination of high P (~650 W or 950 W), high V_L (~650 mm/s or 950 mm/s), a top-hat profile laser and a suitable stripe scanning strategy is ideal for printing a fully dense sample with limited content of unmelted Nb inclusions. These parameters result in a slow moving, large melt pool, with a small aspect ratio and melt pool angle, in a single stripe. This ensures uniform mixing of constituents and also eliminates keyhole porosities. In addition, these samples have a {100} textured columnar β -Ti microstructure with a few randomly oriented stray grains. The proportion of stray grains increases with Nb content as it is an inoculant for heterogeneous nucleation. Since a stronger {100} texture yields the optimum combination of low E , a lower unmelted Nb inclusion

content is desirable. However, irrespective of the Nb inclusion content, the ϵ_f and strain hardening ability of the alloys are sub-par as planar slip in β -Ti occurs without hinderance, leading to flow localization. Further studies are required to develop strategies that homogenize deformation and mitigate planar slip in LPBF printed Ti-Nb, without compromising the strength or E . The broader implication of the study is that the porosity-inclusion dilemma can be resolved by adopting a parameter optimization strategy, which prioritizes ideal melt pool characteristics in a single stripe as opposed to those in a single track. This is expected to inspire a paradigm shift in devising processing windows that can minimize or completely eliminate defects in materials manufactured via LPBF methods, regardless of the material's composition.

Chapter 5 Fracture Behavior of Laser Powder Bed Fusion

Fabricated Ti41Nb via *In-situ* Alloying

5.1 *Introduction*

The research on LPBF fabricated biomedical β -Ti has been trending, but with the availability of pre-alloyed feedstock remains as one of the major challenges. As previously mentioned, the common characteristics of *in-situ* alloyed β -Ti is the occurrence of compositional macro-segregation due to incomplete melting and diffusion of β -stabilizing particles [124, 126], contributed by the fast cooling rate of LPBF process ($\sim 10^6$ K/s) [22]. The macro-segregation and incompletely melted particles contribute to the mesostructure characteristics of the material, which could affect its resultant FCG and fast fracture behavior. However, study on the fatigue and fracture behavior of *in-situ* alloyed β -Ti is scarce. Only one such study has been conducted by Brodie et al. on the uniaxial low cycle fatigue behavior of Ti25Ta (wt.%) [138]. It was found that the unmelted Ta particles does not contribute to the fatigue crack initiation of the material. Aside from the uniaxial low cycle fatigue behavior, the FCG behavior and fracture toughness of *in-situ* alloyed β -Ti were not explored at all. As the AM technology enables frequent modification in implant design, stress concentration features could accidentally be introduced. The design flaw can eventually causes detrimental fatigue and fracture of the implant [163]. On top of that, incorporation of lattice structure in an implant will provide opportunity for crack initiation at the strut intersections. Hence, it is essential to understand the fracture behavior of *in-situ* alloyed implant material to improve its reliability.

Fortunately, past studies on LPBF induced mesostructured was found to be beneficial in improving the fracture response of a material, in particular the fracture toughness. For instance, wavy melt pool boundary of Al12Si and AlSi10Mg imparts high crack tortuosity and toughens the resultant material [164, 227]. Similarly, when the crack propagation direction is perpendicular to the BD, prior- β columnar grain in Ti6Al4V toughens the material by inducing tortuous crack path [194]. Hence, it is reckoned that the incompletely diffused β -stabilizer and compositional macro-segregation associated with *in-situ* alloyed β -Ti can be beneficial for the fracture behavior of the material.

In this chapter, the fracture behavior of *in-situ* alloyed Ti41Nb (wt.%) was studied. In the previous chapter, Ti34Nb (wt.%) shows poor ε_f ($< 5\%$). This could be due to the lack of athermal ω_{ath} suppression by Nb after rapid cooling, which limits the twin/SIM formation upon deformation [120]. Hence, the composition of Ti41Nb was chosen in an attempt to improve the ε_f . To study the fracture behavior of the *in-situ* alloyed Ti41Nb, parts with sufficient quality, i.e. $< 0.5\%$ porosity and minimal amount of unmelted Nb particles, were first fabricated. To achieve high quality *in-situ* alloyed components, the porosity-inclusion dilemma needs to be addressed. Past study had utilized the remelting technique to approach the dilemma but the method is rather energy and time inefficient [124]. Through the usage of high powered laser ($> 650W$) with top-hat profile, the porosity-inclusion dilemma can be effectively resolved, as shown in Chapter 4. However, the usage of top-hat profiled high powered laser is uncommon to the general users at this point of time, in addition to causing insufficient unmelted Nb particles required for the study of segregation effect on fracture behavior.

As such, a small h fast V_L strategy was demonstrated using the commonly available

400 W Gaussian profiled laser to obtain parts with sufficient quality. Thereafter, tensile, FCG and fracture toughness tests were conducted and explained based on the material's structural characteristics.

5.2 *Experimental Details*

5.2.1 *Laser Powder Bed Fusion*

The samples were fabricated using an in-house developed Ti-Nb elemental powder blends with 41 wt.% Nb. The Ti41Nb (wt.%) powder blend was obtained by mixing spherical gas atomized commercially pure titanium (CP Ti) and Nb powders (> 99.8%). The CP Ti powder (Grade 2 ASTM B348, LPW Technology Ltd, United Kingdom) particles have a median diameter of 43.5 μm while the Nb powder (Tecnisco Advance Material Pte Ltd, Singapore) has a particle size distribution that ranges between 20 to 63 μm . The two elemental powders were mixed and blended for 12 hours at a rate of 30 rpm using a tumbler mixer (Inversina 2 L, Bioengineering AG). The blending process was conducted under an Ar atmosphere.

The sample fabrication process was carried out using the SLM 280 HL machine (SLM Solutions Group AG). The machine is equipped with a dual fibre laser system, with each laser having a Gaussian beam profile (1064 nm) with a focus diameter of 80 μm and a maximum P of 400 W. All fabrication processes were carried out in an Ar environment of < 1000 ppm O_2 to minimize oxidation and interstitial element contaminations. The samples were built on Ti base plates with area dimensions of 100 $\times$ 100 mm^2 . Also, all samples were prepared using the rotated stripe scanning strategy. A schematic of the rotated stripe scanning strategy is shown in Figure 51. In every subsequent new layer, the stripes will be rotate clockwise by $\sim 79^\circ$ with respect to the previous layer. A total of four parameter sets were used to demonstrate and suitably

152

optimize the benefit of small h fast V_L (see Figure 51a), in comparison to a scanning strategy with h close to the laser focus diameter (see Figure 51b). The details of the scanning parameters associated with each sample can be seen in Table 12. The parameter names were based on the associated E_d and the h . The “L” and “H” in the names stand for low and high E_d respectively, while the “20” and “40” is the h in μm .

Figure 51 Schematic of rotating stripe strategy with stripe scanning corresponding to (a) normal h normal V_L stripe scanning strategy and (b) fast h fast V_L stripe scanning strategy.

Table 12 Different combinations of LPBF process parameters utilized for manufacturing the Ti41Nb alloy samples.

Sample name	Power, P (W)	Hatch, h (μm)	Stripe Width (mm)	Scanning Velocity, V_L (mm/s)	Layer Thickness, t (μm)	Rotation ($^\circ$)	Energy Density, E_d (J/mm^3)	Laser Profile
L20	390	20	1	1147	50	79	340	Gaussian (80 μm)
H20	390	20	1	951	50	79	410	Gaussian (80 μm)
L40	390	40	1	574	50	79	340	Gaussian (80 μm)
H40	390	40	1	476	50	79	410	Gaussian (80 μm)

Based on the results from the parameter optimization study, H20 was chosen as the parameter to fabricate the specimens for mechanical testing. Blocks with the size of 35 mm (width) $\times$ 40 mm (length) $\times$ 35 mm (height) were first fabricated via LPBF. The blocks were then cut into multiple CT specimens and customized tensile coupons via EDM. The resultant specimens are illustrated in Figure 52a, with the z-axis defined as the BD. The CT specimens were machined to be tested in three different orientations and were named after their orientation as lay (sample lay flat with respect to substrate), $\perp$ (crack perpendicular to BD) and $\parallel$ (crack parallel to BD) specimens. Meanwhile, the customized tensile coupons were machined to be tested in the vertical (tension parallel to BD) and horizontal (perpendicular to BD) direction. Lines were drawn perpendicular to the BD on the illustrations of CT specimens in Figure 52a, to represent the layered structural characteristic as a consequence of the layered LPBF manufacturing. Meanwhile, the dimensions for the customized tensile coupons can be seen in Figure 52b.

Figure 52 (a) Schematic of CT specimens and tensile coupons on a LPBF substrate and (b) Dimensions of the customized tensile coupon.

5.2.2 Sample Evaluation

The percentage volume fraction porosity and percentage volume fraction of unmelted Nb in the fabricated samples were analyzed via XCT (SKYSCAN 1173, Bruker, Germany). X-ray scans were performed at a voltage of 130 kV, using a brass filter. The 3D reconstructed volumes are made up of isotropic cube voxels with a side length of 5.7 μm . To minimize the probability of false segmentation, only pores/inclusions with at least 9 voxels were considered. three threshold values were taken during the analysis to account for the error [200], in which the standard errors were obtained.

5.2.3 Metallographic Characterization

The CT specimens were examined to reveal the cross-sectional area characteristics parallel and perpendicular to the BD. Grit #320 SiC-paper were used to grind the cross-sections followed by a fine grinding with MD-Largo (DiaPro Largo 9 μm suspension, Struers). Finally, the samples were polished to a mirror finish using MD-Chem (OPS 0.04 μm suspension + H_2O_2 , Struers). The identification of constituent phases in the specimen was done by analyzing the specimen with XRD (PANalytical Empyrean, Netherlands) using $\text{Cu-K}\alpha$ radiation and a step size of 0.05° . Meso and microstructural characterization was conducted with a FESEM (JEOL 7600F, JEOL, Japan) equipped with a BSE detector. EDS was done to ascertain the composition at certain regions. Texture analysis was done with EBSD analysis using FESEM equipped with an AZtecHKL Oxford detector. The EBSD mapping was conducted with a maximum scanning step size of 1.5 μm . Furthermore, nanostructure of the specimen was revealed with TEM (JEOL-2100, JEOL, Japan). The TEM sample was prepared using the focused ion beam (FIB) lift out technique at the matrix region with nominal composition.

5.2.4 Mechanical Properties Characterization

To examine the mechanical behavior of LPBF manufactured Ti41Nb, tensile stress-strain responses, fracture toughness and FCG resistance were evaluated.

The tensile stress-strain response was acquired by performing uniaxial tensile test on a series of tensile coupons. An UTM (Zwick Roell, Germany) was utilized with a cross-head displacement rate of 0.006 mm/min. The strain response of tensile coupons was measured with a laser extensometer during the tests. To evaluate the repeatability, a minimum of three tests were performed for each loading orientation.

Experiments to evaluate K_{IC} and FCG characteristics were conducted on Chevron notched CT specimens. The CT specimens used in this study have a thickness (b) of 12 mm and width (W) of 24 mm. The dimensions of CT specimens used in this study are approximately half of the standard CT specimen, hence they are often referred as the half CT specimen. For each orientation, two samples were tested for their FCG and fracture toughness characteristics. Both sides of the CT specimens were mirror polished prior to the tests, so as to allow crack growth monitoring using a long-distance optical microscope with 60X magnification. The long distance optical microscope is attached with a high-resolution camera, capable of achieving a resolution of 1920×1440 pixels. To test the fracture toughness, the CT samples were fatigue pre-cracked using a servo hydraulic testing machine (MTS810, MTS Systems Corp., USA) to reach a/W of 0.45-0.55, where a is the crack length. The fatigue pre-crack procedure was performed using a sinusoidal wave form with a frequency of 10 Hz at a load ratio, R_{load} of 0.1, as prescribed in the ASTM E399-12 [228] and ASTM 647-15 [229]. After the pre-cracking procedure, the CT specimens were loaded in tension under a quasi-static mode until fracture, at a cross-head displacement rate of

156

0.002 mm/s. The readings from the load cell were then extracted to evaluate the K_{IC} associated with each CT specimen.

The load shedding method, as prescribed in ASTM 647-15, was utilized to determine the threshold for fatigue crack initiation, ΔK_o , of the CT specimens. Here, the stress intensity factor range (ΔK) was reduced by ~10% after each crack length increment of 0.2 mm, until the crack growth rate per cycle, da/dN , reaches a value below 4×10^{-9} m/cycle. Upon reaching a da/dN below the designated value, the ΔK was taken as the ΔK_o . The data obtained from the load shedding procedure was also used to determine the FCG characteristic of each specimen. The da/dN vs. ΔK data generated during the steady-state crack growth regime was analyzed using the Paris equation: $da/dN = C(\Delta K)^m$, where C and m are material properties and are referred to as Paris constant and Paris exponent respectively. Standard procedures as described in the ASTM 647-15 standard were utilized to estimate m from the experimental data.

Post-mortem analyses were performed on all the tensile fractured coupons, fatigue pre-cracked CT specimens and mode-I fractured CT specimens, so as to ascertain the dominant failure mechanisms. Fractography of tensile coupons were performed with a FESEM in the SE mode. EDS was also performed on the fracture surfaces of tensile coupons to ascertain the effect of compositional segregation on fracture behavior. Post-mortem EBSD and BSE analysis were performed on the side surfaces of the tensile coupons and pre-cracked CT specimens. The EBSD mapping was conducted with a maximum scanning step size of 1.5 μm .

5.3 Results

5.3.1 Parametric Study

Parametric study is essential to build samples with minimal defects for further mechanical characterization. The study was also done to ascertain the effectiveness of small h fast V_L strategy to address the porosity-unmelted inclusion dilemma. The XCT reconstruction of the samples for parametric study can be seen in Figure 53, in which the volume % unmelted Nb and volume % porosity associated with each sample were visualized and quantified. Due to the relatively large $E_d \sim 360$ and 410 J/mm^3 , pores associated with the samples are dominated by keyhole porosity. When the E_d was held constant, parts with $h \sim 20 \text{ }\mu\text{m}$ have V_L that is twice that of samples with $h \sim 40 \text{ }\mu\text{m}$. At constant h , increasing E_d led to the reduction of volume % unmelted Nb, which is however accompanied by an increase in volume % porosity. Nevertheless, simultaneous reduction of % unmelted Nb and porosity can be observed when E_d was held constant, through the implementation of smaller h and faster V_L . This observation demonstrates the effectiveness of small h fast V_L strategy in addressing the porosity-unmelted inclusion dilemma, regardless of the E_d .

As depicted in Chapter 4, porosity-unmelted inclusion dilemma can occur during *in-situ* alloying of elements with drastically different melting point, e.g. Ti ($1668 \text{ }^\circ\text{C}$) and Nb ($2477 \text{ }^\circ\text{C}$). The key to approach the dilemma lies in melt pool manipulation strategy [230]. The approach in this study was inspired by melt pool manipulation via a parameter known as the normalized enthalpy [199], which is a value proportional to $P/\sqrt{V_L}$ with the assumption of constant material properties and laser specifications. By suppressing the $P/\sqrt{V_L}$ ratio through faster V_L , the tendency of keyhole melting can be suppressed, thereby reducing keyhole porosity formation. To compensate for the

lesser energy input due to faster V_L , the h was reduced to maintain the E_d . As such, keyhole melting can be reduced while maintaining the total energy input, in which the energy is essential for homogenization of the alloy during the *in-situ* alloying process. The attempt to reduce $P/\sqrt{V_L}$ ratio while maintaining E_d led to 6.6 fold porosity reduction from H40 to H20, and 3.8 fold porosity reduction from L40 to L20. At the same time, minor reduction of unmelted Nb can be observed, indicating better effectiveness of the small h fast V_L strategy in homogenizing the resultant alloy. Despite being inferior to the strategy proposed by Huang et al. [230], the strength of the strategy proposed in this study lies in its general applicability to other LPBF systems due to the usage of commonly available laser system with Gaussian profile. Based on the simple parametric study, the H20 parameter was chosen for having the least % unmelted Nb $\sim 0.391\%$ and with $> 99.95\%$ density.

Figure 53 XCT reconstruction showing the 3D unmelted Nb and porosity distribution in the L20, H20, L40 and H40 samples. Quantification of unmelted Nb and porosity in each sample is summarized in a bar chart. Unmelted Nb and pores are marked in blue and red, respectively. All values are quoted with a confidence interval of 99.7%.

5.3.2 Phase Constituents and Structural Characteristics

XRD and EDS data were examined to evaluate the phase and elemental constituents in the 35 mm (width) $\times$ 40 mm (length) $\times$ 35 mm (height) blocks manufactured based on the H20 parameter, in which the results are displayed in Figure 54. Peaks corresponding solely to the BCC phase were detected upon indexing the XRD scan, indicating stabilization of β -Ti in the sample. EDS was performed via mapping to include all regions inclusive of the matrix and the unmelted Nb inclusions. The Nb content in the sample is $\sim 41.2\%$ and is within $\pm 0.5\%$ of the targeted composition. Based on the Ti-Nb phase diagram [190], the thermodynamically stable phase constituent for Ti41Nb is α (HCP) + β (BCC) phase at room temperature. Stabilized β -Ti as seen in the XRD result is normally obtained only when the temperature is above the β transus $\sim 620^\circ\text{C}$. However, if the cooling rate is suitably adjusted, metastable β phase can be fully retained at lower temperatures, usually accompanied with minute amount of other metastable phases such as the ω phase. The full retention of β phase at room temperature as seen in this study is facilitated by the inherent fast cooling rates associated with the LPBF process.

The nature of *in-situ* alloying via LPBF led to the formation of structural characteristics at different length scale. Under the BSE imaging mode, the mesostructure of *in-situ* alloyed Ti41Nb can be easily visualized due to the compositional contrast, as seen in Figure 55 and Figure 56a. The overall investigation of structural characteristics is depicted in Figure 56, which illustrates the representative mesostructure, microstructure and nanostructure in mm, μm and nm length scale respectively. Being a binary alloy, the brighter pixel in a BSE image represents higher Nb concentration and vice versa. The compounding effect of high

cooling rate in a LPBF process, relatively high melting point and relatively high density of Nb particles led to poor homogenization near the bottom region of every single build layer. As the laser scans the powder bed, some Nb particles settle and freeze early near the melt pool boundary region, prematurely halting the homogenization process via Marangoni convection and diffusion. This resulted in the formation of banded mesostructure with alternating Nb deprived layer and matrix layer, in which the matrix layer is the region with close-to-nominal composition. The Nb deprived layer is often accompanied by incompletely diffused Nb particle. Meanwhile, columnar grain structure was observed in the as-built Ti41Nb despite the formation of banded mesostructure (Figure 56b), which the columnar structure is typically associated with the usage of high E_d input during the manufacturing of metastable β -Ti via LPBF [122, 135].

Figure 54 Phase and elemental constituents of the in-situ alloyed Ti41Nb alloy via LPBF.

A closer look at the matrix region of the banded mesostructure reveals cellular dendritic microstructure induced by constitutional supercooling (Figure 56c) — a

feature commonly seen in LPBF manufactured part [216]. Meanwhile, the orthorhombic α'' phase was occasionally found in the Nb deprived region as depicted in Figure 56d, which is a metastable phase typically observed in Ti-Nb alloys with approximately 20 to 35 wt.% Nb [29, 231]. Nevertheless, the signal of α'' phase could not be identified via the XRD analysis due to its low volume fraction in the as-built Ti41Nb sample.

Figure 55 (a) BS image depicting mesostructure of Ti41Nb. (b) Thresholded image of (a) to highlight banded mesostructure.

Furthermore, TEM observation was carried out on the matrix region to investigate the nanostructure of the as-built sample. The selected area diffraction (SAED) pattern as observed in Figure 56e reveals the existence of isothermal ω phase (ω_{iso} phase) that could lead to ductile-to-brittle transition in β -Ti [153]. The identification of ω_{iso} phase is based on the sharp ω spots in the SAED image that formed due to a complete collapse of $\{222\}$ β planes [153]. This can be differentiated from the athermal ω_{ath} phase that exhibits displacive partial collapse of $\{111\}$ β planes, which would be instead presented as fuzzy streaks on the SAED image [232]. The usage of conventional XRD technique in this study has insufficient sensitivity to detect the ω_{iso} phase and requires the usage of synchrotron XRD to accomplish such feat [233]. The

162

dark field image of the ω_{iso} phase as shown in Figure 56f shows homogeneously distributed nanoscale precipitates with a mean size of < 4 nm.

Figure 56 (a) BS image and (b) grain orientation mapping with IPF-Z coloring to depict the mesostructure of the in-situ alloyed Ti41Nb part. (c) and (d) magnifies the matrix region and Nb depleted region respectively in (a), representing the microstructure of the part. (e) SAED image and (f) bright field TEM image of ω_1 and ω_2 variant, representing the nanostructure of the part. The yellow arrows in (c) and (d) point towards incompletely diffused Nb particle. The white arrows in (d) point towards α'' laths which appear as faint streaks. The white discontinuous circle in (e) is the selected area for dark field TEM image. The zone axis (ZA) of TEM image is given at the bottom of image (e).

Upon further analysis of the data from EBSD, the grain width distribution and $\{100\}$ pole figure associated with H20 were derived as respectively seen in Figure 57a and b. A relatively large mean grain width $\sim 148.9 \mu\text{m}$ was obtained in comparison to past studies on *in-situ* alloyed Ti-Nb alloys [122, 135], with the mean grain width $< 100 \mu\text{m}$. The large mean grain width in H20 is due to the usage of high $E_d \sim 410 \text{ J/mm}^3$ in comparison to the past studies with $E_d < 291.67 \text{ J/mm}^3$. The high E_d usage led to larger extent of remelting which facilitated the coarsening of grains. Furthermore, H20 sample shows strong $\{100\}$ fiber texture based on the $\{100\}$ pole figure, implying that the grains have preferential orientation of $\{100\}$ plane axes along the BD. The fiber texture is deemed beneficial for implant applications requiring low E , as β -Ti possesses minimum E along the $\langle 100 \rangle$ loading direction [212]. The MUD value describes the relative strength of a specific orientation in the sample with respect to a sample with randomized grain orientation, which can also be referred to as the ‘texture strength’, is calculated for $\{100\}$ and presented in the pole figure.

Figure 57 (a) Grain width distribution and (b) texture distribution represented by the $\{100\}$ pole figure of *in-situ* alloyed Ti41Nb via LPBF.

5.3.3 Tensile Behavior

To assess the tensile response at different tensile orientations, tests were performed on the coupons with the tensile direction perpendicular and parallel to the BD. The associated coupons are respectively known as the horizontal and vertical tensile coupons. Their representative engineering stress, σ_e , against engineering strain, ϵ_e , responses are shown in Figure 58. The values of YS, UTS, E and ϵ_f were subsequently derived and are displayed in Table 13.

Notably, all coupons demonstrated brittle response with negligible plasticity, $\epsilon_f < 2\%$. The brittle response is accompanied by relatively large fluctuation in UTS for coupons within the same tensile orientation. The ϵ_f of the horizontal and vertical coupons are significantly lower than those of conventionally and LPBF manufactured Ti-Nb alloys [117, 121, 135], which have $\epsilon_f > 8\%$. Nevertheless, vertical coupons demonstrate ϵ_f that is 15% higher than the horizontal coupons, signifying strong anisotropy in the as-built Ti41Nb in terms of ductility. Meanwhile, the horizontal coupons exhibit marginally higher YS of 3.7% as compared to the vertical coupons. The value of YS and UTS are similar for coupons in both orientations due to their negligible work hardening behavior. Similar to the YS, the horizontal coupons have E that is merely 3% higher than that of vertical coupons. The underwhelming difference in E was unexpected given the fiber texture in the coupons, which was expected to exhibit strong anisotropy in the value of E [212]. Moreover, the $E \sim 76.3$ and 74.1 GPa with respect to the horizontal and vertical coupons in this study are significantly higher than the E of LPBF manufactured Ti42Nb (wt.%) using pre-alloyed feed stock [134], ~ 60 GPa. The undesirable increment in E is pleasantly accompanied by an increment

in YS ~814 and 785 MPa for horizontal and vertical coupons, in comparison to the previous study on Ti42Nb, ~675 MPa.

Figure 58 Representative tensile stress-strain response of horizontal and vertical tensile coupon.

Table 13 Tensile properties of horizontal and vertical tensile coupon. All values are quoted with confidence interval of 99.7%.

Sample	YS (MPa)	UTS (MPa)	E (GPa)	ϵ_f (%)
Horizontal	814 ± 69.3	830 ± 117.2	76.3 ± 7.1	1.43 ± 0.9
Vertical	785 ± 31.6	787 ± 32.0	74.1 ± 8.5	1.65 ± 0.5

The fracture surfaces of the tensile coupons were subsequently investigated and the representative fracture surface for both orientations are shown in Figure 59. The fracture surfaces under the SE imaging mode for horizontal and vertical coupons can be seen in Figure 59a and b respectively. Both the fracture surfaces displayed cleavage

fracture characteristic, which is consistent with the brittle tensile response of the tensile coupons. In addition, the fracture surface of the horizontal coupon depicts cleavage fracture with the characteristic of columnar grains, hinting the significance of grain structure on the tensile stress-strain response. The unmelted Nb particles in Ti-Nb matrix can induce stress localization [126], which may lead to early failure of the tensile coupon. To investigate the suggested possibility, EDS mapping was done on the fracture surfaces of horizontal and vertical coupons, as seen in Figure 59c and d respectively. For both cases, the fracture surface cleaved across only a few particles, signifying negligible role of Nb delamination in determining the ε_f .

Figure 59 The representative fracture surface of (a) horizontal and (b) vertical tensile coupon. (c) and (d) are the EDS maps corresponding to Nb of fracture surface (a) and (b) respectively. The red dotted circle is used to highlight the cleavage fracture along an elongated grain. The yellow arrows are used to indicate the incompletely diffused Nb particles.

Furthermore, post-mortem analysis on the side surface was conducted for the tensile coupons in both orientations, under BSE imaging mode and EBSD mapping, as shown

in Figure 60. The BSE images revealed the crack on the horizontal coupon as predominantly surface crack (Figure 60a), while the vertical coupon is accompanied by secondary cracks beneath the fracture surface (Figure 60b). EBSD mappings were conducted in the selected regions of Figure 60a and b, as seen in Figure 60c and d respectively. Post-mortem EBSD map of the horizontal coupon reveals the formation of SIM and twins. The twins were identified as the $\{332\}\langle 113 \rangle$ variant based on the rotation angle between the twin and matrix lattices, $\sim 50.5^\circ$ [234]. Meanwhile, the α'' SIM was identified as the β phase by the EBSD software due to pseudosymmetry but can be distinguished based on the contrast of the BSE image. Despite not being shown on the EBSD map, α'' SIM/ twins formation was found in the post facto vertical coupon. However, α'' SIM/twins formation in coupons of both directions were heavily suppressed due the presence of ω_{iso} phase [153, 234]. The suppression of α'' SIM/twins led to the lack of interference with dislocations in the material, as evident from the lack of work hardening based on the stress-strain response for both horizontal and vertical tensile coupons.

Moreover, in Figure 60c, mixed transgranular and intergranular fracture can be observed for the horizontal coupon. In contrast, Figure 60d revealed predominantly transgranular fracture for the vertical coupon. The fully collapsed ω_{iso} precipitate is known to suppress dislocation slips to only along isolated $\{112\}$ slip planes, which contributes to localized planar deformation bands in β -Ti alloy [153]. Subsequently, stress concentration due to localized dislocation pile up against the grain boundary can lead to early fracture along the grain boundary. In the horizontal sample, the grain boundaries are perpendicular to the tensile direction and facilitates early intergranular fracture. However, intergranular fracture is difficult when the direction of tensile

168

stress is parallel to the long axis of columnar grains, which is why the vertical coupon can sustain slightly more deformation prior to failure. It is also good to note that the intergranular fracture in both samples happened predominantly along the $\{112\}$ slip planes. In conjunction with the poor ductility, the suppression of dislocation slip by the ω_{iso} phase enhanced the YS. At the same time, the ω_{iso} is responsible for the stiffening and isotropization of E in the H20 sample [235].

Figure 60 Post facto BSE micrograph on the side surface of tensile-tested (a) horizontal and (b) vertical tensile coupon. Post facto EBSD mapping on the side surface of tensile-tested (c) horizontal and (d) vertical tensile coupon. The EBSD maps (c) and (d) were taken from the region covered by the boxes with discontinuous outline in (a) and (b) respectively. The 3D boxes in (d) with discontinuous outline represent the crystallography orientation associated with each grain. The BD and tensile direction are indicated wherever applicable.

5.3.4 Fatigue Crack Growth

Representative results of the FCG tests on Ti41Nb lay, $\perp$ and $\parallel$ CT specimens are displayed in Figure 61 as da/dN vs. ΔK plots (also known as the Paris curve). Values

of m and ΔK_o were extracted from the CT specimens and summarized in Table 14. Based on the Paris curve, the $\perp$ and $\parallel$ CT specimen exhibit similar FCG characteristics, contrasting that of lay CT specimen. The lay CT specimens have m value ~ 4.0 , which is significantly higher than the m value for $\perp$ and $\parallel$ CT specimen, which is ~ 2.8 and ~ 2.9 correspondingly. The differences signify significant anisotropy in the FCG property of *in-situ* alloyed Ti41Nb via LPBF. Different values of m reveals the existence of crossover – higher value of m in lay CT specimen meant higher da/dN at high ΔK region in comparison to $\perp$ and $\parallel$ CT specimens; lower da/dN value at low ΔK region in comparison to $\perp$ and $\parallel$ CT specimens. As a consequence, Lay CT specimen has the $\Delta K_o \sim 4.3 \text{ MPa}\sqrt{\text{m}}$, which is higher than $\perp$ and $\parallel$ CT specimens with ~ 3.7 and $\sim 4.1 \text{ MPa}\sqrt{\text{m}}$. The high ΔK region and low ΔK region were defined based on the crossover point as seen in Figure 61, $\sim 6.5 \text{ MPa}\sqrt{\text{m}}$. However, the exact crossover ΔK value changes when different samples are compared.

Representative EBSD band contrast maps of lay, $\perp$ and $\parallel$ CT specimens encompassing the fatigue pre-crack region were investigated to understand their corresponding FCG behavior (Figure 62). To ease the discussion, an indicative cutoff line was drawn on Figure 62 to separate the high and low ΔK region. In the high ΔK region, lay CT specimen exhibited relatively straight planar crack growth, contrary to the $\perp$ and $\parallel$ CT specimens with crack branching and tortuosity. In the low ΔK region, the crack in all specimens experienced transition into faceted/serrated crack, with lay sample exhibiting the most serrated characteristic. The similarity in FCG behaviors of $\perp$ and $\parallel$ CT specimens is in agreement with the similarities in their corresponding Paris curve.

Figure 61 Representative Paris curve for lay, $\perp$ and $\parallel$ CT specimen, where FCG rate per cycle, da/dN , is plotted as a function of the applied stress intensity factor range, ΔK , in each sample.

Table 14 Summary of the FCG properties and fracture toughness of in-situ alloyed Ti41Nb in three orientations, based on the experiments conducted on CT specimens. The data in parenthesis indicates the value obtained from individual experiment.

Sample	ΔK_o (MPa $\sqrt{m}$)	m	r_{max} (μm)	K_{IC} (MPa $\sqrt{m}$)
Lay	4.3(3.8,4.8)	4.0(4.2,3.9)	3.75(2.90,4.61)	37.4(38.1,36.8)
$\perp$	3.7(3.7,3.7)	2.8(2.9,2.6)	2.94(2.93,2.95)	22.6(26.3,19.0)
$\parallel$	4.1(3.9,4.4)	2.9(2.8,3.0)	3.37(2.93,3.82)	41.2(41.8,40.6)

Figure 62 EBSD band contrast map on the fatigue precracked region of (a) lay (b) $\perp$ and (c) $\parallel$ CT specimen.

The FCG characteristic of lay, $\perp$ and $\parallel$ CT specimens in the high ΔK region was observed under the BSE imaging technique (Figure 63a-c), to reveal the interaction of crack with structural characteristics of the material. Figure 63d and e are the magnified SE images corresponding to Figure 63b and c, which helps in differentiating the secondary cracks from the slip traces. The specimens were mirror polished prior to tests, hence the slip traces can be observed after the tests. Secondary cracks can be identified for having 2 edges, with the aid of “edge” effect commonly associated with SE imaging. Meanwhile, slip steps have only a single edge. The CT specimen in the lay orientation has relatively homogenous compositional distribution on its surface, with minute amount of slip traces in the vicinity of the crack (Figure 63a). As seen in Figure 63b and c, the crack propagation in the $\perp$ and $\parallel$ direction at the high ΔK region was accompanied by markedly more slip traces than the lay specimen. The heavy slip formation is associated with the Nb deprived region, indicating that the region has higher tendency to slip. It is not possible to pinpoint an accurate composition for the region due to the limited compositional accuracy of EDS and severe inhomogeneity in the region. Nevertheless, a good estimation of Nb content in the Nb deprived region is $\sim 33.1\%$. In all cases, the slip traces were generally planar and forms along the $\{112\}$ slip planes.

The crack propagation in all samples was always preceded by one or multiple slip lines, which may be in a single direction or multiple directions. In the case of lay specimen, short planar slip traces typically form ahead of the crack tip at 45° relative to the mode I propagation direction. The crack propagates either as a sawtooth-like crack or smooth planar crack. In contrast, the crack propagation in $\perp$ and $\parallel$ specimen was accompanied by heavy planar slip traces in multiple directions in the Nb deprived

region. The crack tends to grow along one of the slip traces but can be arrested, followed by crack propagation in slip traces of alternative directions. This led to heavy crack deflection as seen in the $\perp$ and $\parallel$ specimen (Figure 63b and c). In the occasion where the crack front meets a Nb particle, the particle delaminates and led to large deviation from mode I crack growth as seen in Figure 63c. Such crack tip deviation is not favorable for crack propagation in mode I loading, hence favoring alternative crack tip propagation, leading to crack branching. In all cases, there was negligible interaction between the crack propagation and melt pool boundaries.

Figure 63 BSE micrograph on the high ΔK fatigue precracked region of (a) lay (b) $\perp$ and (c) $\parallel$ CT specimen. (d) and (e) are the magnified SE images of (b) and (c) respectively, which aid in the differentiation of secondary cracks and slip traces. White arrows in (a), (b) and (c) point the slip traces. Yellow discontinuous arrows in (d) and (e) point the secondary cracks.. The red box in (a) indicates the sawtooth-like crack. Red shading on CT specimen illustration located at the bottom left corner of (a), (b) and (c) shows the corresponding location of BSE micrograph.

Meanwhile, OM images of the fatigue fractured surface including the low ΔK region were investigated as shown in Figure 64. The lay CT specimen is comprised of highly serrated fracture surface as observed in Figure 64a. The serrated fracture surface is made up of cleavage planes with self-similar characteristic in the direction perpendicular to the crack growth. On the other hand, the fracture surface for $\perp$ specimen (Figure 64b) is consists of cleavage planes with random and equiaxed characteristic. Similarly, the fracture surface of $\parallel$ specimen exhibits random cleavage planes that is slightly elongated towards the direction of crack propagation (Figure 64c). To put it simply, fracture surface feature associated with all specimens strongly resembles that of the grain characteristics. The fracture surface characteristic of the lay specimen is found to be consistent with the serrated FCG characteristic in the low ΔK region, as observed from the side surface (Figure 62).

Figure 64 Optical micrograph on the fatigue fractured surface of (a) lay (b) $\perp$ and (c) $\parallel$ CT specimen. The shaded region on the illustration of CT specimen located at the top right corner of each image shows the location where the fractography is extracted from.

5.3.5 Fracture Toughness

The mode I fracture toughness, or K_{IC} associated with each sample is given in Table 14. Representative fracture surface corresponding to each specimen orientation in the fast fracture region were analyzed, as observed in Figure 65. The average K_{IC} value is indicated in each image to ease the correlation between fracture surface characteristic and K_{IC} value. The $\perp$ specimens exhibit an unsurprisingly poor average K_{IC} of 22.6 MPa $\sqrt{m}$, given their close-to-perfect elastic stress-strain response with minimal plasticity. The poor fracture toughness is accompanied by a flat fracture surface in the fast fracture region (Figure 65b). However, an astounding improvement in fracture toughness was observed among the lay and $\parallel$ specimens despite the poor tensile ductility, demonstrating K_{IC} of ~ 37.4 and ~ 41.2 MPa $\sqrt{m}$ respectively. The improvement of fracture toughness can be related to the fracture surfaces of lay and $\parallel$ specimen that exhibits significant crack deflection features (Figure 65a and c). The crack deflections are largely associated with the layers of Nb deprived region, giving hints on the role of layered mesostructured in the toughening of *in-situ* alloyed Ti41Nb. The as-built Ti41Nb parts demonstrated large anisotropic behavior in their fast fracture response despite the similarity in tensile stress-strain response along different orientations.

Figure 65 Fracture surface of the fast fracture region associated with (a) lay (b) $\perp$ and (c) $\parallel$ CT specimen. The shaded region on the illustration of CT specimen located at the bottom left corner of each image shows the location where the fractography was extracted from.

5.4 Discussions

5.4.1 Composite Effect of *In-situ* Alloying

The inherently fast cooling cycles of LPBF process led to incomplete melting and diffusion of Nb. As the melt pool forms, the heavy Nb particles have the tendency to be situated at the lower side of the melt pool. The subsequent premature freezing of Nb particles near the boundary of the laser induced melt pool led to the formation of partially molten Nb particles. Without sufficient supply and diffusion of Nb into the frozen area, the Nb deprived region forms around the Nb particles. Nevertheless, the subsequent laser hatch remelts a portion of the melt pool side boundary, leaving the

bottom of the melt pool highly associated with Nb deprived area. The upper region of a melt pool is given more time for Nb diffusion and homogenization, thereby forming the matrix region with close-to-nominal composition.

Consequently, interesting mesostructured component with alternative layers of Nb deprived layer and nominal matrix region is formed, as depicted by the lines in the schematic of CT specimens (Figure 52a). In reality, the depicted layered structure is for illustration only and is not perfect. The Nb deprived region has high tendency to be found across a layer but does not occupy the entire layer. Nonetheless, the assumption of perfectly layer structured Ti41Nb greatly simplifies the discussion on the orientation dependency of its mechanical behaviors.

In the matrix region, fully collapsed ω_{iso} phase led to highly suppressed dislocation slip systems. As shown in Figure 63b and c however, the Nb deprived region has better propensity to slip, owing to the reduced amount of β -stabilizer that suppresses the tendency for diffusional ω_{iso} formation [190]. Hence, the layered structure is akin to a composite with alternating easy and difficult-to-slip regions. This layered structure in turn affects the mechanical behaviors especially in terms of FCG and fracture response.

5.4.1.1 Fatigue Crack Growth

FCG characteristics of *in-situ* alloyed Ti41Nb was strongly affected by the composite-like mesostructure. The Nb poor region brought drastic change to the crack growth behavior and the extent of its effect is strongly dependent on the specimen's orientation relative to the crack growth direction. The summary of crack growth

mechanism in the high ΔK region along different orientations can be seen in Figure 66.

The negligible work hardening behavior of Ti41Nb enables the assumption of elastic-perfectly plastic material behavior, which the maximum plastic zone size, r_{max} , of Ti41Nb at a certain ΔK value under plane strain conditions and within the continuum mechanics framework is given as $r_{max} = \frac{1}{3\pi} \left(\frac{\Delta K}{(1-R)Y_S} \right)^2$. Assuming a ΔK value of 11 MPa $\sqrt{m}$ in the high ΔK region, the r_{max} for lay, $\perp$ and $\parallel$ specimen is $\sim 23.93 \mu m$, $\sim 23.93 \mu m$ and $\sim 25.72 \mu m$ respectively. These values are notably smaller than the average grain width of $148.9 \mu m$. For the lay specimen, the large grain size in comparison to r_{max} led to slip traces only near the crack tip upon cyclic loading. The slip traces typically formed in two directions along $\{112\}$ planes and were approximately 45° to the Mode I FCG direction. The angle of slip traces corresponds to the maximum shear stress direction ahead of the crack tip under mode I loading condition. The crack propagates in a sawtooth-like fashion as seen in Figure 63a, which can be explained by the single crystal crack growth model [236], owing to the relatively large grain size in the material. In the model, the work hardening of one slip plane leads to alternating shear on another. Due to the kinematic irreversibility of cyclic slip, net planar crack growth occurs along the intersecting line of two slip planes.

As for the $\perp$ specimen, despite having relative small r_{max} value of $25.72 \mu m$ as compared to average grain size, heavy slip traces were observed spanning a few grains away from the crack front when the crack is in the Nb poor region. These slip traces can be wavy and were not necessarily orientated at 45° to the mode I direction, owing to the change in maximum shear stress direction when the slip line is away and at an

angle from the mode I crack growth direction. The relatively extensive formation of slip traces indicate the inaccuracy of r_{max} value to estimate the plastic zone size of Nb deprived region. The calculation of r_{max} is based on the tensile data that encompasses the contribution from both matrix and Nb deprived region. However, at this point of time, it is not possible to isolate the Nb poor region and obtain its associated r_{max} value. Similar to the lay sample, the cyclic loading led to crack propagation along the slip traces in the $\perp$ specimen. The slip traces were generally along one direction within a grain and changed direction across grain boundaries, leading to crack propagation with severe deflection. In addition, the Nb distribution in the Nb deprived region is inhomogeneous and the crack propagation can occasionally be blocked by the Nb-rich traces. The Nb poor region is akin to a maze for the crack, inducing crack tortuosity that deviates the crack from mode I propagation direction which effectively slows down the crack growth rate. It was also noted that crack tends to grow into the Nb poor region at high ΔK , possibly due to the easy slip formation that “attracts” crack propagation into the region.

Meanwhile in the $\parallel$ specimen, the spatial arrangement of layered composite mesostructure gave it a different FCG characteristic at high ΔK . The crack that propagated in the $\parallel$ specimen met periodical “barriers” of Nb deprived zone that have higher propensity of shearing than the matrix region, leading to crack deflection similar to that observed in the $\perp$ specimen. As the unmelted Nb particles is closely associated to the Nb deprived region, the crack front also encountered Nb particles as it propagates. As the crack passes, the Nb particle delaminates from the matrix and guides the crack in an unfavorable direction for propagation. The wrongfully guided crack was eventually stopped where alternative crack branched out and grew in the

direction typically observed when a far-field mode I loading is applied. The crack branching mechanism brought about deviation from mode I loading and the need of extra load cycles to create new surface, hence delaying crack propagation. Such crack branching can also be seen in $\perp$ sample but with less frequency, as the crack was not forced to pass through the Nb particles which typically reside near the bottom of the melt pool boundary.

One may argue that the lay specimen has layers of Nb deprived region beneath the surface and should have induced tortuous FCG and crack branching at high ΔK . However, unlike other specimens, the Nb deprived region does not span the entire crack front in the lay specimen. Hence, the effectiveness of Nb deprived region to promote crack tortuosity and branching in lay specimen is relatively insignificant.

Figure 66 FCG mechanism in the high ΔK region associated with Lay, $\perp$ and $\parallel$ CT specimens.

As the ΔK lowers, the r_{max} approaches 2.94 – 3.75 μm for all specimens and was less sensitive to the mesostructure characteristics. Hence, transition into a crystallographic, serrated mode of fracture was observed in all specimens. The arrangement of grains dominated the FCG behavior at low ΔK , subsequently led to anisotropic FCG response in the near threshold region. For the lay specimen, the grains have their long axis arranged along the crack front. This minimized the crystallographic variation associated with crack growth in the lay specimen, in contrast to the $\perp$ and $\parallel$ specimen, as depicted in Figure 64. Hence, the crack in the lay specimen experienced favorable condition to form highly serrated crack, which helped in reducing the rate of FCG through roughness-induced closure.

In short, a transition from mesostructure to microstructure crack interaction were observed as ΔK reduces, causing change to the FCG characteristic. At high ΔK , Nb deprived region in $\perp$ and $\parallel$ specimen led to crack tortuosity and branching, which reduced the effective ΔK and lowered the driving force for FCG. At low ΔK , the grain arrangement characteristic promoted highly serrated crack in the lay specimen, causing roughness-induced closure that benefited the FCG rate. The change in mechanism led to crossover in the Paris curves, where lay specimen exhibited $m \sim 4.0$ significantly lower than that of $\perp$ and $\parallel$ specimen, ~ 2.8 and ~ 2.9 respectively. The discovery provides valuable insights for defect-tolerant-design in parts manufactured via the *in-situ* alloying route by considering the direction of crack propagation with respect to the orientation of specimens.

5.4.1.2 Fracture Toughness

Moving on to the fast fracture response of the CT specimens, all specimens satisfied the plane strain condition for K_{IC} , which is largely expected due to the poor ductility

exhibited by the as-built part. The absence of crack blunting mechanism is accompanied by an unsurprisingly low fracture toughness $\sim 22.6 \text{ MPa}\sqrt{\text{m}}$ in the $\perp$ specimen. The fracture toughness obtained is comparable to a past study on Ti-15Mo (wt.%) β -Ti with fully collapsed ω_{iso} phase, $\sim 22 \text{ MPa}\sqrt{\text{m}}$ [237]. The lack of plasticity in the $\perp$ specimen corresponded to the clean and smooth fracture surface without formation of dimple (Figure 65b).

It is noteworthy that when the crack propagated along different directions, the K_{IC} markedly increased by nearly two fold to $\sim 37.4 \text{ MPa}\sqrt{\text{m}}$ and $\sim 41.2 \text{ MPa}\sqrt{\text{m}}$ for lay and $\parallel$ specimen respectively. A closer look at the fracture surfaces in the fast fracture region revealed crack deflection induced by the layered composite mesostructure (Figure 65a and c). As the crack passed through the interface of easy and difficult-to-slip regions, the crack deflected from its nominal mode I growth direction. Under the same far field K_I , the effective driving force for a deflected crack is typically smaller than that of a straight crack of the same projected length. As such, an apparently larger driving force is required to fracture a specimen with deflected crack in comparison to a straight crack. Consequently, the layered composite-like mesostructure toughened the lay and $\parallel$ specimens. This improved the K_{IC} of the brittle *in-situ* alloyed Ti41Nb lay and $\parallel$ specimen to a range similar to the as-built Ti6Al4V fabricated via LPBF process $\sim 37.5 \text{ MPa}\sqrt{\text{m}}$, which exhibits ductility in the excess of 4% [238]. The schematics of fast fracture behavior associated with each specimen orientation are shown in Figure 67a. The crack deflection caused by layers of easy and difficult-to-slip regions in the $\parallel$ specimen can be observed in Figure 67b.

The toughening mechanism as discovered in the *in-situ* alloyed Ti41Nb is significant due to the fact that K_{IC} can be improved despite the lack of plasticity/ductility. This further highlights the importance to investigate the fracture toughness of an AM material instead of merely investigating on the uniaxial tension properties. The poor ductility of a material does not immediately translates to poor fracture toughness, where the relation of both is connected by intrinsic toughening mechanism [239]. The intrinsic toughening mechanism relies mainly on the material's ability to blunt the crack tip, making it more operative in ductile metals. For a less ductile metal, extrinsic toughening mechanism that relies on crack growth resistance needs to be utilized. In the case of LPBF, the unique ability to induce mesostructure can be leveraged to resist fracture. For instance, wavy melt pool boundary induced by multiple laser scans imparted high crack tortuosity and toughened the resultant material, as seen on the Al12Si and AlSi10Mg alloys [14, 15]. Similarly, when the crack propagation direction is perpendicular to the BD, prior- β columnar grain in Ti6Al4V deflected crack propagation and toughened the material [16]. Extrinsic toughening mechanism is important in LPBF fabricated materials as it decouples toughness from the need of plasticity. The fracture toughness of a typical high strength and low ductility material associated with LPBF can be improved with extrinsic toughening mechanism, without the need to sacrifice the strength in the name of ductility through heat treatment. The LPBF as a near net shape processing technology does not require further forming procedure, hence the fracture toughness can be a more important metric in comparison to the ductility.

To further improve the K_{IC} of the specimen in the $\perp$ orientation, incorporation of Nb deprived region in a controlled fashion throughout the specimen can be done. One

way is to selectively scan and melt the powder bed with a checkerboard pattern of alternating high and low E_d region. This in turn creates alternate regions of matrix and Nb deprived region across the same layer, which effectively toughens the resultant part in all directions. The inherently fast cooling cycle and flexibility of LPBF process enables the possibility of mesostructure control in the manufactured component to a certain extent, thereby offering tremendous opportunity in the conquest of material toughening.

Figure 67 (a) Schematics showing the fast fracture behavior of lay, $\perp$ and $\parallel$ CT specimens. (b) The SEM image of tilted $\parallel$ CT specimen was captured under the SE mode to illustrate the effect of Nb deprived region on crack deflection. The black arrows are pointing toward bands of Nb deprived region. The discontinuous line traces the representative fracture surface in the fast fracture region.

5.4.2 Build Size Effect

Up to this point, the discussions had been on the mechanical properties of *in-situ* alloyed Ti41Nb without questioning the unusual existence of ω_{iso} phase. In fact, the

selection of 41 wt.% Nb was based on past study where similar range of Nb addition could lead to alloy with the combination of low $E \sim 57$ GPa, moderate YS ~ 600 MPa and reasonable $\varepsilon_f \sim 13\%$ [117]. Similarly, a past study on LPBF manufactured Ti42Nb (wt.%) using pre-alloyed powder demonstrated $E \sim 60.51$ GPa, YS ~ 674.08 MPa and $\varepsilon_f \sim 11.65\%$ [134]. The negligible effect of ω_{iso} phase in the past studies prompted further investigation into the cause of brittleness exhibited by Ti41Nb alloy in this study.

The effect of heat accumulation during LPBF process had been demonstrated via SS316L, which the effect can be substantial and brought about fast increase in the temperature of a part-in-progress as the number of build layers increases [240]. The part's temperature at the top surface can reach ~ 250 °C at 300 layers build height and ~ 500 °C at 1000 layers build height. The observation of heat accumulation is highly relevant to Ti41Nb due to the similar thermal conductivity possessed by the two materials. In the Ti41Nb alloy, the detrimental ω_{iso} phase can precipitate at a temperature as low as ~ 250 °C [190]. Therefore, it is entirely possible for *in-situ* ω_{iso} aging to occur in Ti41Nb alloy under the effect of heat accumulation. In this study, the CT specimens required at least 600 layers to build, which could easily bring the surface temperature of the specimens to more than 250°C. Therefore, we hypothesized the existence of a build size effect that could lead to part's brittleness as a result of *in-situ* ω_{iso} precipitation. It should be noted that, the high E_d required for homogenization of *in-situ* alloyed component in this study (410 J/mm^3) could induce significantly greater effect of heat accumulation, as opposed to that required for pre-alloyed Ti42Nb [134] (40 J/mm^3) or SS316L [240] (48.5 J/mm^3). The relatively small h in

this study likely does not contribute to the significant increment in heat accumulation due to the accompanying V_L increment

Unfortunately, the build size effect was not expected and the LPBF machine was not equipped with *in-situ* temperature monitoring device. To verify the theory of *in-situ* ω_{iso} aging based on the build size effect, parts with relatively small build size of 12 mm (width) $\times$ 30 mm (length) $\times$ 7 mm (height) mm were built with H20 parameter, in comparison to the large part of 35 mm (width) $\times$ 40 mm (length) $\times$ 35 mm (height) used for the machining of CT specimens. At the same time, one of the large part was solution heat treated to explore the possibility of ductility recovery. The solution heat treatment was carried out above the Ti41Nb β -transus temperature (750 °C) for an hour to dissolve the ω_{iso} phase, which was achieved with a 5 °C per minute ramp in a box furnace followed by water quench. Horizontal tensile coupons were then machined out of the small part, large part and solution treated large part. Three replications of tensile tests were conducted for each part for repeatability study. The representative stress-strain responses associated with each part can be seen in Figure 68. The corresponding tensile properties of the parts are summarized in Table 15.

Figure 68 Representative tensile stress-strain response of horizontal tensile coupon extracted from large, small and solution treated large sample.

Table 15 Tensile properties of horizontal tensile coupon extracted from large, small and solution treated large sample. All values are quoted with confidence interval of 99.7%.

Sample	YS (MPa)	UTS (MPa)	E (GPa)	ϵ_f (%)
Large	785 ± 31.6	787 ± 32.0	74.1 ± 8.5	1.65 ± 0.5
Small	751 ± 3.5	N/A	66.0 ± 15.7	13.26 ± 4.8
Solution Treated	321 ± 90.3	684 ± 5.1	94.5 ± 60.9	10.71 ± 6.2

The as-built small Ti41Nb part had significantly improved ϵ_f of ~13.26% while possessing great E ~66 GPa and YS ~751 MPa. The reduced part build size lessened the heat accumulation and limited the extent of *in-situ* ω_{iso} aging, as evident from the ductility improvement. The improvement serves as a solid evidence for the detrimental build size effect associated with Ti41Nb alloy, or metastable β -Ti in

general. Likewise, the solution treated part showed significantly improved ε_f to ~10.71% by dissolving the ω_{iso} . In the meantime, SIM characteristic can be observed on the stress-strain response of heat treated part, which resulted in significant reduction of YS to ~321 MPa. Large variation in tensile properties can also be observed after solution heat treatment due to the compositional inhomogeneity in the *in-situ* alloyed part. In turn, the *in-situ* alloyed part had different heat treatment response at different locations. Hence, heat treatment for *in-situ* alloyed Ti41Nb needs to be further optimized despite the improved ductility, which is however not within the scope of this study.

Extending the premises of discussion further, the awareness of build size effect is critical in ensuring the safety and reliability of as-built metastable β -Ti product. Based on the effect, several process related improvements need to be done where a few related examples will be suggested here. Firstly, actively cooled substrate platform can be employed to reduce heat accumulation especially in the process of building a large structure. Moreover, care should be taken in the spatial orientation of a part to reduce the extend of heat accumulation, e.g. a solid component built on top of a lattice structure could lead to severe heat accumulation due to the poor heat conduction through the lattice structure. Furthermore, *in-situ* temperature monitoring should be deployed to aid in product certification or process intervention when required. Time delay between scans can be adjusted to enable heat dissipation based on the monitored temperature data. Last but not least, a standardize heat treatment procedure should be developed to ensure reliable properties in the resultant part regardless of the build size.

All in all, reliable process needs to be developed to cater for the change in build size and geometry, especially for high E_d process as seen in the *in-situ* alloying process.

5.5 Summary

The employment of small h fast V_L strategy to obtain high quality *in-situ* alloyed Ti41Nb was shown to be effective, where the amount of unmelted Nb can be minimized ($\sim 0.391\%$) while reasonable porosity level of $< 0.5\%$ was achieved. Blocks with the dimensions of 35 mm (width) x 40 mm (length) x 35 mm (height) were fabricated with the suitably optimized H20 parameter set and characterized for structural characteristics, uniaxial tensile properties, FCG properties and fracture toughness. Based on the results, the key findings can be summarised:

- 1) The *in-situ* alloying approach led to structural characteristics at different length scales for the Ti41Nb blocks. The mesostructure of the fabricated blocks is comprised of columnar grains and composite structure with layers of Nb deprived region and matrix region. Meanwhile, typical cellular dendritic structure made up the microstructure of the resultant material. Interestingly, nanoscale ω_{iso} precipitation can be observed and constitute the nanostructure of the material.
- 2) The tensile properties of the resultant material were relatively anisotropic. The parts demonstrated a combination of high YS (> 780 MPa) and low E (< 76.3 GPa). However, the parts were surprisingly brittle with $\epsilon_f < 1.65\%$, which can be explained by the existence of nano-sized ω_{iso} phase.
- 3) The FCG rate at high ΔK was strongly influenced by the layers of Nb poor regions. Depending on the sample's orientation, the extent of Nb poor region

along the crack front varied. Large extent of Nb poor region ahead of the crack front led to crack deflection and slowed down the FCG rate, as seen in the $\perp$ and $\parallel$ CT specimens. On the other hand, the FCG rate at low ΔK was strongly influenced by the local slip systems. Therefore, highly serrated crack path that is beneficial for FCG rate was observed in the lay CT specimens, for its lesser crystallographic variations ahead of the crack tip as compared to the $\perp$ and $\parallel$ CT specimens.

- 4) The $\perp$ CT specimens exhibited an unsurprisingly poor average K_{IC} of ~ 22.6 MPa $\sqrt{m}$, given the material's close-to-perfect elastic stress-strain response with minimal plasticity. However, the interface between Nb poor region and matrix region facilitated crack deflection, which brought up the average K_{IC} value to ~ 37.4 MPa $\sqrt{m}$ and ~ 41.2 MPa $\sqrt{m}$ for lay and $\parallel$ specimen respectively.
- 5) Ti41Nb can be embrittled due to build size effect. The increased build size of a part is accompanied by thermal accumulation, followed by *in-situ* heat treatment effect that led to precipitation of fully collapsed ω_{iso} phase.

In short, the build size effect signifies an urgent need to deal with the detrimental *in-situ* ω_{iso} precipitation. Nevertheless, the brittleness induced by ω_{iso} precipitation provided the opportunity to unravel the extrinsic toughening mechanism induced by compositional segregation, which is unique to *in-situ* alloying process. The as-mentioned toughening mechanism is significant due to its applicability to virtually all alloys and not limited to just β -Ti alloys.

Chapter 6 Conclusions and Future Work

The research works carried out for the completion of this thesis are summarized in this chapter. Feasible future work is then proposed.

6.1 Conclusions

In this thesis, studies had been conducted to address the research gaps associated with *in-situ* alloying of β -Ti with LPBF. Firstly, the effects of Ta addition were investigated on the *in-situ* alloyed Ti-Ta alloys. Thereafter, a new laser scanning strategy was proposed to successfully resolve the porosity-inclusion dilemma. The mechanism behind the breakthrough was revealed via experimental observations and thermal simulations on Ti34Nb (wt.%). Finally, the fracture behavior of Ti41Nb (wt.%) was studied and correlated with the structural characteristics of the material. The detailed conclusion associated with each study will be elaborated in the following subsections.

6.1.1 Laser Powder Bed Fusion of Ti-Ta Alloys: Compositions and Designs for Biomedical Applications

Effect of Ta addition on samples' characteristics

With a constant E_d , the addition of Ta affected the defects evolution from keyhole induced porosity to incomplete fusion of melt pool. The volume % porosity and volume % unmelted Ta increased with the amount of Ta. Additionally, the phase(s) present in the alloys changed from $\alpha \rightarrow \alpha' \rightarrow \alpha'' + \alpha' \rightarrow \beta + \alpha'' + \alpha'$ for 0, 10, 30, 50 wt.% Ta respectively. The dominant phase(s) detected in the alloy matrix is in bold text. The size of the lath/acicular phase was also refined with the increment of Ta content. The big difference in melting point between Ti and Ta served as the main culprit behind the increasing defects with Ta addition.

Effect of Ta addition on mechanical properties

Ti30Ta provides the optimal mechanical properties for orthopaedic applications due to its lowest $E \sim 73$ GPa while having the highest YS ~ 950 MPa. Lath/acicular phase size refinement and solid solution strengthening improved the YS of the Ti-Ta alloy up to Ti30Ta. Further Ta addition to Ti50Ta retained coarse β (BCC) phase, accompanied by slight drop in YS. The decrease in ε_f with Ta addition is due to the increased amount of porosity and unmelted Ta in the alloy matrix. Strain incompatibility and stress concentration can be expected at the lath- α' (HCP)/Ta(BCC) boundary due to the lattice mismatch between the two phases. Such mismatch possibly led to interface rupture and subsequently contribute to void formation and coalescence.

6.1.2 Resolving the Porosity-unmelted Inclusion Dilemma During *In-Situ* Alloying of Ti34Nb via Laser Powder Bed Fusion

Resolving porosity-inclusion dilemma

The combination of high P (~ 650 W or 950 W), high V_L (~ 650 mm/s or 950 mm/s), a top-hat profile laser and a suitable stripe scanning strategy is ideal for printing a fully dense Ti34Nb sample with limited unmelted Nb inclusions content. These parameters resulted in a slow moving, large melt pool, with a small aspect ratio and melt pool angle, propagated in a direction perpendicular to the scanning direction. This ensures uniform mixing of constituents and also eliminates keyhole porosities. The simultaneous densification and homogenization signify a breakthrough in resolving the porosity-inclusion dilemma. In addition, the resultant low angle melt pool boundary is beneficial in facilitating $\{100\}$ textured β -Ti microstructure formation. These findings are expected to inspire a paradigm shift in devising processing

windows that can minimize or completely eliminate defects in materials manufactured via LPBF methods, regardless of the material's composition.

Microstructure formation mechanism

At constant E_d , the resultant part produced with a Gaussian profiled laser and low $P \sim 350$ W had weaker texture and refined grain in comparison to the part associated with top-hat profiled laser and high $P \sim 950$ W. The primary factor for the difference was related to the amount of unmelted Nb particles, which acted as inoculants. Nevertheless, thermal history was extracted from the thermal simulations to eliminate the possibility of CET as the dominant mechanism of microstructural evolution. The role of Nb particles as inoculants were further confirmed through meticulous experimental observations.

6.1.3 Fracture Behavior of Laser Powder Bed Fusion Fabricated Ti41Nb via In-situ Alloying Build size effect

The extent of heat accumulation increases with part's build size especially the build height. The heat accumulation led to *in-situ* ω_{iso} precipitation that embrittled the large 35 mm (width) $\times$ 40 mm (length) $\times$ 35 mm (height) Ti41Nb block, which exhibited $\epsilon_f \sim 1.65\%$, YS ~ 785 MPa, $E \sim 74.1$ GPa. With small build size of 12 mm (width) $\times$ 30 mm (length) $\times$ 7 mm (height), significantly better ductility was observed at $\epsilon_f \sim 13.26\%$, with slightly reduced $E \sim 66$ GPa and YS ~ 751 MPa. Meanwhile, solution heat treatment of the large part can recover ϵ_f to $\sim 10.71\%$, but at the same time deteriorated the YS to ~ 321 MPa due to SIM. The discovery of build size effect points toward the urgent need to develop mitigation measures for the detrimental *in-situ* ω_{iso} precipitation, such that the fabrication of superior β -Ti implant materials can be done.

Composite effect

The formation of layered composite-like mesostructure with alternated Nb deprived region and matrix region was observed, due to the inherently fast cooling rate of LPBF that limits the melting and diffusion of Nb. The crack interactions with the composite-like mesostructure strongly affects the FCG rate and fracture toughness in an anisotropic fashion. At high ΔK ($> 7 \text{ MPa}\sqrt{\text{m}}$), the FCG underwent severe deflection in the Nb deprived region and slows down the FCG rate depending on the propagation direction. Meanwhile, crack deflection can occur along the interface of Nb deprived region and matrix region during fast fracture. Without crack deflection, the brittle as-built Ti41Nb sample shows poor $K_{IC} \sim 22.6 \text{ MPa}\sqrt{\text{m}}$. Despite exhibiting negligible plasticity, fast fracture along directions that induced crack deflection improved the K_{IC} by almost two fold. This finding is significant in demonstrating the potential of *in-situ* alloying to induce extrinsic toughening mechanism, despite having a material that exhibits negligible ductile response.

6.2 Future Work

The following future research directions are recommended to propel the reliable application of *in-situ* alloyed β -Ti as an implant material.

6.2.1 Compositional Design for *In-Situ* Alloying

The inherent characteristic of *in-situ* alloying with LPBF to produce parts with compositional segregation calls for the need to rethink the compositional design approach. If a homogenous part is required, the powder feedstock needs to be designed for such purpose while not compromising the resultant material's properties. Meanwhile, parts with compositional segregation was shown to be beneficial. In this case, compositional design should be made to leverage the benefits of compositionally

segregated components. Nevertheless, the dependency of mechanical behavior on partially melted particles needs to be further studied and understood. In order to achieve this, innovative means to isolate the voids and particles are required, such that the matrix interaction with them can be better investigated.

6.2.2 Modelling of *In-situ* Alloying Process

Numerical analysis approach such as computational fluid dynamic is essential to better understand the *in-situ* alloying process. However, the modelling is still limited due challenges such as inability to obtain thermomechanical properties of transitional composition as well as the complexity to impart diffusion process.

6.2.3 Understanding Strengthening Mechanism of Heterogenous *In-situ* Alloyed Component

Quantitative description of different strengthening mechanisms in a compositionally heterogenous component is difficult. For example, the inhomogeneous distribution of composition meant different lattice parameter everywhere within the material, giving extra complexity to estimate dislocation density based on the XRD peak broadening phenomenon. Establishing a method to estimate/quantify the role of different strengthening mechanism in an heterogenous *in-situ* alloyed material will certainly yield better understand on relevant material design methodology. Moreover, TEM analysis should also be conducted to aid the identification of SIM, twinning systems, dislocation interactions and any mechanisms related to strengthening behavior.

6.2.4 Develop Methodology to Obtain Elastic Modulus of Heterogenous *In-situ* Alloyed Component via Ultrasound Device

Most of the time, ultrasonic measurement device can provide a more accurate value of Young's modulus in comparison to tensile test. However, the inhomogeneous compositional distribution and unmelted particles in an *in-situ* alloyed component led

to extra complications to the suggested approach. For instances, commercially available ultrasonic Young's modulus measurement system assumes a material to be homogenous. Hence, approaches to reliably quantify the Young's modulus of an inhomogeneous material (with compositional macro-segregation) needs to be studied, which requires the development of new soundwave-material interaction model.

6.2.5 Explore and Understand Capabilities of Top-hat Laser

The usage of top-hat laser provides the opportunity to create unique melt-pool that is beneficial for *in-situ* alloying. However, the processing window involving such melt pool using top-hat laser is yet to be explored. Laser scanning parameters such as beam diameter, P, V_L , h , stripe spacing etc. can affect the resultant melt pool formation, microstructural features and mechanical properties of the final part. Hence, more studies are required in this area to ensure the reliable usage of top-hat laser.

6.2.6 Leverage on the Nucleation Phenomena of Partially Melted Particles

The partially melted particles could be leveraged to produce part with equiaxed grains. Hypothetically speaking, under a constant set of laser parameter, the usage of smaller particles size (while retaining constant composition) can lead to more nucleation and lesser volume fraction of partially diffused particles in an *in-situ* alloyed material. However, further reducing the particles size can cease the nucleation if they are dissociated sufficiently. Besides, there are other factors that can affect the beneficial nucleation phenomena such as laser parameters and scanning strategy. Hence, more studies will be required to understand the topic.

6.2.7 Develop Post-fabrication Heat Treatment Procedure

Reliable post-fabrication heat treatment process needs to be developed as part of the β -Ti component fabrication process. The availability of heat treatment procedure

enables predictable and tunable material's properties that could not be achieved by LPBF process alone.

6.2.8 Understand Fracture Behavior under Operating Condition

The fracture behavior of β -Ti could behave differently under an implant's *in-vivo* operating condition. For instances, testing a β -Ti in air will yield different fracture responses as compared to that in a body fluid or when osseointegration occurs on the material. Extensive and all-rounding understanding on the fracture behavior of implant material should be established before the material's mass deployment to humankind.

Appendix A Thermophysical properties of Ti34Nb (wt.%)

T (K)	ρ (kg/m ³)	K (W/(m K))	C _p (J/(kg K))
298.15	5380.31	18.54654	451.16
300	5380.07	18.53658	451.16
400	5366.74	18.33851	467.92
500	5352.85	18.60066	481.45
600	5338.42	19.139	493.7
700	5323.48	19.85589	505.41
800	5308.06	20.69465	514.67
873.15	5296.49	21.36465	1144.11
945.36	5293.7	20.29665	667.55
1000	5285.18	20.98681	500.32
1100	5269.16	22.25059	508.8
1200	5252.59	23.51512	517.91
1300	5235.47	24.78025	529.59
1400	5217.83	26.04587	543.82
1500	5199.67	27.31189	560.36
1600	5181.02	28.57825	579.02
1700	5161.9	29.8449	599.68
1800	5142.31	31.11181	622.24
1900	5122.27	32.37894	650.69
2015.75	5098.54	33.84591	675.2133
2067.79	4909.72	26.45497	765.61
2100	4899.95	26.86315	767.79
2200	4869.13	28.13027	771.18
2300	4837.6	29.39739	774.77
2400	4805.4	30.66451	778.54
2500	4772.56	31.93163	782.51
2600	4739.11	33.19875	786.72
2700	4705.1	34.46587	790.55
2800	4670.55	35.73299	791.12
2900	4635.5	37.00011	791.12
3000	4599.98	38.26723	791.12

Appendix B Melt Pool Evolution of 350W Ti34Nb (wt.%)
Sample

Appendix C Melt Pool Evolution of 950W Ti34Nb (wt.%) Sample

Appendix D Slip Plane Associated with 350W Ti34Nb (wt.%)

(a), (b) and (c) are EBSD band contrast overlaid images with IPF-X coloring. $\{110\}$, $\{112\}$ and $\{123\}$ pole figures in (d), (e) and (f) correspond to the grains containing the pointed slip lines in (a), (b) and (c) (The planes manifests themselves as dots on the pole figures). $\{110\}$, $\{112\}$ and $\{123\}$ planes are the possible crystallographic slip

planes of the BCC material. Note that the universal axis of the pole figure and the associated image is the same. The vector of slip trace must be parallel to its slip plane, hence can be taken as the zone axis of all the possible slip planes. These possible slip planes will manifest itself as a straight line on the stereographic projection (also the pole figure, though strictly speaking is a series of dots), which is perpendicular to the zone axis vector. This straight line can be referred as the line of possible slip planes. Hence, by drawing the line of possible slip planes on the pole figure (that is perpendicular to the vector of slip trace), it is possible to examine the hypothesis of slip plane activation on a particular crystallographic plane associated with the pole figure. The line of possible slip planes are the red discontinuous lines in (d), (e) and (f). If the line of possible slip planes intersect with one or more dots in a pole figure of a particular crystallographic plane, that means the activation of that particular crystallographic plane is possible based on the observed slip trace vector (as shown by the red circles in (d), (e) and (f)).

Appendix E Simulated Thermal Profiles of Melt Pools Formed with Different Profiles and Spot Diameters Associated with 950W Ti34Nb (wt.%) Sample

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