Linköping Studies in Science and Technology
Licentiate Thesis No. 1896

Alloy Design and Characterization

of

γ' Strengthened
Nickel-based
Superalloys

for

Additive Manufacturing

Jinghao Xu

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Linköping 2021

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Date: February 12, 2021
Location: ACAS, Linköping University

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ISBN: 978-91-7929-726-8

ISSN: 0280-7971

Printed by LiU-Tryck 2021

Nickel-based superalloys, an alloy system based on nickel as the matrix element with the addition of up to 10 more alloying elements including chromium, aluminum, cobalt, tungsten, molybdenum, titanium, and so on. Through the development and improvement of nickel-based superalloys in the past century, they are well proved to show excellent performance at the elevated service temperature. Owing to the combination of extraordinary high-temperature mechanical properties, such as monotonic and cyclic deformation resistance, fatigue crack propagation resistance; and high-temperature chemical properties, such as corrosion and oxidation resistance, phase stability, nickel-based superalloys are widely used in the critical hot-section components in aerospace and energy generation industries.

The success of nickel-based superalloy systems attributes to both the well-tailored microstructures with the assistance of carefully doped alloying elements, and the intently developed manufacturing processes. The microstructure of the modern nickel-based superalloys consists of a two-phase configuration: the intermetallic precipitates $(\text{Ni},\text{Co})_3(\text{Al},\text{Ti},\text{Ta})$ known as γ' phase dispersed into the austenite γ matrix, which is firstly introduced in the 1940s. The recently developed additive manufacturing (AM) techniques, acting as the disruptive manufacturing process, offers a new avenue for producing the nickel-based superalloy components with complicated geometries. However, γ' strengthened nickel-based superalloys always suffer from the micro-cracking during the AM process, which is barely eliminated by the process optimization.

On this basis, the new compositions of γ' strengthened nickel-based superalloy adapted to the AM process are of great interest and significance. This study sought to design novel γ' strengthened nickel-based superalloys readily for AM process with limited cracking susceptibility, based on the understanding of the cracking mechanisms. A two-parameter model is developed to predict the additive manufacturability for any given composition of a nickel-based superalloy. One materials index is derived from the comparison of the deformation-resistant capacity between dendritic and interdendritic regions, while another index is derived from the difference of heat resistant capacity of these two spaces. By plotting the additive manufacturability diagram, the superalloys family can be categorized into the easy-to-weld, fairly-weldable, and non-weldable regime with the good agreement of the existed knowledge. To design a novel superalloy, a Cr-Co-Mo-W-Al-Ti-Ta-Nb-Fe-Ni alloy family is proposed containing 921,600 composition recipes in total. Through the examination of additive manufacturability, undesired phase formation propensity, and the precipitation fraction, one composition of superalloy, MAD542, out of the 921,600 candidates is selected.

Validation of additive manufacturability of MAD542 is carried out by laser powder bed fusion (LPBF). By optimizing the LPBF process parameters, the crack-free MAD542 part is achieved. In addition, the MAD542 superalloy shows great resistance to the post-processing treatment-induced cracking. During the post-processing treatment, extensive annealing twins are promoted to achieve the recrystallization microstructure, ensuring the rapid reduction of stored energy. After ageing treatment, up to 60-65% volume fraction of γ' precipitates are developed, indicating the huge potential of γ' formation. Examined by the high-temperature slow strain rate tensile and constant loading creep testing, the MAD542 superalloy shows superior strength than the LPBF processed and hot isostatic pressed plus

heat-treated IN738LC superalloy. While the low ductility of MAD542 is existed, which is expected to be improved by modifying the post-processing treatment scenarios and by the adjusting building direction in the following stages of the Ph.D. research.

MAD542 superalloy so far shows both good additive manufacturability and mechanical potentials. Additionally, the results in this study will contribute to a novel paradigm for alloy design and encourage more γ' -strengthened nickel-based superalloys tailored for AM processes in the future.

Keywords: Nickel-based superalloy; Alloy design; Laser powder bed fusion; Cracking susceptibility; Additive manufacturability; Heat treatment; γ' precipitate; High-temperature mechanical property; Creep.

Populärvetenskaplig Sammanfattning

För tusentals år sedan började alkemister på olika kontinenter, som Europa, Asien och Afrika, att söka nya vägar att göra vissa material. På ett tidigt stadium var alkemins syften vanligtvis att göra ädla metaller av basmetaller eller att skapa odödlighetens elixir. Dessa mål låter främmande ur ett modernt vetenskapligt perspektiv, men alkemi har haft stor betydelse för mänsklighetens historiska utveckling. Alkemi, som en forntida gren av naturfilosofin, har som grundtanke att rätt kombination av basämnen skapar material med mer värdefulla egenskaper. Denna enkla men filosofiska inblick uppmuntrar metallurgister och materialtekniker att utveckla mer avancerade material som är fördelaktiga för mänskligheten.

När man tittar historiskt på den relativa betydelsen av tekniska materialen, som de fyra huvudkategorierna: metaller, polymerer, kompositer och keramer, ser man att metaller hade sin topp mellan 1920- och 1980-talet. Men från och med millennieskiftet saktar utvecklingen av nya metaller ner. Utöver utvecklingen av nya materialkompositioner fick andra aspekter som kvalitetskontroll och tillverkningsprocessutveckling stor betydelse. Nickelbaserade superlegeringar är inget undantag. Nickelbaserade superlegeringar är en grupp legeringar där nickel fungerar som baselement och som dopas med mer än 10 legeringselement. Den magiska kombinationen av dessa element i superlegeringar säkerställer dess framgångsrika applicering i kritiska heta komponenter vid en förhöjd temperatur som till och med är nära deras smältpunkter. Utvecklingen av nickelbaserade superlegeringar blomstrande under 1950-90-talet precis som andra metaller. Under de senaste två decennierna har den snabba utvecklingen av additiv tillverkning, även känt som 3D-printning, revolutionerat tillverkningstekniken för ett brett spektrum av metalliska material. Dessa material är attraktiva för denna nya teknik på grund av dess fördelaktiga möjlighet att minska materialavfall och tillhandahålla komponenter nära deras slutgiltiga form, vilket ofta inte är möjligt med konventionella tillverkningstekniker. Inte heller denna gång är nickelbaserade superlegeringar något undantag. Den stora utmaningen är emellertid sprickbenägenheten vid additiv tillverkning av partikelhårdade superlegeringar, vilket gör det utmanande att nå full täthet hos materialen på ett robust sätt.

Vid additiv tillverkning, till exempel vid lasersmältning i pulverbädd, en av de mest använda processerna, övergår den smälta metallen till fast form under 10^{-3} sekunder, vilket är två storleksordningar snabbare än en ögonblinkning. Denna extremt snabba kylhastighet ger utan tvekan problem vid tillverkning av höglegerade nickelbaserade superlegeringar. Sprickor börjar attackera de svaga punkterna i det stelnade bulkmaterial. Dessutom, trots den höga avkylningshastigheten, undertrycks inte segregeringar helt, varför koncentrationen av elementen periodiskt förhöjs eller reduceras över en längdskala på flera hundra nanometer, vilket motsvarar en hundradel av tvärsnittsdiаметern av ett människohår. I det här arbetet är den första uppgiften att identifiera dessa utsatta platser och deras kompositionssärdrag. Genom mikrostrukturundersökningar och beräkningsmetoder, för en given kemisk sammansättning, kan en legering delas in i två områden som innehåller olika element. För att få en legering lämpad för additiv tillverkning är huvudstrategin att förbättra sprickmotståndet i det svaga området. Inspirerad av detta kunde två dominerade aspekter formuleras: motståndet mot deformation och motståndet mot värme. Genom en jämförelse av skillnaderna mellan svaga och starka områden kan

legeringens lämplighet för additiv tillverkning kvalitativt illustreras, och detta överensstämmer väl med de existerande resultaten för olika superlegeringar.

Efter att ha fastställt det grundläggande urvalskriteriet för materialval tas en matris med nästan 1 miljon materialsammansättningar fram som täcker spännvidden för de huvudelement som vanligtvis används i superlegeringar. Att hitta den mest optimala legering bland en miljon kandidater är som att hitta en nål i en höstack. Förutom att väga in lämpligheten för additiv tillverkning, vilket är viktigast i denna studie, beaktas även andra faktorer, som fasstabilitet och fraktion av förstärkningspartiklar, för att filtrera bort olämpliga legeringar.

Till slut föreslås en slutgiltig legering. Förutom den teoretiska urvalsprocessen, valideras den föreslagna legeringen experimentellt. Genom en försöksmatris med olika processparametrar sorteras det lämpliga processfönstret för denna nya legering fram vilket kan tillhandahålla ett sprickfritt bulkmaterial. Därefter undersöks lämpliga värmebehandlingar för att skräddarsy mikrostrukturen hos materialet. Slutligen visar mekaniska tester vid förhöjda temperaturer att den nya legeringen har stor potential att utnyttjas vid temperaturer högre än 65% av dess smältpunkt.

Det är fascinerande att ta fram ett nytt material med förbättrade egenskaper genom en annan kombination av legeringselement. Kanske kommer den i detta arbete föreslagna nya legeringen inte att vara den mest enastående i superlegeringsfamiljen, men förhoppningsvis kommer den att bidra till en tydligare förståelse för förhållandet mellan additiv tillverkning och sprickbildning. Beskrivningen av den här nya legeringen kommer dock förhoppningsvis att bidra till utvecklingen av nickelbaserade superlegeringar optimerade för additiv tillverkning.

Popular Science Summary

Back thousands of years ago, alchemists in different continents, like in Europe, Asia, and Africa, started to practices demanding making certain materials. At the early stages, the common purposes of alchemy are to make noble metals from base metals or to create the elixir of immortality. These goals sound out of ordinary from a modern science perspective, while alchemy indeed made a great difference throughout the long path of human history. Alchemy, as an ancient branch of natural philosophy, generally holds the influential wisdom that the proper combination of base substances creates more valuable properties. This plain but philosophical insight keeps encouraging metallurgists and materials engineers to promote more advanced materials beneficial for humankind.

Looking at the relative importance evolution of engineering materials, like the four major categories: metals, polymers, composites, and ceramics, as the developing curves against time scale, among them, metals underwent the peaks between the 1920s and 1980s. However, starting with millenniums, the development of metal slows down. Beyond the new promotion of materials composition, other aspects like quality control and manufacturing process development overtook the account. Nickel-based superalloy is not an exception. Nickel-based superalloy is a group of alloys where nickel serves as the base element and doped with more than 10 alloying elements. The magical combination of these elements in superalloys ensures its successful application on the critical hot components at an elevated temperature which is even close to their melting points. The development of nickel-based superalloy had a flourishing history in the 1950s-1990s like other metals. In the past two decades, the rapidly developed additive manufacturing technology, also known as three-dimensional printing, enables this disruptive manufacturing manner for a wide range of metallic materials. These materials are open to embracing this new technology owing to its beneficial potentials for providing net-shape components which could not be achieved by the conventional ways, and the reduction of materials waste. This time, nickel-based superalloy is not an exception as well. However, the lied ahead challenge is the vulnerable crack resistance of particle enhanced superalloy during the additive manufacturing, resulting in it could barely be provided full dense part robustly.

During additive manufacturing, for example, laser powder bed fusion, one of the most used process, the melted liquid metal finishes the condensation to solid with 10^{-3} second, which is two orders of magnitudes faster than an eye blink. This extremely fast cooling rate undoubtedly brings troubles for fabricating the highly alloyed nickel-based superalloy. Cracks start attacking the weak places in the solidified bulk materials. Additionally, even under this magnitude of cooling rate, the element redistribution is not fully suppressed, thus, the concentration of elements is periodically enriched and poor across several hundred nanometers' scales, which corresponds to the length of 1 part per 100 of the cross-sectional diameters of human hair. In this work, the first urgent task is to isolate these vulnerable places according to their compositional features. By microstructural characterization and computational approaches, for given chemical composition, the alloy could be subdivided into two substances containing different elements. To make the alloy survive from the additive manufacturing induced cracking, the core strategy is to improve the crack resistance of weak points. Inspired by this, two dominated aspects could be formulated: the resistance to deformation and the resistance to heat. Comparing the differences between

weak and strong points, the alloy's additive manufacturability is then qualitatively illustrated, and it agrees well with the existed results from various superalloys.

After establishing the fundamental material selection criterion, a materials universe with almost 1 million recipes is built which covers the spans of major elements used in superalloy. To find a talented alloy among 1 million candidates is like to find a needle in a haystack. Besides the consideration of additive manufacturability, which is most important in this study, other factors, as well as the phase stability and strengthening particles fraction, are taken into account and used for filtering out those unsuitable alloys.

In the end, 1 alloy is finally proposed. Beyond fighting a war on paper, the proposed alloy is validated experimentally. By a group of additive manufacturing testing, the decent processing window for this new alloy is sorted out for providing the crack-free bulk material. Afterward, post-additive-manufacturing-processing treatments are investigated to tailor the microstructure. In addition, examined by high-temperature mechanical testing, this new alloy shows excellent potential on the service at a temperature higher than 65% of its melting temperature.

It is fascinating to bring up new material with improved properties by a different combination of elements. Perhaps this new alloy proposed in this work will not be the outstanding one among the superalloy family, but it hopefully will contribute to a clearer understanding of the relationship between additive manufacturing and cracking forming. The story of this new alloy hopefully will encourage more talented nickel-based superalloy for additive manufacturing.

Acknowledgements

This research is financially supported by the Swedish Governmental Agency for Innovation Systems (Sveriges innovationsmyndighet, Vinnova) MADAM project (grant 2018-00804), and the Vinnova Competence Center for Additive Manufacturing – metal (CAM²). I would like to acknowledge the organizations for providing me travel fund, that is Agora Materiae Graduate School for multidisciplinary PhD students at Linköping University, and Stiftelsen Axel Hultgren.

It has been a serendipitous story three years ago for me to decide to take the adventure here at Linköping University, Sweden. I am very grateful for everybody I met here, every minute I spent here, and every place I stepped here.

Foremost, I would like to thank my main supervisor, Johan Moverare, who offered me this opportunity to involve into this interesting PhD project. I appreciate the immense coaching and mentoring you gave me. I also appreciate your support of my self-development and decision-making. I would like to thank my co-supervisor, Ru Lin Peng, for your valuable remarks and helpful inputs. Thank you both my supervisors, and your contagious passion for science which always encourages me to explore deeper in this field.

Special gratitude goes to Dr. Hans Gruber, and Dr. Fiona Schulz from Chalmers University of Technology/CAM2, for printing my LPBF samples and for the close collaboration. I would like to appreciate my other project partners, Dr. H. Brodin from Siemens Energy AB, Dr. S. Bengtsson from Höganäs AB, K. Minet and A. Shaikh from EOS Finland Oy, Dr. A. Eklund and J. Gårdstam from Quintus Technologies AB, and Prof. E. Hryha from Chalmers University of Technology for the fruitful and helpful discussions on this project and the efforts on the new materials. I would like to thank Dr. V. Luzin from ANSTO, Australia for the neutron diffraction measurements.

I am very grateful to work with all my colleagues in the Division of Engineering Materials at Linköping University. Thank you all for creating this wonderful working environment. Thank you Ingmari, our administrator, for taking care of every detailed administration works excellently. Thank you, Rodger and Patrik, for your technical supports, without you my characterization and mechanical testing works could not be carried out that smoothly. I would like to thank you my fellow peers (and alumni), Dunyong, Pimin, Hank, Prabhat, and so on, I really enjoy the discussions and the ‘A-ha’ moments with you guys.

I would like to deeply thank my family and family in law for the kind support and understand of me. It has been ten years since I left my hometown, but the cherished personalities you taught me will influence my whole life no matter where I am. Thanks my friends for the enjoyable and relaxing moments and the attitudes that you pretend to not care about my works at all haha.

A huge acknowledgment and love express to my wife, Yao (瑶), for your support through the years. I could not forecast the future, and every decision we had made together brings me the best at this moment. See you and Feiji soon!

Linköping, December 2020

List of Publications

Publications appended in this thesis

Paper I

J. Xu, H. Gruber, D. Deng, R.L. Peng, J.J. Moverare, Short-term creep behavior of an additive manufactured non-weldable Nickel-base superalloy evaluated by slow strain rate testing, *Acta Mater.* 179 (2019) 142–157.

Contribution: Performed the microstructure and fractography characterizations, data analysis, mathematic formulating, and manuscript writing and revising.

Paper II

J. Xu, H. Gruber, R. Boyd, S. Jiang, R.L. Peng, J.J. Moverare, On the strengthening and embrittlement mechanisms of an additively manufactured Nickel-base superalloy, *Materialia*. 10 (2020) 100657.

Contribution: Performed the tensile testing, microstructure and fractography characterizations, data analysis, mathematic formulating, and manuscript writing and revising

Paper III

J. Xu, H. Gruber, R. Lin Peng, J. Moverare, A Novel γ' -Strengthened Nickel-Based Superalloy for Laser Powder Bed Fusion, *Materials (Basel)*. 13 (2020) 4930.

Contribution: Performed the microstructure characterizations, chemistry measurements, data analysis, manuscript writing and revising.

Manuscript IV

J. Xu, H. Brodin, R. L. Peng, V. Luzin, J. Moverare, Effect of heat treatment temperature on the microstructural evolution of CM247LC superalloy by laser powder bed fusion, In manuscript. (2020).

Contribution: Performed the microstructure characterizations, data analysis, mathematic formulating, and manuscript writing.

Summary of appended papers/manuscript:

In paper I and II, the studied materials were laser powder bed fused (LPBF) IN738LC superalloy. In paper I, the high-temperature short-term creep deformation mechanism of polycrystalline LPBF superalloy is discussed. Based on this, the understanding of grain boundary sliding as the controlling aspect that dominates the creep deformation is established. In paper II, the strengthening and embrittlement mechanisms of LPBF IN738LC superalloy are discussed for both as-built and post-processing treated states. In paper III, the

composition, LPBF window, microstructure of the newly design MAD542 superalloy firstly reported. In manuscript IV, by investigating the microstructural evolution of LPBF CM247LC superalloy during post-treatments, the mechanism of sluggish grain boundary migration was discussed.

The whole picture of this project includes alloy design, microstructural, and mechanical property validation. Even though the above-listed papers/manuscript investigated different LPBF nickel-based superalloys, the knowledge and understanding generated from them did help on this project from different perspectives.

Publications not included in this thesis

Paper V

H. Wärner, J. Xu, G. Chai, J. Moverare, M. Calmunger, Microstructural evolution during high temperature dwell-fatigue of austenitic stainless steels, Int. J. Fatigue. (2020) 105990.

Contribution: Operated the transmission electron microscopy characterizations.

Paper VI

L. Cui, S. Jiang, J. Xu, R. Peng, R. Mousavian, J. Moverare, Revealing relationships between microstructure and hardening nature of additively manufactured 316L stainless steel, Mater. Des. 198 (2021).

Contribution: Operated the transmission electron microscopy characterizations.

List of Abbreviations

AC	Air Cooling
AM	Additive Manufacturing
AMSE	American Society of Mechanical Engineering
BC	Band Contrast
BCT	Body-Centered Tetragonal
BD	Building Direction
BSE	Backscattered Electron
BTR	Brittle Temperature Range
DC	Dendrite Core
DDC	Ductility-Dig Cracking
DF	Dark-Field
DMLM	Direct Metal Laser Melting
DMLS	Direct Metal Laser Sintering
DoE	Design of Experiment
DS	Directional Solidification
EBM	Electron Beam Melting
EB-PBF	Electron Beam Powder Bed Fusion
EBSD	Electron Backscatter Diffraction
EDS	Energy Dispersive X-ray Spectroscopy
FCC	Face-Centered Cubic
FCC	Furnace Cooling
FE-SEM	Field Emission Scanning Electron Microscope
GB	Grain Boundary
GOS	Grain Orientation Spread
HAADF	High-Angle Annular Dark-Field
HAGB	High-Angle Grain Boundary
HCS	Hot Cracking Sensitivity
HIP	Hot Isostatic Pressing
HRTEM	High-Resolution Transmission Electron Microscopy
HT	Heat Treatment
I.D.	Identity
ID	Interdendrite
IPF	Inverse Pole Figure
LBW	Laser Beam Welding

LMF	Laser Metal Fusion
LMP	Larson Miller Parameter
LPBF	Laser Powder Bed Fusion
NIMS	National Institute for Materials Science
OM	Optical Microscopy
PDAS	Primary Dendrite Arm Spacing
PHACOMP	PHase COMPutation
PM	Powder Metallurgy
PMZ	Partially Melted Zone
PPM	Parts Per Million
RS	Residual Stress
RX	Recrystallization
SAC	Strain-Age Cracking
SE	Secondary Electron
SEBM	Selective Electron Beam Melting
SGB	Solidification Grain Boundary
SLM	Selective Laser Melting
SSRT	Slow Strain Rate Tensile
SSS	Solid Solution Strengthening
STEM	Scanning Transmission Electron Microscopy
TB	Twin Boundary
TCP	Topologically Close-Packed
TEM	Transmission Electron Microscopy
TGM	Temperature Gradient Mechanism
TSR	Thermal Shock Resistance
XRD	X-Ray Diffraction

Nomenclature

ΔT_b	Undercooling to approaching coalescence
$\Delta \Gamma_b$	Energy difference of liquid/solid and grain boundary interfaces
δ	Thickness of an isolated solid-liquid interface
ΔS_f	Entropy of fusion
γ_{gb}	Grain boundary energy
γ_{sl}	Solid/liquid interfacial energy
τ_{Oro}	Orowan shear stress
τ_{Cut}	Shear stress required for dislocation cutting
G	Shear modulus
b	Magnitude of Burger's vector
$L_{\gamma'-\gamma'}$	Spacing between γ' particles
$d_{\gamma'}$	Average size of precipitates
γ_{APB}	Anti-phase boundary energy
$d\gamma$	Unit shear strain
ρ	Dislocation density
l	Average length of dislocation
$\alpha_{Tay.}$	Materials constant for Taylor's strengthening
M	Taylor's factor
M_{creep}	Merit index for creep resistance
x_i	Atomic fraction of solute i
$\tilde{D}_i$	Appropriate interdiffusion coefficient
T	Absolute temperature in Kelvin
c_{LM}	Larson-Miller constant
t	Time
χ	Crack susceptibility index
σ_{UTS}	Ultimate tensile strength
σ_T	Thermal stress
E	Young's modulus
α_{CTE}	Coefficient of thermal expansion
ΔT	Temperature difference
ν	Poisson's ratio
σ_0	Lattice stress
σ_{YS}	Yield strength
k_d	Hall-Petch coefficient

σ_{ss}	Solid solution strength
σ_p	Peierls stress
d	Average grain size
C_s^*	Solid composition at the solid/liquid interface
k	Equilibrium distribution coefficient
C_0	Nominal composition
α	Fourier number
f_s	Fraction solid
D_s	Diffusivity of solute in the solid
t_f	Local solidification time
λ_1	Primary dendrite arm spacing
μ	Dendrite arm spacing constant
V	Solidification velocity
G_T	Thermal gradient
k^i	Equilibrium distribution coefficient of solute i
C_0^i	wt. % of i th element in the nominal composition
C_s^i	wt. % of i th element in the solid phase
f_{DC}	Volume fraction of the dendrite core
f_{ID}	Volume fraction of the interdendrite
C_{DC}^i	wt. % of i th element in the dendritic core region
C_{ID}^i	wt. % of i th element in the interdendrite region
$\Delta\sigma_y$	Difference of yield limit
$\sigma_{y,ID}$	Yield strength of interdendrite
$\sigma_{y,DC}$	Yield strength of dendrite core
σ_{GB}	Grain boundary strengthening
$\sigma_{\gamma'}$	γ' precipitation strengthening
$\sigma_{Dis.}$	Dislocation strengthening
d_c	Size of cellular structure
$\sigma(P)$	LPBF parameter dependent strength
C	Process constant
χ_{ID}^i	Atomic fraction of i th solute at the interdendrite
χ_{DC}^i	Atomic fraction of i th solute at the dendrite core
$d\sigma/\sqrt{d\chi^i}$	Strengthening coefficient for i th solute
ΔT_m	Difference of melting temperature
T_m^i	Melting point of the i th element
$\overline{Md}$	Average d orbital energy
$(Md)_i$	The d orbital energy value of i th elements
E_V	Energy density of laser powder bed fusion

P	Laser power
V_s	Scan speed
H	Hatching distance
L	Layer thickness

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1 General introduction

This thesis book for licentiate of engineering degree (Tekniska Licentiat) includes the research results by the author Jinghao Xu for his PhD study since September of 2018 at the Division of Engineering Materials in Linköping University.

1.1 Research background

Precipitation strengthened nickel-based superalloys have been developed for several decades for engine usage in critical hot section components, owing to its outstanding mechanical properties, oxidation resistance, and phase stability at elevated temperatures. In contrast to conventional manufacturing methods, based on incremental layer-by-layer manufacturing, additive manufacturing (AM) provides advantages and opportunities to fabricate the component with a complicated structure. More specifically, the air-cooling channel in the turbine blade could be optimized using AM methods. Until recently, the major interests for the AM community have been on commercial superalloys, such as Inconel 718, Inconel 625, and Hastelloy X, since they can be additively manufactured with a few critical defects successfully.

Owing to the excellent high-temperature chemical and mechanical properties of γ' -strengthened superalloys, the fabrication of them by the AM process has always been a great vision of the AM community. However, because of their high crack susceptibility during the AM- and/or the post-processing, the AM-processing of γ' -strengthened superalloys still remains a great challenge. The solid relationship between the composition-related materials index and the additive manufacturability is urgently demanded. Based on the established additive manufacturability diagram in this work, a novel alloy composition, MAD542, is proposed from 921,600 candidates with the consideration of suppressing the formation of undesired phases and optimizing the volume fraction of γ' precipitates as well. The AM processing window, microstructures, and high-temperature mechanical property of this new superalloy are examined experimentally, indicating that the MAD542 superalloy shows good AM cracking resistance, post-processing heat treatability, the higher amount of γ' phase with greater than 60% volume fraction, and appreciate creep resistance.

1.2 Research objectives

In this PhD research project, a novel γ' strengthened nickel-based superalloy for the LPBF process with good creep performance will be designed. The primary objectives of this work are:

1. To propose a new alloy design criterion regarding the manufacturability of nickel-based superalloys by additive manufacturing. (In chapter 4)
2. To design a novel composition of a γ' strengthened nickel-based superalloy which could be adapted to the LPBF process with good metallurgical quality and limited in-process defects. (In chapter 4 and 5)
3. To examine the microstructures and creep properties of the new nickel-based superalloy. (In chapter 5 and 6)

2 Literature review

2.1 Laser powder bed fusion (LPBF): a metallic additive manufacturing technique

According to the standard of the International Organization for Standardization (ISO) / ASTM [1], 7 processes are included in the additive manufacturing categories: binder jetting; directed energy deposition; material extrusion; material jetting; powder bed fusion; sheet lamination; vat photopolymerization. By applying these AM techniques, the most commonly used materials are plastics, metallic, organic, and ceramics [2]. LPBF is one of the important subcategories of powder bed fusion, which manufactures metallic materials. There are several more terminologies with different naming systems, mostly according to the trademark of the manufacturers of the printing systems, referring the similar process, for example, selective laser melting (SLM) [3], direct metal laser sintering (DMLS) [4], laserCUSING [5], laser metal fusion (LMF) [6], direct metal laser melting (DMLM) [7]. In LPBF, the laser beam is the energy source for melting the powder bed. Another popular powder bed fusion process is electron beam powder bed fusion (EB-PBF), also known as electron beam melting (EBM) [8], which has an electron beam as the energy source.

2.1.1 LPBF process

Fig. 2.1. Schematic illustration of the LPBF system.

As mentioned above, although the LPBF has been given various names, the key features of the LPBF process are the same: the laser beam as the thermal source for melting the powders, and the powder bed. As the schematic illustration shows in Fig. 2.1., besides the powder-bed chamber, there is also a dispenser bin that serves as the reservoir of powders.

Besides the very necessary laser beam source and the powder bed, other important parts in the LPBF system helps to conduct the build. The LPBF starts with the distribution of powders on the build platform which supports the powder bed and the built parts. After

selective laser fusion of each layer, the build platform moves down for filling another layer of powders. The selective fusion here indicates that only part of the powder bed is fused. Then, the recoater blade is moving back and forth from the dispenser bin to the powder bed to spread a new layer of powders on the top of the melted/fused one.

The typical size of powders for LPBF is between 20-50 μm . To build the component, pre-alloyed powders, with the alloying elements doped before the powder supply, are generally used. Thanks to the mechanical movement of scanning mirrors, the build speed of LPBF could be increased. Besides, different scanning strategies could be achieved, which severely influence the process defects, microstructure, crystallographic anisotropic behavior, surface roughness, and residual stresses [9]. To control the oxidation of the material, the LPBF process is commonly conducted under a protective atmosphere with inert gas [10], such as N_2 , Ar, and even He (Helium) [11].

2.1.2 LPBF application

The application of LPBF-processed components is heavily dependent on the materials being printed and its potential application condition. As the focus of this work is the nickel-based superalloy, this alloy is designed to withstand the harsh service environment at high-temperature. Obviously, more design flexibility of the components subjected to the high temperature is of great importance, for example, a more advanced internal cooling system of the gas turbine parts helps to reduce the combustion emission. In this sense, the LPBF processed nickel-based superalloy undoubtedly could be useful. The General Electric Company gets the patent, regarding the fuel nozzle part processed with a batch of AM techniques including LPBF for a gas turbine engine, filed in March 2015 [12]. In 2017, the American Society of Mechanical Engineering (AMSE) awarded SIEMENS for its achievement on the first successfully 3D-Printed gas turbine blades, which are tested in a demanding working temperature higher than 1250 $^{\circ}\text{C}$ [13].

2.2 Post-AM-processing treatments

The post-AM-processing treatments here indicate the treatments which are necessarily applied after the printing of the part. In this section, two important post-AM-processing treatments are discussed, which significantly influence the printed part in the micro-to-macro scale.

2.2.1 Hot Isostatic Pressing

Hot isostatic pressing (HIP), as a primary materials shaping process, has been developed before the 1960s [14]. The material subjected to the HIP simultaneously undergoes both high temperatures and high isostatic pressures. What distinguishes the HIP process from other materials manufacturing processes is the applying of inert gas as the pressure-transmitting medium to implement the three-dimensional equivalent changes. Therefore, near-net-shape components are commonly supplied by HIP.

Typically, two kinds of materials are used for HIP, the powders, or the pre-shaped part. Powder metallurgical turbine discs made from nickel-based superalloys is one of the most important cases for the implementation of the HIP. To manufacture the powder metallurgical part by HIP, pre-alloyed powders which are sealed in the can condensate

under the high temperature/pressure. After HIP, other thermomechanical processing including hot extrusion, isothermal forging may be applied for the near-net-shape turbine disc fabrication. Additionally, HIP is also heavily used for healing the defects in Ti alloys and superalloys castings before the service. The HIP is also used for the rejuvenation of the retired components. During the HIP process which couples both high temperature and pressure, the microstructure of nickel-based superalloy evolves and localized chemistry changes. After HIP, the degraded microstructure served in long-term rejuvenates owing to the homogenization of dendrite microstructure [15]. It demonstrated that rejuvenating effects introduced by HIP not only heal the defects but also reset dislocation densities, then further improve the creep resistance of a deformed superalloy [16].

The as-AM-processed parts usually uncertainly contain internal defects, HIP unsurprisingly acts as a necessary procedure to provide the parts of higher quality. For γ' strengthened nickel-based superalloys, HIP effectively acts as the approach in healing the in process-induced cracks [17]. The HIP pressure is normally in between 1000-2000 bar (100-200 MPa), while the HIP temperature varies according to mainly the γ' solvus temperature. By applying the super-solvus temperature, creep occurs in the material under the single austenite condition. Generally, plastic flow also happens since the HIP pressure exceeds the yield strength at the HIP temperature. Although the super-solvus HIP shows excellent crack-healing coupled with recrystallization which reduced the general crystallographic anisotropy, the expense is that the grains extensively grow. To maintain the fine grain structure, HIP could be conducted at the sub-solvus temperature, in which the γ' would not fully be dissolved and then pin the grain boundary (GB) migration and prevent the dramatic grain growth [18]. By the combination of both high temperature and HIP pressure, the cracks could be highly healed. According to the pioneering research by Carter et al. [19], the internal cracks of LPBF processed CM247LC superalloy are effectively healed by HIP, while the surface-connected cracks remain.

2.2.2 Heat treatment

What made the HIP as one of the post-AM-process routes of γ' strengthened nickel-based superalloys is the 'difficult-to-weld' feature of them, and thus the demand for crack healing. For those nickel-base superalloys with good additive manufacturability, the HIP is not always necessary.

Heat treatment (HT) is a significant process that tunes the chemistry composition distribution and tailors the microstructure. Commonly, there are primarily two-fold purposes for conducting HT in γ' strengthened nickel-based superalloys: 1) to achieve chemistry homogenization and promote precipitates, which will be described as solutioning treatment in this work; 2) to further adjust the morphology and more important the volume fraction of γ' phase, which will be described as an ageing treatment in this work. The solutioning treatment is conducted at a higher temperature than ageing treatment.

For the AM processed γ' strengthened nickel-based superalloy, the HT scenario is different from the conventionally manufactured counterparts, because the initial microstructural is very different. Firstly, owing to the high cooling rate of the AM process, the solidification dendrite arm spacing in the as-built state is restrained into sub-micron size for LPBF, and several micrometers for EB-PBF. For the highly alloyed material systems such as a nickel-based superalloy with refractory elements addition, the solutioning treatment is challenging. For example, the solutioning treatment of single crystal superalloy involves

several steps of dwell of temperature and precisely designed heating scenarios [20,21], in order to, on the one hand, dissolve the γ/γ' eutectic region and accelerate the chemical homogenization, and on the other hand, avoid the occurring of incipient melting at the lower solidus region caused by the elemental segregation.

However, the fine dendrites could be taken as an advantage for the solutioning treatment. By Ramsperger et al. [22], the solutioning treatment of EB-PBF processed CMSX-4 superalloy becomes much easier comparing with the casting counterpart. First, no special heating ramps are required, and incipient melting would not appear. Second, the complete chemical homogenization could be achieved by just a few minutes which requires several hours for cast CMSX-4. Both the conveniences could be attributed to the two orders magnitude finer dendritic structure in the EB-PBF alloy, indicating that the elemental segregation is not severe dimensionally and only constrained into the micrometer scale [23]. The shorter dendrite arm spacing also reduced the diffusion distance for the elements. Secondly, in particular to the LPBF processed γ' nickel-based superalloy, the single FCC austenite phase configuration is generally obtained, which sets a huge difference to the conventionally manufactured ones. For example, in the as-LPBF-built IN738LC superalloy, which displays 43 vol. % γ' phase [24] after solution treatment, γ' is barely observed [25]. Moreover, for higher γ' contained superalloy, e.g. CM247LC (γ' vol. % up to 65% [26]), shows only 1.5 vol. % γ' phase in the as-built condition which could be confirmed by atomic resolution micrographs via high-resolution transmission electron microscopy (HRTEM) in nanoscale [27]. On this basis, the fine dendrite and nearly FCC single-phase configuration offer the heat treatment of LPBF processed γ' superalloys more possibilities.

2.3 Problem characteristics in the LPBF process

Several significant features of the LPBF process are considered as problem characteristics, which either reduce the component integrity or damage the mechanical performance.

2.3.1 Residual stresses

Residual stresses (RS) are the stresses that remain inside a solid material where no external stresses being applied. The AM parts are considered as vulnerable to RS generally owing to its extremely high-temperature gradient during printing, which leads to the detrimental effect of the component integrity via geometrical distortions or cracking [28].

According to different scales of RS, they are generally classified into three types: 1) Type I RS, which vary across over large distance in macro size, namely, the type I RS occur at the size that is comparable to the dimensions of the material part; 2) Type II RS, which is restricted into the micro size, involving with the differently oriented grains or different phases within the material; 3) Type III RS, which is related with defects at the atomic size, such as the dislocation lines. Commonly, type II and type III are named as the micro-stress [29]. In the AM processed part, the type I RS plays a significant role in controlling the component integrity. To explain the generalization of the type I RS in a selectively laser melting component, Mercelis and Kruth [30] proposed the temperature gradient mechanism (TGM). Owing to the rapid heating of the upper surface plus the slow heat conduction, a steep temperature gradient close to the laser beam region is obtained. The strength of the material decreases with the increasing temperature, indicating the possibility of plastic

deformation if the RS exceeds the yield strength at the 'hot' area. To separate the laser process into heating and cooling phases, compressive and tensile RS are developed. During heating, the lower-temperature underlying material constricts the expansion of heated top layer, introducing the compressive strain. While during cooling, the underlying material constricts the shrinkage of the top layer, where the tensile strain occurs.

2.3.2 Porosity

Porosity is a pore-like defect within the volume of the material and is commonly observed in AM processed parts. The remaining porosities in the AM parts are detrimental to the mechanical properties, acting as the potential crack initiation sites, which may lead to premature failure [31].

The porosity could be sub-categorized into the metallurgical pores and the keyhole pores. It is generally accepted that the origin of the metallurgical pores comes from the aggregation of entrapped gases [32]. While the keyhole pores are related to the insufficient melt overlapping. Xiao et al. [33] attributed the keyhole pores to the incomplete filling of the gaps with the molten materials, which apparently associated with the print parameters, due to the rapid solidification process. Additionally, the lack of fusion comes not only from the un-robust printing process but also from the nature of printed materials. For example, the LPBF Al alloys are susceptible to the keyhole pores because the good affinity between the Al and the oxygen in the build chamber. The formed oxide potentially acts as the initial site for keyhole pores [34]. Regarding the size and morphology of porosity, the metallurgical pores usually appear like spherical shape with the diameter generally less than 100 μm , while the keyhole-like pores look more irregular and commonly have a size greater than 100 μm .

In the LPBF of nickel-based superalloy, the keyhole-like porosity seems not a severe issue. In the early study (the year of 2013) of LPBF of IN738LC superalloy by Rickenbacher et al. [35], by optimizing the printing process parameters, this kind of porosity could be dramatically reduced from over 50% to less than 0.5%.

2.3.3 Process induced cracking

The cracks introduced during the AM process is one of the most challenging issues hindering the further development of the advanced alloy systems, like high-strength aluminum alloys and γ' strengthened nickel-based superalloy.

2.3.3.1 Solidification cracking

From powders to bulk materials, solidification acts as an important part of the AM process. Solidification cracking, also known as hot tearing or hot cracking, appears during the solidification process [36]. Its mechanisms have attracted extensive research in the field of casting and welding [37,38]. Specifically, in the AM process, the solidification cracking emerges in the melt pool, where it represents the formation of irreversible failure in a partly solid state.

Generally, the mechanism of solidification cracking can be considered as the combination of impeded compensation by liquid flow with thermal stresses during the solidification shrinkage [36]. Solidification cracking comprises two main processes, cracking initiation, and propagation, like any other cracking mechanisms. It can be summarized from many research [39,40] that the solidification cracking initiate above the solidus temperature

and then propagate along with the interdendritic liquid film, where the liquid phase has barely any stress bearing capacity. In the semisolid mushy zone, insufficient liquid flow compensates for the solidification shrinkage where cavities of pores are prone to form [41]. Then cracks can initiate on these defects. In addition, the solidification process causes strong thermal gradients which leads to thermal contraction, promoting the condition for solidification crack propagation. Pellini [42] proposed 'Strain Theory' to describe the crack occurrence, thus interdendritic liquid film barely bears the strain exceeded the critical value.

As abovementioned, the mushy zone serves as the critical microstructure for the solidification cracking susceptibility. However, it may be a misunderstanding regarding the slurry and mush, where both zones are in a semisolid mixture state. The difference is that the newly formed grains freely suspended in liquid flow in the slurry zone but interact and tangle with each other in the mushy zone. In several models [42,43] refer that the extended mushy zone will suffer more solidification shrinkage strain and be more susceptible to solidification crack initiation. On this basis, on the thermodynamic consideration, it is worth noting that, the solidification range, can be referred to as a brittle temperature range (BTR), which plays a significant part in solidification cracking susceptibility. BTR can be defined as the difference value between liquidus and solidus temperature [44]. Flemings [45] concluded that a narrow solidification range leads to solidification as a nearly uniform mush, which results in only very small differences in the fraction of solid. The two-phase mushy zone can be estimated as the solidification temperature divided by the thermal gradient [45]. Shankar [46] reported that crack density increased from 0.1 mm/mm² to 1.1 mm/mm² with the brittle temperature range increasing from 21 °C to 68 °C for 304L-B and 304L-A stainless steel, respectively.

It can be concluded that to reduce the size of the mushy zone, one way is to decrease the solidification range, which means to decrease the temperature difference between liquidus to solidus. However, for most non-equilibrium solidification, the solidus temperature depends on the eutectic phase with a low melting point. Segregation of impurity elements lower solidus temperature by forming eutectic phases, which is deleterious to solidification cracking resistance [47]. Such as sulfur in steel drastically lower the solidus from 1365 °C to 988 °C [48,49] as the formation of low melting Fe-S eutectic films along the interdendritic and grain-boundary regions [50]. Another important approach for the reduction of the mushy zone is to increase the thermal gradient. Goodwin suggested [47] that increasing heat input (low thermal gradient) increases the susceptibility of cracking in the welding of 316 stainless steel.

Talking about the solidification cracking, it is inevitably worth mentioning the theoretical model developed by Michel Rappaz, who correlates the solidification microstructure with the grain structure. At the end of solidification, grain boundary has a large influence on the solidification cracking susceptibility. Grain boundary coalescence improves the intergranular strength of solidifying dendritic structure to resist solidification crack [51]. Rappaz [52,53] supposed that planar liquid/solid interface coalescence to a grain boundary can be described by the following equation.

$$\Delta T_b = \frac{\Delta \Gamma_b}{\delta} = \frac{\gamma_{gb} - 2\gamma_{sl}}{\Delta s_f} \frac{1}{\delta} \quad (2.1)$$

Where ΔT_b is an undercooling to approaching coalescence, $\Delta \Gamma_b$ is the difference between the two energies, δ is the thickness of an isolated solid-liquid interface, Δs_f is the entropy of fusion. It is worth to be noted that coalescence mainly is determined by the difference between grain boundary energy, γ_{gb} and twice the solid/liquid interfacial energy,

$2\gamma_{sl}$. Thus, the 'attractive' and 'repulsive' behavior of boundaries rely on a different value. When $\gamma_{gb} - 2\gamma_{sl} < 0$, the liquid film is unstable and serves as a bridge between dendrite arms. In this case, poor wetting occurs, the bridging droplets resist strain, thus decrease crack susceptibility. It is supported by experimental evidence in Borland's [54] research on Al-alloy, poor wetting features with larger dihedral angle were found to be more weldable. If $\gamma_{gb} - 2\gamma_{sl} = 0$, it refers to 'neutral' state, which means coalescence occurs with no extra undercooling. However, when $\gamma_{gb} - 2\gamma_{sl} > 0$, it means liquid film remains stable at lower temperature until the undercooling exceeds the corresponding critical value. The interfaces are 'repulsive'.

According to the last stage solidification process, some alloying elements contribute to a deleterious effect on hot cracking of nickel-based superalloys, such as Zr and B, even in a very small amount. Two factors of the active detrimental elements can be summarized, the strong segregation tendency to grain boundaries [55] and the lowering of solid/liquid interface energy [56]. As supported by Grodzki [51], solidification crack susceptibility decrease with Zr content decreasing from 0.09 wt. % to 0 in Nickel-based superalloy. Heydari [57] reported a similar tendency and explained that Zr segregates at grain boundaries to form a eutectic phase in the IN738LC superalloy. With the help of atom probe tomography, Cadel [58] suggested that grain boundaries act as preferential sites for the precipitation of bodies.

2.3.3.2 Liquation cracking

Layer by layer additive manufacturing brings the intrinsic re-heating to the layers beneath the melt pool. Different from solidification cracking occurrence in the fusion zone, liquation cracking occurs at a partially melted zone (PMZ) where the sites are a bit away from the melt pool [59]. From the crack morphology perspective, liquation cracking shows intergranular features but does not reveal any dendritic morphology [60]. Typically, liquation cracks are small in length, ranging from crossing several grains to a few millimeters long.

The formation of liquation cracks is considered as the semi-continuous liquid film along grain boundaries in PMZ that cannot hold the tensile stresses induced by thermal gradient [61]. The re-heating temperature in PMZ is lower than the solidus temperature. However, as discussed before, some low melting eutectic phases remain in the solid matrix and can be melted at temperatures below the solidus. However, it is worth highlighting here that at least in LPBF of γ' containing nickel-based superalloy, the γ/γ' eutectic constitute is hardly found in the as-built condition.

In the superalloy IN718, Nb and Ti residually segregate at interdendritic regions to promote a greater quantity of low-melting liquid [62]. When the re-heating temperature reaches the eutectic temperature, liquation initiates by the eutectic reaction. The formation of liquation in PMZ is crucial to promote a liquation crack. Besides the low-melting eutectic remelted again, Pepe and Savage [63,64] proposed the well-known constitutional liquation. In Nickel-based superalloy Udimet 700, Waspaloy, Hastelloy X, and IN718, the formation of constitutional liquation can interact with particles of carbide or other intermetallic compounds and the matrix from the reference [63,65–69]. In nickel-based superalloy with a high volume fraction of γ' precipitates, constitutional liquation could be a well-contributing factor to liquation cracking. It has been reported that superalloy IN738 cracked on PMZ grain boundary along resolidified γ/γ' eutectic constituent from liquated γ' phase [70]. Furthermore, Shahsavari [71] provided microstructural evidence using XRD mapping to

confirm that the liquid film formed from constitutional liquation causes liquation cracking in superalloy Rene80 weldments.

Microsegregation results in the formation of secondary solidification constituents, such as carbides, γ/γ' eutectic, borides, and other intermetallic compounds in interdendritic regions during the welding process of IN738 [72]. Ojo [73] suggested that active boron atoms increase wetting behavior which reduces the liquation cracking resistance in commercial nickel-based superalloy IN738. As reported in Qian's research [74], the increased liquation cracking susceptibility of IN718 can be considered as δ phase dissolution-promoted liquation, boron carbide constitutional liquation, and grain boundary segregation.

Only constitutional liquation can barely penetrate most grain boundaries in the PMZ. Coupled with grain boundary migration, liquation cracking is highly promoted. Liquation cracking occurs with the simultaneous occurrence of constitutional liquation and GB migration. The moving grain boundaries intersect with constitutional liquation, which means liquid penetrates these grain boundaries. Grains growth occurs under high temperature and sufficient solute-rich liquid entrap the grain boundaries to form grain boundaries films [63]. This phenomenon could be supported in a nickel-based superalloy 690 weldments [75].

In some other engineering alloy systems, the weldability of aluminum alloys remains a difficult problem as well. Kou [76–78] summarizes the liquation cracking mechanism as (i) wide PMZ due to wide solidification temperature range and high thermal conductivity, (ii) larger solidification shrinkage due to difference between solid/liquid density, and (iii) large thermal contraction caused by large thermal expansion coefficient.

2.3.4 Anisotropic behavior

From the crystal growth perspective, owing to the strong heat dissipation during the AM process, the preferred grain growth direction is parallel to the solidification direction. As a result, the columnar grains are usually found in the LPBF alloys. By adjusting the printing strategy, different types of crystallographic textures could be developed. For example, the unidirectional long scans generally lead to the $\langle 011 \rangle$ dominated grain orientation parallel to the building direction [79,80], while rotated non-directional scans result in the $\langle 001 \rangle$ texture [81]. The texture attributes strongly to the anisotropic mechanical properties. The most significant comparison of anisotropic behaviors could be discovered in the horizontally and vertically built samples. For example, as reported by Yu et al. [82], the horizontally built LPBF Hastelloy X superalloy shows slightly higher yield strength than the vertically built parts while the elongation is highly reduced under tensile testing at 700 °C.

2.4 Problem characteristics in post-process treatment

Post-LPBF-process treatments play an important role in tailoring the properties of the materials. However, several problematic phenomena are worth noting.

2.4.1 Sluggish recrystallization

The sluggish recrystallization behavior of LPBF superalloys in this work is defined as the as-built material that is difficult to recrystallize during the post-processing thermal treatment. Generally, the static recrystallization temperature of the nickel-base superalloy

is in the range of 1000-1100 °C and under this temperature range, recrystallization will gradually take place [83]. However, according to extensive investigations, for example, Kunze et al. [25] reported that the as-laser deposited IN738LC superalloy retains the strong cubic texture although it went through a super-solvus hot isostatic pressing (HIP) at 1180 °C for 4 h. Similarly, in the previous study on LPBF IN738LC superalloy [84], a combination of thermal treatments including 1210 °C HIP for 4 h plus 2-h solutioning at 1120 °C and 24-h aging at 850 °C failed to bring a fully recrystallized microstructure. Moreover, to eliminate the crystallographic texture induced by LPBF in IN738LC, Geiger et al. [85] applied a full heat treatment including a super-solvus heat treatment at 1250 °C for 3 h followed by a 1200 °C HIP for 4 h, and 1120 °C solution treatment for 2 h, and a 20 h aging at 850 °C. In the report by Messé et al. [86], the recrystallization of LPBF IN738LC occurs at around 60 °C above the γ' solvus with a narrow recovery to recrystallization transition temperature window around 10 °C. Conversely, in the conventionally processed γ' strengthened nickel-base superalloy, Dahlén et al. [87] reported that at a sub- γ' -solvus temperature of 1120 °C (45 °C below the γ' solvus (~ 1165 °C)), the cold deformed IN738LC gradually recrystallized and $\sim 80\%$ recrystallization and full recrystallization were achieved after 2 h and 4 h, respectively. Another commonly printed non-weldable nickel-base superalloy CM247LC exhibits a narrow gap of recovery to recrystallization transition temperature as well. According to Muñoz-Moreno et al. [88], the as-built CM247LC superalloy keeps the strong (001) fiber texture after 2-hour heat treatment at 1230 °C, however after treatment at 10 °C higher (1240 °C for 2 h) the recrystallization occurred extensively and reduced the crystallographic anisotropy, at a mesoscale across the investigated sample.

The challenging part of the sluggish recrystallization of LPBF nickel-based superalloy is the lack of driving force for grain boundary migration plus, maybe, more importantly, the dominating dragging force from the compositional gradient across the dendrite/interdendritic regions which is trapping the grain boundary. The discussion of the sluggish recrystallization is available in the appended manuscript IV, where the solid microstructural evidence and careful mathematic validation are included. Interestingly, a recently published paper [89] on LPBF 316L stainless steel found that the grain boundary migration is less influenced in the sparser solute-segregation network region, which supports the interdendritic trapping effect on the recrystallization process.

2.4.2 Post-process treatment induced cracking

Besides the cracking induced during the LPBF process, i.e., solidification and liquation cracking. The γ' strengthened nickel-based superalloys show high crack susceptibility for cracking during the post-processing treatment as well.

2.4.2.1 Strain-age cracking

During the post-processing thermal treatment, in particular at the ageing temperature, the formation of precipitates reduces the ductility of the material. In the γ' strengthened nickel-based superalloys, the precipitation of the intermetallic γ' phase, on one hand, strengthens the materials, while on the other hand, decreases the ductility. As a consequence, the un-released RS plus the precipitation stress could induce the strain-age cracking (SAC) when the strain exceeds the ductility limit [90]. Partly owing to this critical problem, the AM processing of γ' strengthened nickel-based superalloys remains a big challenge.

2.4.2.2 Ductility-dip cracking

In the γ' strengthened nickel-based superalloys, a certain temperature range, generally intermediate temperatures such as 700 to 900 °C as reported by Kim et al. [91], is critical because the ductility is highly reduced (ductility dip). For example, in the Monel K-500 superalloy, the ductility is largely reduced from higher than 20% elongation at 300 °C to around 2% elongation at 650 °C [92]. The ductility-dip cracking (DDC) is supposed to be generated during the AM fabrication process [19], and provide intergranular cracking features [93]. Similar to the SAC, DDC would occur once the material is undergoing this low-ductility region with high enough strain applied [94].

2.5 History and development of nickel-based superalloys

2.5.1 Development of alloy composition

The terminology 'superalloy' was introduced in the 1950s, for describing alloys with both good high-temperature mechanical and chemical properties [95]. Comparing with the other nomenclatures, like 'heat resisting alloys' or 'high-temperature alloys', the meaning of 'superalloy' seems to be rather obscure. In Tien and Caulfield's textbook [96], they attribute to the usage of the term 'superalloy' as influenced by the popular fictional character, superman, which makes the word 'super' a popular descriptor. At the earlier stage before the superalloy being accepted as the name 'superalloy', the superalloy-like high-temperature alloys already are adapted for providing the high-temperature component. For example, in 1905, Marsh [97,98] developed the Nichrome alloy comprising 80% of nickel and 20% of chromium as the material for producing turbine blades. In the year of 1921, a patent including the HASTELLOY® B nickel-molybdenum alloy composition was filed, and it was still used in the space capsule and the Atlas rocket in 1961 [99]. In the 1930s, a British austenitic iron-based Cr-Ni-W alloys alloy, KE965, was served as the standard alloy for exhaust valves in both the aircraft and automobile industries [100]. Like HASTELLOY® B and KE965 superalloys, the early-stage superalloys are austenitic base alloys. To further improve the mechanical properties at the elevated temperature, Pfeil [101] developed the Nimonic 80 superalloy in 1941, by adding aluminum and titanium in the Nichrome base alloy. Till then, Nimonic 80 is 'literally' the first nickel-based superalloy strengthened by the $\text{Ni}_3(\text{Al}, \text{Ti})$ γ' phase. The development of the Nimonic 80 superalloy laid the foundation for the philosophy of γ' as the primarily inevitable strengthening phase at the elevated temperature for superalloys, even though various alloying elements have been doped for the different expected properties. In 1958, Eiselstein [102] developed the Inconel 718 superalloy, first-time introducing Ni_3Nb γ'' as the strengthening phase. Till now, Inconel 718 and its derivative alloys are still active in the superalloy's arena attracting both metallurgists' and engineers' focus. With more and more diverted nickel-based superalloys being proposed, the high-temperature components are offered better and better performing materials.

The understanding of the nickel-based superalloys are not straightforward. The development of early superalloys has highly relied on the metallurgical experience and expertise, hypothesis, and even accidental luck. Pfeil developed the first γ' strengthened Nimonic 80 in 1941, while the γ' phase was firstly recognized by Taylor and Floyd by the working on Ni-Ti-Al ternary system in 1952 [103]. Moreover, the first observation of γ' precipitates in a superalloy was conducted by Betteridge and Franklin using micrography in

1957 [104]. Hereafter, with the development of phase diagram theory, physical metallurgy, and advanced microstructural characterization, the nickel-based superalloy developer focuses more on the microstructure tailoring by composition adjustment with the assistance of these powerful scientific tools. One of the most famous cases is the development of RR1000 superalloy for turbine disc applications. Based on the thermodynamic modeling from phase diagram analytics, Hardy et al. [105] in Rolls-Royce plc., proposed the RR1000 superalloy with a good combination of damage tolerance and creep resistance, which abandons the traditional iteration involved empirical alloy design method. In recent years, with the assistance of high-throughput computational thermodynamics coupled with a physics-based approach, e.g. Alloy-by-Design® (ABD) [106], γ' -strengthened cracking-resistant ABD-850AM and ABD-900AM nickel-based superalloys were developed for the AM process [107].

2.5.2 Development of manufacturing processes

The better performances of nickel-based superalloys cannot be achieved by the composition development solely, while the manufacturing processes also play an important role. With the flourishing development of superalloy composition since the 1950s, the manufacturing processes experienced the corresponding rapid development. The first milestone is the introduction of glass lubrication for extrusion by Sejournet in 1948 [108], enabling the larger ingot being extruded to bars for machining or to billets for the following forging steps. The wrought related manufacturing processes were extensively used for the superalloy production, while with the development of casting techniques, complicated internal cooling superalloy blades were fabricated by castings. In 1952, Darmara [109] firstly developed the commercial vacuum melting technique, which importantly improved the cleanliness and more precious composition control than the air melting. With vacuum melting, the contamination from the atmosphere, in particular of nitrogen, was significantly reduced. Moreover, the higher number of alloying elements, especially refractory elements, becomes possible to add. Then, the casting superalloys started to replace the wrought ones on the turbine blade application, even though the wrought parts show lower compositional segregation and better mechanical and cyclic properties at the lower temperature regime, while the casting parts are superior on the high-temperature performance partly owing to the coarser grain size. Till now, vacuum melting is adopted as the standard manufacturing route to provide nickel-based superalloy ingots. In the late 1960s, Versnyder et al. [110] further developed a new precision investment casting technique, thus directional solidification, based on Bridgman–Stockbarger method by controlling the direction of the temperature gradient during solidification, to produce the nickel-based superalloy. By applying the grain selector or the monocrystal ‘seeding’ in the directional solidification process, the nickel-based superalloy can be provided in columnar grain or single crystal form, which has a highly reduced number of transverse grain boundaries (to the loading direction), ensuring a dramatic improvement of the creep resistance at elevated temperature. Another important nickel-based superalloy manufacturing branch is the powder metallurgy approach. In the late 1960s, powder metallurgy was developed as a near-net-shaping manufacturing technique with low-mass waste. The process of powder metallurgy for nickel-based superalloys generally contains a route of powder production, powder consolidation, and thermomechanical processing [111]. Owing to the pre-alloyed powder used, the elemental segregation is restricted in the powder-size level. In addition, the equiaxed fine

grains are always promoted in the powder metallurgy processed superalloys. Based on these benefits of the powder metallurgy process, the corresponding superalloys parts show good fatigue resistance which is one of the major critical requirements for the turbine disc component.

2.6 Physical metallurgy of nickel-based superalloy

In this section, the physical metallurgy of nickel-based superalloy is discussed, which includes the integrated picture of composition (alloying elements) -microstructure (phases) -properties (mechanical and chemical properties).

2.6.1 Phases and microstructures

Typically, the microstructure of a certain superalloy consists of different phases. In a typical modern γ' strengthened superalloy, the common phase configuration including the disordered austinite FCC phase (γ phase) and ordered FCC phase with $L1_2$ structure (γ' phase). The γ phase majorly comprises of Ni atoms with other atoms of alloying elements randomly occupying the FCC lattice sites. While in the γ' phase, alloying elements Al, Ti, or Ta are substituting the vertices of FCC cubic cells and form the sublattice. In the γ' phase, the Ni atoms are occupying the centers of the faces of the FCC cell. In some other nickel-based superalloy, such as IN718, IN625, and Rene220, the more common precipitate phase is γ'' (gamma double prime). The structure of the γ'' phase is body-centered tetragonal (BCT) with the $D0_{22}$ crystal structure and the chemical composition form is Ni_3Nb . It should be noted that γ'' phase is a metastable phase, which decays to its thermodynamic stable form (the δ phase with $D0_a$ crystal structure, sharing the same chemical composition of Ni_3Nb) at the elevated temperature above 650 °C [112]. Owing to this, it impedes the service temperature limit of γ'' strengthened superalloys to around 650 °C.

Beyond the γ phase matrix and the γ' precipitates as the major phases, there are other phases in a smaller amount that still play a significant role. Firstly, the carbides. Here the carbides in superalloys are categorized into two types: the primary carbide and the secondary carbide. Primary carbide, in the form of MC (M stands for metallic element), formed during the solidification process and acting as the major carbon reservoir for the following heat treatment and service condition. The MC carbide spread throughout the alloy at both grain bulk and grain boundaries. The commonly observed MC carbide is HfC, TaC, NbC, and TiC, according to the Gibbs free energy of MC carbide formation and the experimental observations [113]. The secondary carbides are decomposed slowly from the MC-type carbides at the elevated temperature, for example, the M_6C and $M_{23}C_6$ type carbides. The M_6C carbides form at 815-980 °C, while the $M_{23}C_6$ carbides form at a slightly lower temperature of 760-980 °C [114]. In contrast to the MC carbides, secondary carbides prefer to reside in an intergranular way. Owing to the preferential sites of these secondary carbides, they have a beneficial effect as they pin grain boundaries and therefore improve the mechanical properties at elevated temperature. In addition, because of the pinning effect of secondary carbides, it is also considered as an advantage to control the grain size by controlling grain boundaries migration during the thermomechanical processing of superalloys. Another feature of secondary carbides which is different from the MC carbide is the enriched alloying elements. The enrichment of Cr, Mo, and W are generally found.

Secondly, the borides. Boron is another commonly doped minor element. In nickel-based superalloys, boron is prone to segregate at the grain boundaries because of the low solubility in the nickel matrix. Similar to the grain boundary carbides, the intergranular borides improve the high-temperature mechanical properties. The common form of boride is $M_2M'B_2$, where M represents the boride forming elements with larger atomic radius like Mo and Ti, and M' represents those smaller elements like Cr, Ni, and Co [115].

Thirdly, the topologically close-packed (TCP) phases. The TCP phases in superalloys form during the heat treatment or long-term service. These phases often have the plate-like or needle-like morphology. The formation of the TCP phase, like σ , μ , and P phase, is detrimental to the phase stability of superalloys. The excessive quantities of Cr, Mo, W, and Re (a common solutioning element in single crystal superalloy) are prone to develop TCP phases. For example, the ideal stoichiometry of the σ phase is A_2B , where A and B stand for the transition metals, like $Cr_{61}Co_{39}$, $Re_{67}Mo_{33}$; of μ phase is A_6B_7 , like W_6Co_7 , and Mo_6Co_7 ; one of the compositions for P phase is $Cr_{18}Mo_{42}Ni_{40}$ [116].

2.6.2 Alloying elements effects

In the chemical recipe of a modern nickel-based superalloy, up to more than 10 alloying elements are intentionally added. The choice of elemental additions primarily serves the goal of modifying the properties at high temperatures. The typical alloying elements in nickel-based superalloys and their features are summarized as follows [117,118]:

- **Cr**: improve the hot corrosion and oxidation resistance; solid solution strengthener; σ phase former; secondary carbide former.
- **Co**: high solubility in Ni matrix; increasing γ phase solidus; precipitates modifier.
- **Mo**: strong solid solution strengthener; boride former; MC and M_6C carbide former; σ and μ phase promoter.
- **W**: strong solid solution strengthener; M_6C carbide former; σ and μ phase promoter.
- **Al**: primary γ' former; improve high-temperature oxidation resistance by forming alumina.
- **Ti**: γ' former; strong MC carbide former.
- **Ta**: MC carbide former; increasing γ' phase fraction; strong solid solution strengthener.
- **Nb**: strong solid solution strengthener; increasing γ' phase fraction; MC carbide former; typical γ'' former.
- **Re**: solid solution strengthener; precipitates modifier.
- **Ru**: solid solution strengthener; phase stabilizer in Re containing superalloys.
- **C**: carbide source; solid solution strengthener.
- **B**: boride source; grain boundary strengthener; increasing creep strength and ductility.
- **Hf**: strong MC carbide former; grain boundary strengthener.
- **Zr**: grain boundary strengthener.

2.6.3 Strengthening mechanisms

There are several distinct mechanisms involved in the strengthening of nickel-based superalloys.

2.6.3.1 Solid solution strengthening

The origin of solid solution strengthening comes from the local stress field caused by the solid solutes in the base pure metal matrix, which impedes the movement of dislocations. As aforementioned, since up to more than 10 different alloying elements could be doped into the nickel-based superalloy system, the contribution of solid solution strengthening on the strength is significant.

To quantitatively estimate the solid solution strengthening, the coefficients fitted model from experiments are generally used, for example as described in detail by Roth et al. [119].

2.6.3.2 Precipitation strengthening

The γ' phase is the primary precipitation strengthener in superalloys, in particular to the high-temperature strength. The $L1_2$ γ' compound shows an anomalous temperature-dependent yield effect [120]. At higher temperatures, e.g. at 900 °C the γ' materials display the peak yield strength, which is double of the strength at the room temperature [116,121].

On the other hand, the γ' precipitates within the γ matrix play various roles in the interaction with dislocation motion. First, the γ' phase can be sheared by dislocations. Owing to the ordered feature of γ' , a large energy penalty would be generated if one full dislocation ($a/2 < 1\bar{1}0 > \{111\}$) enter the γ' phase. This energy is known as the anti-phase boundary (APB) energy, which in this case could be considered as the Al-Ni bond being forced to be replaced by the Al-Al bond. In this sense, dislocations go through the γ' in a pair, where the APB created by the first dislocation will be removed by the second dislocation. Among this dislocation shearing case, it can be further categorized into weakly coupled and strongly coupled dislocation cases [122]. In the weakly coupled dislocation case, the separated spacing between the dislocation pair is larger than the diameter of γ' phase, while the strongly coupled dislocation case indicates that the spacing between the paired dislocations is smaller than the diameter of γ' phase, thus, the leading and trailing dislocations could be somewhat observed at the same particle [123]. Second, if the size of precipitate exceeds a critical value, dislocation bypassing by Orowan looping [124] is more operative than dislocation shearing owing to the stress required for bypassing (τ_{oro}) is lower than the stress required for cutting (τ_{cut}).

Here, for a given diameter of γ' , e.g. 300 nm, one could give the estimated τ_{cut} by strong pair coupling as: $\tau_{cut} = Gb/(\pi L_{\gamma'-\gamma'}\sqrt{(\pi d_{\gamma'}\gamma_{APB}/(Gb^2) - 1)})$ [125], where G is the shear modulus (taken as 75 GPa), b is the magnitude of Burger's vector (0.257 nm), $L_{\gamma'-\gamma'}$ is the spacing between particles (taken as 112 nm as the case in the appended paper I), $d_{\gamma'}$ is the average size of precipitate (300 nm), γ_{APB} is the anti-phase boundary energy (0.2-0.3 J/m²). While the shear stress for Orowan looping is written as: $\tau_{oro} = Gb/L_{\gamma'-\gamma'}$. It results in $\tau_{cut} > 333$ MPa. However, τ_{oro} is around 170 MPa. It indicates that in the coarse γ' precipitates condition, dislocation bypassing is more common.

2.6.3.3 Grain boundary strengthening

That the polycrystalline alloys gets strengthened by the grain boundary network is an old topic. The most famous relationship between the increment of yield strength and the grain size is the Hall-Petch equation [126,127].

2.6.3.4 Dislocation strengthening

Dislocation is a typical line defect in crystals. Considering the shear strain caused by the sweeping of dislocation in a small volume, it can be expressed as [128]:

$$d\gamma = \rho b l \quad (2.2)$$

Here the $d\gamma$ is the unit shear strain, ρ is the dislocation density, b is the magnitude of Burger's vector, and l is the average length of dislocation. Assuming the dislocation distributes homogeneously, the length of dislocation l is given by the reciprocal of the square root of dislocation density as:

$$l = \frac{1}{\sqrt{\rho}} \quad (2.3)$$

Introducing the shear modulus G , the strengthening contribution from dislocations is rewritten as:

$$\Delta\sigma = \alpha_{ray} M G b \sqrt{\rho} \quad (2.4)$$

Where α_{ray} is a constant and M is the Taylor's factor. This equation is well known as Taylor's equation [129]. According to Taylor's equation, the increment of strength is proportional to the square root of dislocation density. In the LPBF alloys, especially in the as-built condition, the strengthening effect of dislocations is significant. For example, the as-built IN738LC superalloy shows good yield strength even though it lacks the γ' strengthening contribution. The appended paper II [18] gives a more detailed discussion on the strengthening mechanisms.

2.7 Creep in nickel-based superalloys

Creep of materials is defined as the solid materials deforms slowly and time dependent under the persistent mechanical stresses at the elevated temperature, which is normally higher than 50% of its melting temperature.

2.7.1 Creep mechanism

From the classical Ashby deformation mechanism map [130], the creep mechanism could be categorized into diffusional creep and dislocation creep. In the diffusional creep regime, the creep rate is controlled by the diffusional flow rate. The consideration is based on the that the grain boundaries in polycrystalline materials act as the major sources and sinks for vacancies. Then the diffusional creep could be further subdivided into Nabarro-Herring [131,132] and Coble [133] creep. In Nabarro-Herring creep, the lattice diffusion is only considered, while in Coble creep, the grain boundary diffusion is the consideration.

In particle strengthened alloys, such as the γ' strengthened nickel-based superalloys, the dislocation creep is more operative. The dislocation travels along the slip plane until it encounters a precipitate obstacle, then dislocation climbing must occur [134]. For example,

in the region of dislocation climb controlled creep, Reed [135] denote M_{creep} as a suitable merit index for creep resistance of single crystal superalloys:

$$M_{creep} = \sum_i \frac{x_i}{\tilde{D}_i} \quad (2.5)$$

Where x_i is the atomic fraction of solute i in the alloy, and $\tilde{D}_i$ is the appropriate interdiffusion coefficient. It should be noted that more slow diffusion elements indicate better creep resistance and decreasing dislocation climbing rates.

In contrast, in creep of the polycrystalline nickel-based superalloys, the grain boundary sliding acts as the dominant role in controlling the creep rate, which is discussed in detail in the appended paper I.

2.7.2 Creep performance of LPBF processed superalloy

Larson and Miller [136] proposed a method to estimate the time-temperature relationship under creep stress, and it is the most widely used parameter. Larson Miller Parameter (LMP) can be described as the following:

$$LMP = T \times (c_{LM} + \log_{10} t) \quad (2.6)$$

Where T is the absolute temperature in Kelvin; c_{LM} is the Larson-Miller constant, which varies between 15 and 25, and is taken to be 20 in this study; t is the time to rupture. According to this equation, LMP directly depends on creep temperature but has a weaker logarithmic dependence of rupture time.

Fig. 2.2. Larson-Miller-Parameter creep comparisons of CM247LC, Mar-M-247, IN738 nickel-based superalloy, as well as SLM fabricated IN738LC (data from references [25,35,137–142])

In Fig. 2.2., the LMP plots of cast superalloys IN738, CM247LC, Mar-M247 as well as LPBF processed IN738LC are compared. Generally, cast Mar-M247 superalloy shows better creep resistance properties than cast IN738LC, since the higher γ' precipitates volume fraction in Mar-M247. In addition, Mar-M247 comprises higher refractory elements Mo, W, Ta, and Hf with a sum of more than 15 wt. %, which can improve the creep performance of superalloys owing to their slowly diffusing natures. In contrast, the sum of Mo, W, Ta is less than 10 wt. % for IN738LC. Comparing the cast Mar-M247 with its derivative form for directional solidification (DS) CM247LC, the DS CM247LC shows superior creep performance

because of the heavy reduction of the grain boundary transverse to the loading direction. Here, CM is a trademark of Cannon-Muskegon Corporation, and Mar-M is a trademark of Martin Marietta Corporation. In the early study of LPBF IN738LC, Rickenbacher et al. [35] reported the creep performance at 850 °C. The bars were post-processing treated with HIP and standard heat treatment. The bars are examined by vertically (Z-plane) and horizontally (XY-plane) built. The creep resistance of LPBF IN738LC is generally worse than the cast ones. However, it should be noted here that the vertically built samples show obviously better creep performance than the horizontally built samples since the columnar grains in the vertical sample are more parallel to the creep loading direction.

2.8 Chapter summary

In this chapter, the background regarding the LPBF process and nickel-based superalloy is reviewed. The nickel-based superalloy is one of the significant and well-developed alloy systems. However, the AM techniques boosted in the past 2-3 decades acting as the disruptive manufacturing process against the conventional ones. From lots of aspects, the AM processed parts show a big difference with the well-understood knowledge, especially the difference in the cellular structure, chemical distribution, and phase configuration. This allowed and stimulated the proposing of the new composition of a superalloy adapted to the AM process. Although few success cases were reported on this topic and apparently the knowledge gap is huge, the attempt to the chemical alternation should be encouraged.

3 Experimental methodology

3.1 Materials

There are multiple nickel-based superalloys used in this study including the newly designed MAD542, and legacy superalloys IN738LC and its derivatives, and CM247LC. IN738 was first developed by Bieber [143] in 1969, as an investment casting nickel-based polycrystalline superalloy. This superalloy is divided into two different versions according to the Carbon content, the low carbon and high carbon grades from 0.11 to 0.17 wt. % [144], which are designated as IN738LC and IN738C. The compositions of the powder grades of these superalloys are listed close to where the experimental results are presented.

3.2 LPBF process

To fabricate as-built samples with a minimum defect level, optimized LPBF parameters were used. For example, in section 5.1, the printing parameters optimized for the MAD542 superalloy are described in detail with the validation of microstructural inspections. A 67° rotation-scan strategy was used for all the printed parts in this study, indicating the scanning vector rotates 67° for each layer. To provide the MAD542 superalloys for high-temperature mechanical testing, a three-layer stacked hexagonal geometry was used. As shown in Fig. 3.1., the side-to-side diameter of the hexagon is 9 mm and the length of the bar is 70 mm. The MAD542 bars are printed by using an EOS M100 system equipped with a round base plate of which the diameter is 100 mm.

Fig. 3.1. (a) illustration of the three-layer stacked hexagonal bars (b) digital photography of the as-built bars.

3.3 Metallographic preparation

The conventional mounting-grinding-polishing routine was used for metallographic sample preparation for a batch of different microstructural characterization methods, such as optical microscopy, and scanning electron microscopy. First, the hot mounting, the carbon-based thermosetting resin, PolyFast, was used for preparing the 30 mm mount. Then, the mount undergoes the grinding process by using #220 SiC sandpaper under the lubrication of water. Three-step polishing was used: starting with a 9 μm and then 3 μm abrasive, then the final finish is polishing by Struers® OP-U colloidal silica suspension.

3.4 Optical microscopy

In this work, the micrograph of the well-polished sample by optical microscopy (OM) is generally used for the inspection of the defects induced by the LPBF process. A Leica DM6 optical microscopy (Leica Microsystems GmbH, Wetzlar, Germany) was used.

3.5 Electron microscopy

3.5.1 Scanning electron microscopy

A Hitachi SU70 field emission scanning electron microscope (FE-SEM) (Hitachi, Ltd., Japan) was used for the SEM characterization. Commonly, the acceleration voltage of 20 kV was used for imaging secondary electron (SE) micrographs.

3.5.2 Electron backscatter diffraction

Electron backscatter diffraction (EBSD) is an SEM-based characterization method for crystallographic microstructure. In this work, an Oxford NORDLYS EBSD detector (Oxford Instruments, UK) was used for detecting the Kikuchi diffraction patterns. The EBSD data was acquired and indexed in the Flamenco software (Oxford Instruments HKL CHANNEL 5). The post-analysis of the EBSD scan was carried out in an open-source MATLAB® tool-box MTEX [145].

3.5.3 Transmission electron microscopy

Transmission electron microscopy (TEM) analysis was employed on an FEI Tecnai G2 microscope operating at 200 kV accelerating voltage. To prepare the TEM sample, a thin foil was firstly ground down to 50-100 μm in thickness. Then a round foil with a diameter of 3 mm was punched. The final polishing was performed using twin-jet electropolishing on a Struers apparatus. The electrolyte solution was 10% perchloric acid and 90% ethanol. The polishing temperature was -25°C , and the polishing voltage was 20 V.

3.6 High-temperature tensile and creep testing

To perform the high-temperature tensile and creep testing, an Instron 5982 testing system with 100 kN load capacity was used. An extensometer with two ceramic rods attached to the gauge length surface was used for the engineering strain measurement. The gauge length of the extensometer was 12.5 mm.

The bars were tested at 850 °C, which is provided by a 3-zone heat radiation furnace. A type-K thermocouple was attached to the center of the gauge length to monitor the specimen temperature. After the target temperature is reached, more than 1 h soaking time were applied before the testing starts.

4 Alloy design strategy

4.1 Crack susceptibility model for AM processed nickel-based superalloy

As long as decades ago, the weldability of precipitation-hardened nickel-based superalloys were qualitatively predicted in Prager and Shira's book [146] from the year 1968. In their model, the superalloys are separated into different regions according to their composition contents of Al and Ti, as Fig. 4.1. shows. In nickel-based superalloys, the Al and Ti are the primary γ' intermetallic phase formers, which is not surprised that those alloys with a higher amount of Al and Ti lead to the decreasing of weldability because of the higher risk of strain age cracking.

Fig. 4.1. Relationship between estimated weldability in precipitation-hardening Nickel-based superalloy and Al and Ti content, developed by Prager and Shira [146].

Other crack susceptibility models are aiming at quantifying the freezing range of an alloy, based on the knowledge that shortening the size of the mushy zone during solidification would reduce cracking susceptibility. Thus, the sensitivity of the hot tearing of an alloy increases with the broadening of the freezing range [147]. This kind of criteria was widely reported according to casting or welding research. The very common form to express this interval of solidification is by calculating the temperature interval [148] between the point at which the liquid feeding becomes difficult ($\sim 90\%$ solid phase formed) and the point at which the liquid films transformed into droplets ($\sim 94\%$ solid phase formed) [53]. Another

worth mentioning criterion is the hot cracking sensitivity (HCS) proposed by Clyne and Davis [149], in which the relative time interval rather than the temperature interval spent by the mushy zone is used as the index. Based on a similar argument but further considering the shrinkage contribution and then the tensile deformation applied on the perpendicular direction to the dendrite growth direction, Rappaz et al. [150] introduce the critical deformation rate as the indicator to characterize the HCS.

Another model that is worth mentioning here is proposed by Neil Harrison [151]. The ‘processable’ nature of an alloy depends on Thermal Shock Resistance (TSR). Derived from the definition of TSR, Harrison [152] proposed the crack susceptibility of an alloy, χ , as the following equation:

$$\chi = \frac{\sigma_{UTS}}{\sigma_T} \quad (4.1)$$

Where, σ_{UTS} is ultimate tensile strength of the alloy, if it’s ductile material, yield strength is usually chosen, σ_T is the thermal stress, which is a function of temperature, and it can be expressed as:

$$\sigma_T = \left[\frac{E\alpha_{CTE}}{2(1-\nu)} \right] \Delta T \quad (4.2)$$

Here, E is Young’s modulus, α_{CTE} is the coefficient of thermal expansion, ΔT is temperature difference on the heating surface, ν is Poisson’s ratio.

It’s clear from the definition, for a material to withstand hot cracking, σ_{UTS} larger than σ_T should be satisfied, which means $\chi > 1$. However, it is complicated to calculate a certain value of χ . Take the yield strength instead of ultimate tensile strength, and it depends on two parts, lattice stress and grain size strength contribution, as Hall-Petch equation below:

$$\sigma_{YS} = \sigma_0 + k_d d^{\frac{1}{2}} \quad (4.3)$$

Here σ_0 is the lattice stress, k_d is the locking parameter and d is the average grain size. From the lattice stress, it can be separated into the contributions from solid solution, σ_{ss} , and Peierls stress, σ_p , as expressed as:

$$\sigma_0 = \sigma_{ss} + \sigma_p \quad (4.4)$$

Under the identical processing conditions for similar alloys, the $k_d d^{\frac{1}{2}}$ can be assumed to have the same value. Peierls stress has limited contribution and can be assumed to be unchanged in alloys sharing the identical major element contents. So, the difference in yield strength depends on the solid solution only. Taking Hastelloy X as an example, it is a typical solid strengthening Nickel-based superalloy, Gypen, and Deruyttere’s [153] model for multicomponent solid solution hardening can be used to predict the strength. Then, based on the solid solution strengthening (SSS) [154] theory, Harrison [152] modified the composition of Hastelloy X to increase the σ_{UTS} , however, with no obvious σ_T variation. The crack resistance of modified Hastelloy X improved and a 65% reduction in cracking was achieved during LPBF.

4.1.1 Segregation behavior in LPBF

Before going into the alloy design approach, one more argument needs to be understood: is there elemental segregation existing in the as-built LPBF alloys? The solute redistribution behavior can be estimated by Brody and Flemings’ model [155], which evaluate the solid-state diffusion during solidification, as given by:

$$C_s^* = kC_0[1 - (1 - 2\alpha k)f_s]^{\frac{k-1}{1-2\alpha k}} \quad (4.5)$$

Where, α is Fourier number, expressed as:

$$\alpha = \frac{D_s t_f}{L^2} \quad (4.6)$$

Here, k is the equilibrium distribution coefficient, C_0 is the nominal composition, f_s is the fraction solid, D_s is the diffusivity of solute in the solid, t_f is the local solidification time, L is half of the dendrite arm spacing which represents the diffusion distance here. C_s^* is solid composition at the solid/liquid interface. The primary dendrite arm spacing (PDAS), λ_1 , can be estimated as [156]:

$$\lambda_1 = \mu \cdot V^{-\frac{1}{4}} \cdot G_T^{-\frac{1}{2}} \quad (4.7)$$

Where μ is constant, V is the solidification velocity, G_T is the thermal gradient, and the product of $G_T \cdot V$ is the cooling rate. Empirically, derived from the Eq. (4.7), Davies [157] determined the λ_1 as:

$$\lambda_1 = (97 \pm 5) \cdot \left(\frac{\partial T}{\partial t} \right)^{-0.36 \pm 0.01} \quad (4.8)$$

In the LPBF process, the cooling rate could be up to 10^6 K/s. Taken $\partial T / \partial t$ as 1×10^6 K/s, it results in the PDAS λ_1 to be 0.55-0.81 μm . As a consequence, the L is determined to be around 0.3 μm . To estimate the local solidification time, t_f , the solidification freezing range needs to be defined first. In this work, the Scheil solidification model was used, where no diffusion was assumed in the formed solid phases while the diffusion was assumed to be infinitely fast in the remaining liquid phases. Taken the IN738LC superalloy as an example, the Scheil solidification freezing range is determined by thermodynamic calculation (ThermoCalc, TTNi8 database) to be 239 K [84]. Therefore, the localized solidification process is supposed to be accomplished within 3×10^{-4} s, thus, t_f is estimated to be 3×10^{-4} s. For the major elements in IN738LC superalloy, the Nb shows fast diffusion rate [158]. To determine the diffusivity of solutes, D_s , the Arrhenius fits are carried out by using the data from [159]. At the liquidus temperature of IN738LC superalloy (1325 °C/1598 K [160]), the D_s of Nb is calculated to be 5.5×10^{-14} m²/s. Inserting back the D_s , t_f , and L into Eq. 4.6, the Fourier number α is then calculated to be 1.85×10^{-4} . Since the value of α is very close to 0, the solute redistribution behavior can be re-written as well-known Scheil equation:

$$C_s^* = k C_0 [1 - f_s]^{k-1} \quad (4.9)$$

At the very beginning of solidification, take the $f_s = 0$ but slightly larger than 0, the segregation behavior at the onset of solidification can be considered as:

$$C_s^* = k C_0 \quad (4.10)$$

Surprisingly, the above analysis finds that in a rapid cooling regime like for the LPBF process, element segregation still occurs during solidification. This has been supported by extensive researches on the as-LPBF-processed alloys by using high-resolution composition measurement techniques, e.g. Energy Dispersive X-ray Spectroscopy (EDS) in the TEM [161,162].

Therefore, following Eq. 4. 10, once the nominal composition of an alloy is determined, the concentration of i th element at the dendritic core region (which is the first solidified space) is determined by the equilibrium distribution coefficient k^i of this element. To estimate the value of k^i for the major alloying elements in the nickel-based superalloy, 61 different composition recipes from the literature are accessed. It contains more than 40 different nickel-based superalloys including both heritage grades and their derivative grades and experimental grades. The as-solidified compositions measured from experimental methods are checked, where C_0^i represent the wt. % of i th element in the nominal

composition while C_s^i stands for the wt. % of i th element in the dendritic core region. Fig. 4.2. shows the C_s^i as a function of C_0^i for the primary alloying elements inducing Cr, Co, Mo, W, Al, Ti, Ta, Nb, and Fe. By linear regression fitting, the slope of the solid lines in Fig. 4.2. are used to determine the k^i values.

Fig. 4.2. The plots of C_s^i vs. C_0^i of the primary alloying elements in the nickel-based superalloys.

It is apparent that some of the alloying elements are prone to segregate at the dendrite core (DC) region during solidification, such as W and Co, which has a k^i value greater than 1. On the other hand, elements like Nb, Mo, Al, Ti, and Ta segregate at the interdendritic (ID) region which leads to their k^i value less than 1. Elements like Cr and Fe then have a more uniform distribution behavior across dendrites and interdendrites, resulting in the k^i value of these two elements very close to 1. In AM-processed alloys, similar solidification segregations are widely reported in a selective electron beam melted (SEBM) CMSX-4 superalloy [22], an LPBF CM247LC superalloy [161], a laser beam welded (LBW) IN718 superalloy [163], an LPBF 316L steel [164], an LPBF IN718 [162]. Additionally, the next step is

to sort out the elemental concentration profile at the DC and ID regions. The total space of the as-built microstructure is considered as the sum of two parts: the DC and ID, as:

$$f_{DC} + f_{ID} = 1 \quad (4.11)$$

Where f_{DC} and f_{ID} is the volume fraction of the DC and ID regions, respectively. Then, the volume fraction of the DC and ID regions was measured via the image analysis process. As the SEM secondary electron micrograph of an as-LPBF-processed nickel-based superalloy shows in Fig. 4.3., the DC and the ID region were demonstrated by superposing the red and green shades, respectively. By adjusting the threshold of the image, the fraction of DC is determined to be around 70% as the binarized image in the inset in Fig. 4.3.

Fig. 4.3. SEM secondary electron micrograph of an as-LPBF-processed nickel-based superalloy with the DC and ID region highlighted. The binarized image in the inset indicates the DC fraction.

After the determination of f_{DC} and f_{ID} , the relationship between the i th element concentration in the bulk material (nominal composition, C_0^i), at the dendrite core (C_{DC}^i), and at the interdendrite (C_{ID}^i) can be derived according to the rule of mixture, as:

$$f_{DC}C_{DC}^i + f_{ID}C_{ID}^i = C_0^i \quad (4.12)$$

In the realistic case, the composition of the i th element is in a concentration gradient profile across different regions. However, in the simplistic sense, here, the C_{DC}^i is treated as a constant value which is equal to the value of C_s^i , which is the composition of the very first solidified solid during solidification. Similarly, the i th element concentration at the ID region is considered as a constant value as well. Till now, for an alloy with a specific given nominal composition C_0^i , the DC composition C_{DC}^i could be estimated by the elemental segregation behavior as discussed, while the ID composition C_{ID}^i could be calculated by the mixture rule as the Eq. (4.12).

Generally, the AM-process-induced cracking is heavily dominated by the poor cracking resistance in the ID region rather than DC. From extensive research [165–169], the majority of the cracks are observed in the ID spaces. In addition, a high portion of the cracks is specifically identified at the grain boundaries. According to the welding literature, the GBs located in the ID region is categorized into the class of solidification grain boundary (SGB). The last-stage solidified SGBs are coincidentally overlapped with the last-stage solidified interdendrites.

4.1.2 Minor elements effects

The minor element here is defined as the alloying element with the wt. % less than 1%, such as C, B, Zr. Other ‘impurity-like’ elements with the concentration within the PPM level are considered as a trace element, such as S, P, Pb, Sn, and will not be discussed in this work. These minor elements play a significant role in the mechanical properties of a nickel-base superalloy, for example, C and B are generally intentionally doped as the crucial grain boundary strengtheners at the elevated temperature owing to their preferential segregation along the grain boundaries.

Fig. 4.4. Calculated Scheil solidification profiles of NiCrAl alloys (calculated using ThermoCalc software and TCNI10 database)

On the other hand, in the LPBF regime, the minor elements partitioning at the grain boundary deteriorates the additive manufacturability, which leads to the reduction of liquation cracking resistance. Two necessary premises are necessary for the liquation cracking occurrence: 1) tensile stress and the projection of stress on the direction which potentially tears the interdendrite apart, and 2) the liquid film remaining at the interdendritic region, which negligibly carries stress. However, the mechanism of liquid film formation is still controversial. One commonly proposed mechanism of liquation cracking is the formation of low-melting-point phases in the interdendritic space, which

liquifies during the reheating and results in the liquation cracking. For example, the liquation of so-called 'low melting point' phases, like carbide, boride, sulphocarbide, and even γ - γ' eutectic constituents in the heat-affected zone is considered as the primary intergranular liquation according to the reports from welding literature of nickel-base superalloys [170–172].

In addition, recent researches [173,174] attempts to understand the liquation cracking mechanism in the EB-PBF nickel-based superalloy from the atomic-scale evidence. By advanced atom probe tomography characterization, the high-angle grain boundaries, which is the interdendritic region simultaneously, are observed to be prone to accommodate a higher amount of minor elements. The liquation cracking susceptibility then could be attributed to the reduction of solvus temperature by the segregation enrichment of elements, which hardly bear the intrinsic reheating, thus the 'segregation induced liquation' [59]. Therefore, the elemental segregated interdendrite is the space that got liquified rather than the carbide or boride or other 'low melting point' phases. With the solidification profile path calculation, the temperature drops as a function of the solidified phase could be illustrated. As the example shown in Fig. 4.4., two simplified demo compositions of nickel-based superalloy were selected: 1) the B-free: Ni-20Cr-3Al (wt. %), and 2) the B-containing: Ni-20Cr-3Al-0.02B (wt. %). Both two compositions provide a single FCC-phase structure. It is clear to see that with the addition of a minor amount of B, the freezing range, which is defined as the temperature range between the onset and the end of solidification, is broadened from 45 °C to 108 °C in the B-free to B-containing condition. The increase of freezing range would therefore increase the cracking susceptibility by the potential liquefaction.

4.1.3 Two-parameters crack susceptibility prediction

In this present work, the ID and DC are assumed as two different constituents as Fig. 4.5. illustrated. In another word, the 'composite-like' material is assumed; thus, the alloy is comprised of two constituent parts, namely the dendrite core and the interdendrite region. The chemical composition for both DC and ID could be determined as described in the previous section according to the given nominal bulk composition.

Fig. 4.5. Schematic illustration of the unit volume during solidification, the DC indicates the dendrite core while ID indicates the interdendrite. Z is the direction of solidification.

Considering the cracking resistant capacity between DC and ID, normally, ID is the weaker space which has lower resistance to cracking. Here, an indirect evidence is that the in-process cracking primarily occurs at the grain boundaries. As the SEM micrograph and the EBSD scanning maps at the same area of interest of an as-built superalloy containing in-process microcracks shown in Fig. 4.6., the orientation relationship between the adjacent region of the two sides of a crack could be illustrated. The EBSD band contrast (BC) maps are presented to identify the micro cracks. The enlarged view of those cracked areas shown in the red box in Fig. 4.6. (a) are correspondingly provided in Fig. 4.6. (d-g). By superposing the EBSD-BC map with the grain boundary (misorientation angle greater than 10°), it is found that the majority of the cracks show intergranular features. Meanwhile, the transgranular crack could be observed as the white arrow indicating in Fig. 4.6. (g).

Fig. 4.6. (a) SEM-secondary electron imaging of an as-LPBF-processed nickel-based superalloy containing micro-cracks, (b) the EBSD band contrast map of the same region in (a), (c) the EBSD inverse pole figure (IPF) coloring map of the same region in (a), (d-g) the high angle grain boundary (colored in yellow) maps superposing on the corresponding band contrast map of the region indicated by the red boxes in (a).

Fig. 4.7. The grain boundary misorientation profile of all the grain boundaries (red column) and cracked grain boundaries (blue column).

Fig. 4.7. shows the analysis of the misorientation distribution profile from both the whole scan of the area in Fig. 4.6. and cracked GBs. Consistent with the direct observation on the EBSD scan, the cracks primarily occur at the high-angle grain boundaries (HAGBs).

While the misorientations of the whole measuring area appear to have a bimodal distribution behavior. The first peak in the misorientation range lower than 10° is attributed to the largely developed subgrain boundaries or the light distortion of crystals because of the LPBF process. The second peak in the misorientation range between $30\text{--}40^\circ$ is commonly observed in the as-LPBF-processed microstructure owing to the bare development of recrystallized GBs. Comparing the HAGBs misorientation profile from the cracked GBs with the whole area, the distributions are in a similar tendency. On this basis, the in-process cracking occurs somewhat randomly at the HAGBs.

If one considers the fact that the in-process cracking is dominated by the high angle intergranular cracks only, it covers up how important the role interdendrite plays from the chemical composition perspective. Letting us review the as-built microstructure with a special focus on the relationship between interdendritic boundary and GBs. In Fig. 4.8., by combining the backscattered electron (BSE) imaging with a superposed grain boundary map from EBSD measurements at the same location of an as-LPBF-processed CM247LC superalloy (more information in appended manuscript IV), the GBs plots with respect to the dendrite/interdendrite are unveiled. It is not surprising that both the HAGBs (misorientation angle $> 10^\circ$) and the subgrain boundaries are primarily located at the inter-cellular/dendritic region. It is accepted as that during the LPBF process, the (sub)grain boundary interface is formed at the last stage of solidification, which coincides with the location of the interdendritic locations. These grain boundaries are defined as solidification grain boundaries (SGB) in the welding literature [175].

Fig. 4.8. BSE SEM micrograph of an as-LPBF-processed CM247LC superalloy with a superposed grain boundary map from EBSD measurements at the same sample location. The orientations of two adjacent regions projected on (100) pole figure are shown, with their {100} crystallographic planes sketched as well.

According to the microstructural evidence, it is clear that the in-process cracks attack the intergranular sites, in another word, the interdendritic region. Letting us review the in-process critical cracking mechanisms of nickel-based superalloy during the AM processes, one of the key factors to mitigate the cracking susceptibility is to strengthen the interdendritic region. Based on this wisdom, in this model, the first materials index introduced is from the consideration of comparing the mechanical loading resistance from DC and ID region. Different from the previous models considering the solidification natures such as freezing range and solidification time, here solid-state alloys are the premise. Thereafter, one could derive an indicator which compares the elastic load-bearing capacities of the DC and ID region, thus the difference of yield limit of them, $\Delta\sigma_y$, as:

$$\Delta\sigma_y = \sigma_{y,ID} - \sigma_{y,DC} \quad (4.13)$$

In the γ' -strengthened nickel-based superalloys, based on the additive law, the yield strength could be expressed using several individual strengthening factors [18], as:

$$\sigma_y = \sigma_p + \Delta\sigma_{SS} + \Delta\sigma_{GB} + \Delta\sigma_{\gamma'} + \Delta\sigma_{Dis}. \quad (4.14)$$

Where σ_p is the Peierls stress from pure crystal lattice resistance, $\Delta\sigma_{SS}$ is strengthening from solid-solution, $\Delta\sigma_{GB}$ is the strengthening part from grain boundaries, $\Delta\sigma_{\gamma'}$ is the strength contribution from the γ' precipitates, and $\Delta\sigma_{Dis}$ is the dislocation strengthening part. During the LPBF process, the extremely high cooling rate suppress the formation of γ' phases, leading to the absence of $\Delta\sigma_{\gamma'}$ part in Eq. (4.14). In the as-LPBF processed condition, the microstructure is then treated as the solid solutioning with supersaturated alloying elements. By applying the subtraction as in Eq. (4.14), the Peierls stress is considered as a constant value between ID and DC, and the yield strength difference then could be rewritten as:

$$\Delta\sigma_y = (\Delta\sigma_{SS,ID} - \Delta\sigma_{SS,DC}) + (\Delta\sigma_{GB,ID} - \Delta\sigma_{GB,DC}) + (\Delta\sigma_{Dis,ID} - \Delta\sigma_{Dis,DC}) \quad (4.15)$$

The σ_{GB} part is proportional to the reciprocal of the square root of grain size, according to the Hall-Petch strengthening law. While the grain size of an as-LPBF-processed superalloy is dependent upon the printing process-related parameters, making the σ_{GB} composition weakly dependent. Additionally, the σ_{Dis} part is proportional to the square root of dislocation density according to Taylor's equation, under the assumption that material constants and Taylor's factors of each alloy have a similar value. In another word, the σ_{Dis} part is dominated by the dislocation density. The dislocation density of different alloys in the as-LPBF-processed state remains a closely consistent value in the order of magnitude of $10^{14}/m^2$ from a batch of reports [18,176,177]. Another approach to validate the consistency of dislocation densities is to deduce the cellular size of the as-LPBF-processed samples. The dislocation density, ρ , in a cellular structure containing materials is related to the reciprocal of the cubic square of cellular size, d_c^2 , and it could be expressed as $\rho \propto 1/d_c^2$ [178]. In the as-LPBF-processed nickel-based superalloy, the average cellular interspacing is in the narrow range of 400-600 nm, see e.g. LPBF IN718 [162], LPBF IN625 [179], LPBF Hastelloy X [180,181], LPBF IN939 [182], LPBF IN738LC [86], and LPBF CM247LC [183]. Based on these arguments, the σ_{Dis} part can be assumed to be a constant value for various superalloy grades fabricated by the similar LPBF process. Therefore, the yield strength difference in Eq. (4.15) could be rewritten as:

$$\Delta\sigma_y = (\Delta\sigma_{SS,ID} - \Delta\sigma_{SS,DC}) + \Delta\sigma(P) = \Delta\sigma_{SS} + C \quad (4.16)$$

Where $\Delta\sigma(P)$ is the strength dominated by the LPBF process, which is treated as a constant C in this work. To simplify, the yield strength difference here is represented by $\Delta\sigma_{SS}$ only. In this model, the as-LPBF-processed alloy is considered, indicating the single γ phase

condition. Then the solid solution strengthening difference between ID and DC is expressed as:

$$\Delta\sigma_{ss} = \sum_{i=1}^n \sqrt{\chi_{ID}^i} \cdot \frac{d\sigma}{\sqrt{d\chi^i}} - \sum_{i=1}^n \sqrt{\chi_{DC}^i} \cdot \frac{d\sigma}{\sqrt{d\chi^i}} \quad (4.17)$$

Where χ_{ID}^i and χ_{DC}^i are the atomic fraction of i th alloying element segregating at the ID and DC regions, respectively, and $d\sigma/\sqrt{d\chi^i}$ is the strengthening coefficient for each element in the unit of MPa/ $\sqrt{\text{at.\%}}$, which is provided in detail of the work by Roth et al. [119].

Another insight of improving the additive manufacturability is to increase the solidus temperature at the ID region. From the physical perspective, if the ID region shows higher solidus temperature, the lower susceptibility of ID region being liquified by the intrinsic re-heating. In this model, the solidus temperatures are referred to the melting temperature of a mixture containing the alloying elements. Motivated in this way, one could formulate an index which indicates the difference between the melting temperature of ID and DC, ΔT_m , as:

$$\Delta T_m = T_{m,ID} - T_{m,DC} \quad (4.18)$$

To estimate the melting temperature of a mixture, the Harmonic mean is used, which can be written as:

$$\Delta T_m = \frac{1}{\sum_{i=1}^n \frac{\chi_{ID}^i}{T_m^i}} - \frac{1}{\sum_{i=1}^n \frac{\chi_{DC}^i}{T_m^i}} \quad (4.19)$$

Where T_m^i is the melting point of the i th element.

4.1.4 Additive manufacturability diagram

After the determination of the 2 parameters, $\Delta\sigma_{ss}$ and ΔT_m , the additive manufacturability of a nickel-based superalloy could be assessed. With the increasing of $\Delta\sigma_{ss}$ value, the deformation resistance in the ID region increases. With the increasing of ΔT_m value, the heat resistance of ID region increases. Hence, a superalloy with both higher $\Delta\sigma_{ss}$ and ΔT_m combination is expected to have better additive manufacturability. Inspired by the 2-parameter model, the additive manufacturability diagram can now be developed. Fig. 4.9. illustrates the idea: putting $\Delta\sigma_{ss}$ and ΔT_m on the x and y-axis in the x-y plot. Each composition maps to one position on the diagram. To start, the legacy designations of nickel-based superalloys are presented, as shown in the same figure. Not surprisingly, these superalloys with good weldability, which is associated with additive manufacturability, are located at the upper right-hand corner. These superalloys are known as the easy-to-weld superalloys, and they are covered by the blue envelope in Fig. 4.9. For example, IN718 and IN625 are well proved as the superalloys which are ready and prominent for the AM process. Wide research from different groups could achieve the crack-free LPBF IN718 [184,185] and IN625 [186,187] parts in a wide processing window. Among the easy-to-weld superalloys, although Hastelloy X can be successfully fabricated by LPBF in a defect-free condition, process parameter optimization is required [188]. Thereafter, reading from the diagram, Hastelloy X shows lower additive manufacturability comparing with IN718 and IN625. Another superalloy in this envelope is Haynes 242 which is strengthened by the $\text{Ni}_2(\text{Mo}, \text{Cr})$ precipitates with sluggish formation kinetics. Although there is a limited number of reports on this AM processed parts, Haynes 242 is greatly known for its excellent weldability [189].

Other powder metallurgy (PM) and wrought superalloys, which are widely used in the turbine disc component, are marked in a green open circle and enveloped into green cover. In this region, the superalloys are considered as fairly-weldable superalloys. For example,

the advanced disc superalloy RR1000 developed in Rolls-Royce plc. shows fairly good weldability [190,191]. It should be also noted that recent proposed AM γ' strengthened nickel-based superalloys which are designed for the AM process, e.g. ABD850AM, ABD900AM [192] by OxMet technologies and developed by using Alloys by Design® approach [135,193], and ExpAM [194] developed by Carpenter Technology Corporation, are located at this region. These AM superalloys are readily adopted for the LPBF process after processing parameter optimization.

On the lower left-hand corner, the cast superalloys are marked in red. In this region, some of the superalloys are well investigated regarding the LPBF processability. For example, the IN738LC, it is a superalloy designation developed for the casting process. In the additive manufacturability diagram, the IN738LC sits in the region with superposing of both wrought/PM and cast superalloy envelopes. From the extensive study, the crack-free LPBF IN738LC superalloy could be achieved by process parameter optimization [195–197]. Another typical cast superalloy locates in this region that should be discussed is the CM247LC. Superalloy CM247LC has attracted great interest in the LPBF community for the additive manufacturability investigations. In the early attempts to LPBF process the CM247LC, crack-free samples could barely be provided in the as-built condition even after optimizing the printing parameters and laser scan strategies, e.g. as reported by a serial work done by Carter et al. [19,90,198,199]. However, in a recent reported work by Adegoke et al. [200], after searching the LPBF processing window from a statistical DoE (Design of Experiment) matrix containing 30 experiments, the as-built sample with the void and crack density close to zero could be identified. Even though the CM247LC superalloy locates at the far end part of the additive manufacturability diagram, it does not indicate the total impossibility for this alloy to be LPBF processed.

In summary, from the additive manufacturability diagram (Fig. 4.9.), the ability to rank the legacy superalloys with their additive manufacturability with respect to the propensity of in-LPBF-process cracking has been demonstrated.

Fig. 4.9. Additive manufacturability diagram for designations of legacy nickel-based superalloys.

4.1.5 Effect of alloying elements on the additive manufacturability

To extend the implementation of the additive manufacturability diagram, the influences of alloying elements could be qualitatively characterized. In this work, the example chemical composition is taken as Ni-8Cr-8Co-5Mo-4W-5Al-1Ti-3Ta-2Nb, in wt. %, which is given the name MAD542 here for demonstration. Starting with this nominal composition, the additive manufacturability of the MAD542 superalloy is mapped in the diagram in Fig. 4.10. With the nominal composition of MAD542 mapped at the center of the diagram, the calculation results of the addition of 0.5 at. % and subtraction of 0.5 at. % of each alloying element by substitution of the matrix element Ni is illustrated in the gray and violet envelopes, respectively. First, in the element addition scenarios, the Nb shows the most positive influence on improving the alloy's additive manufacturability. Other elements, like Mo, Ti, and Ta are the potential elements that increase the additive manufacturability as well. In the research on the effect of Ti addition on cracking in additively manufactured (laser solid formed) IN625, Hu [201] reported with the increasing of Ti content from 0 to 5 wt. %, the solidification temperature range decreased from 210 to 149 °C. The crack rate of Ti-doped IN625 decreased to nil. As depicted in the diagram, Co, and Cr display nearly no influence, indicating by the positions close to the nominal composition. The addition of W and Al further harms the additive manufacturability. In contrast, the effect of subtraction of alloying elements acts in the opposite way. For example, to improve the additive manufacturability of an alloy, one could either decrease the concentration of W or increase the concentration of Nb, as shown in the upper right-hand corner.

Fig. 4.10. Additive manufacturability diagram of MAD542 superalloy. The influences of addition and subtraction of elements are illustrated as the gray and violet envelopes.

4.2 Phase stability model

Another assessment for the candidate alloys is the phase stability property, thus the potential probability of forming the TCP phase. The major purpose of the phase stability model is to characterize the TCP formation tendency. In 1964, the PHase COMPUtation (PHACOMP) approach was proposed to predict the solid solubility limit of each alloying element in the nickel matrix, based on which the TCP formation propensity could be estimated [202]. In the PHACOMP method, the parameter N_v is used, which indicates the electron vacancies. However, the use of N_v shows a limited number of elements. Two decades later in 1984, Morinaga et al. [203] proposed the New PHACOMP method, which modified the phase prediction model. Instead of using N_v , the New PHACOMP method uses the d orbital energy level, M_d . By calculating the sum of M_d parts from each alloying element, the compositional average of M_d is then expressed as:

$$\overline{M_d} = \sum_{i=1}^n \chi_i \cdot (M_d)_i \quad (4.20)$$

Where χ_i and $(M_d)_i$ are the atomic fraction and M_d value of i th elements, respectively. The $\overline{M_d}$ value is then successfully used for predicting the propensity of TCP phase formation, and more useful, alloy design of nickel-based superalloy [204]. From the physical meaning, the M_d value correlates with the electronegativity, which represents the tendency of electrons being attracted by an atom. The d orbital level M_d value also relates to the atomic radius. To simplify, if a nickel-based superalloy shows lower $\overline{M_d}$, the TCP phase formation tendency is lower. The values of M_d (in the unit of eV) of alloying elements in Ni could be found in reference by Morinaga [205].

4.3 MAD542: a novel nickel-based superalloy for AM process

Considering the common alloying elements in nickel-based superalloy, a Cr-Co-Mo-W-Al-Ti-Ta-Nb-Fe-Ni alloy family is proposed as the basic compositional configuration. Owing to the combination of high uncertainty and normal composition ranges of nickel-based superalloy, broad steps of each possible elements are used, as Table 4.1. listed. By searching the wide range of alloying elements, the alloy space, hereafter refer to all the candidates of alloys, contains $4 \times 4 \times 4 \times 5 \times 4 \times 4 \times 5 \times 6 \times 6 = 921,600$ recipes in total.

Table. 4.1. The designed alloy spaces.

Elements	Cr	Co	Mo	W	Al	Ti	Ta	Nb	Fe	Ni
wt. %	8	8	1	4	3	1	1	0	0	Bal.
	12	12	3	6	4	2	3	0.5	4	
	16	16	5	8	5	3	5	1	8	
	20	20	7	10	6	4	7	1.5	12	
				12			9	2	16	
								2.5	20

Fig. 4.11. (a) Additive manufacturability diagram for the designed alloy space (the grey cloud) together with other legacy superalloys, (b) enlarged view of the most right-hand upper corner of the alloy space.

By inserting the candidate alloy recipes into the two-parameter plot, the additive manufacturability of the alloy space can be estimated. In Fig. 4.11. (a), the location of the alloy space cloud is presented with the superposing of the calculation from the legacy superalloy compositions. The enlarged view of the alloy space with the best additive manufacturability is provided in Fig. 4.11. (b).

From Fig. 4.11. (b), the candidate alloy recipe with the I.D.: 43915 fulfills the requirements to achieve the objective of best additive manufacturability among the compositions in the alloy space. Here, the terminology *objective* indicates the expected goal

of the materials to be designed according to the materials selection approach proposed by Ashby [206]. However, it should be well noted that alloy design of the printable nickel-based superalloy is not a single objective limited procedure. For example, in the designed novel superalloy, the phase configuration of a $\gamma + \gamma'$ dual phase with a limited amount of TCP phase is appreciated. By calculating the phase diagram of I.D.: 43915 alloy, as shown in Fig. 4.12., a certain amount of undesired phases exist.

Fig. 4.12. The thermodynamic equilibrium phase diagram of I.D.: 43915 alloy using the TCNI10 database in the Thermo-Calc software.

On this basis, to consider phase configuration, the New PHACOMP method is introduced into this work. In the three-dimensional contouring plot of alloy space cloud in Fig. 4.13., the 2-parameter additive manufacturability model is presented at the x-y plane, while the z-axis indicates the value of $\overline{Md}$. Here, the critical value of $\overline{Md}$ is set to be 0.98 eV, which is well accepted that $\overline{Md} < 0.98$ eV results in low formation propensity of TCP phases [207]. It is straightforward to illustrate the influence of $\overline{Md}$ on filtering of the alloy candidates. By applying the horizontal plane of $\overline{Md}=0.98$ eV, those alloy recipes above this horizon show higher propensity of TCP formation. Therefore, those alloys beneath this horizon are the potential ones with less TCP formation susceptibility.

Fig. 4.13. Three-dimensional contouring plot of the alloy space, X-Y plane indicating the additive manufacturability diagram and Z-axis representing the $\overline{Md}$ value.

Fig. 4.14. (a) Additive manufacturability plot of alloy space with $\overline{Md}$ lower than 0.98 in colored and $\overline{Md}$ greater than 0.98 in grey, (b) thermodynamic equilibrium phase diagram of 4 candidates of 3 wt. % Al (I.D.: 43339), 4 wt. % Al (I.D.: 29767), 5 wt. % Al (I.D.: 30301), and 6 wt. % Al (I.D.: 16585), as the legend shows.

The projection of the 3D contour map on the 2-parameter additive manufacturability plot is shown in Fig. 4.14.(a). To separate the different levels of wt.% of added Al content, it is colored in different shades of red which is indicated by the arrows. The I.D.s of those alloy recipes with best additive manufacturability with 3 wt.%, 4 wt.%, 5 wt.%, and 6 wt.% Al doping is I.D.: 43339, I.D.: 29767, I.D.: 30301, and I.D.: 16585, respectively, as indicated in the legend of Fig. 4.14.(a).

As in the section of ‘History and development of nickel-based superalloy’ mentioned, the phase configuration with the γ phase serves as the matrix phase plus the γ' precipitates as the primary strengthening phase, has been proposed as the philosophical route to design nickel-based superalloy, and it is well proved by the extraordinary high-temperature mechanical properties of γ' -strengthened superalloys. Here, the γ' precipitates fraction of the superalloys is illustrated by thermodynamic calculation at the equilibrium state using Thermo-Calc® software (version 2020b) with a TCNI10 database. The plot of the molar fraction of phases as a function of temperature is provided in Fig. 4.14.(b). With the increasing of Al content, the liquidus, solidus, and γ' solvus temperature increases. In Fig. 4.14.(b), another important indicator is the solutioning heat treatment window, which is represented by the temperature range between γ' solvus and solidus. In this temperature, the alloys could be heat treated in the single γ phase region without the onset of liquification. The solutioning windows for all 4 alloys are greater than 100 °C, indicating the good solutioning heat treatment potentials. The volume fraction of the γ' phase at the elevated temperature is often considered as a significant index for assessing the high-temperature mechanical properties, e.g. the creep resistance, of superalloys. By assuming that the molar fraction of γ' phase approximates to its corresponding volume fraction owing to the rather small lattice mismatch between γ/γ' , it is obvious that the volume fraction of γ' phase increase with the increasing amount of Al content. Obviously, a superalloy with a higher amount of γ' phase shows better high-temperature strength. In addition, the creep resistance could be improved by increasing the γ' phase volume, e.g. the life to creep rupture increased almost one order of magnitude by increasing 3.1% γ' to 24% γ' via different heat treatment of the same superalloy [208]. In the advanced single-crystal nickel-based superalloys (widely used for the turbine blade applications), the relatively high γ' volume fraction could go up to 60-80% [209]. According to the research from National Institute for Materials Science in Japan (NIMS) [210], the longest creep rupture life at 900 °C is obtained by 70% γ' alloys for TMS superalloys series (TMS is the designation of single crystal superalloy developed in NIMS). In the powder metallurgy processed nickel-based superalloys (widely used for the turbine disc applications), the volume fraction of γ' is in the range of 40-60% [211–213]. Other conventionally cast nickel-based superalloys usually have a broad γ' volume fraction range, e.g. ~35% for cast+wrought [214] IN939, ~46% for cast IN738LC [215], and ~62% for cast CM247LC [137]. However, the alloy with a too high-volume fraction of γ' precipitates (e.g. I.D.: 16585 with 6 wt.% Al addition has higher than 70% γ' in the fully precipitated stated) is not a suitable candidate. The LPBF process fabricates the polycrystalline nickel-based superalloy. First, at the lower temperature, e.g. in the room temperature regime, γ' precipitates hinder the dislocation movements by shear resisting or looping bypassing of dislocations. Based on this, the superalloys are strengthened. If one considers the γ' phase as the hard domains which are difficult to be deformed, the left soft domains (the γ matrix) serve as the space for accommodating the strain which provides the ductility (more detailed discussion in the appended paper II). At the elevated temperature, the deformation mechanism is majorly overtaken by grain boundary sliding (more detailed discussion in

appended paper I). On this basis, pursuing the very high γ' volume fraction of the LPBF superalloy is ruled out. Here, the target volume fraction of γ' is set in the range of 60-65%, according to the commercial cast superalloy, e.g. the conventionally cast CM247LC contains up to 65% volume fraction of γ' phase [26].

To sum up, by carefully considering the combination of 1. additive manufacturability using the novel proposed 2-parameter model, 2. TCP phase formation propensity using the New PHACOMP method, and 3. the γ' precipitates fraction using the thermodynamic calculation approach, one of the candidates, I.D.: 30301, is selected from the alloy spaces containing 921,600 compositions in total. The nominal composition of I.D.: 30301 is listed in Table 4.2. The alloy 30301 is given the name MAD542 superalloy. Here, the MAD stands for Materials for ADditive manufacturing under the scope of the MADAM project (a VINNOVA (the Swedish Agency for Innovation Systems) project which financially supports this work). Here, '542' stands for the critical elemental concentration of 5 (wt.%) Mo, 4 (wt.%) W, and 2 (wt.%) Nb, which significantly improve (Mo, and Nb) or reduce (W) the additive manufacturability.

Table 4.2. The nominal composition of ID: 30301 (MAD542) superalloy in wt. %

wt. %	Cr	Co	Mo	W	Al	Ti	Ta	Nb	Ni
I.D.: 30301 (MAD542)	8	8	5	4	5	1	3	2	Bal.

5 Microstructure validation of MAD542

In this chapter, the LPBF process and microstructures of MAD542 are presented and discussed [216]. The pre-alloyed gas atomized powders of the MAD542 superalloy were supplied by Höganäs AB, Sweden. The raw powder size is in the range of 15-45 μm . In the previous chapter, the major elements of the MAD542 superalloy are designed. To start the initial investigation on the MAD542 superalloy, the powder grade with limited minor elements is fabricated, according to the wisdom from the extensive studies on the minor element effects. The measured composition including minor and trace elements from the powder supplier is listed in Table 5.1.

Table 5.1. The chemical composition of the MAD542 nickel-based superalloy was investigated in this study (Ni in Bal.).

Element	Cr	Co	Mo	W	Al	Ti	Ta	Nb
wt. %	8	8	5	4	5	1	3	2
Element	C	B	Si	P	S	Zr	O	N
wt. %	0.1	<0.001	<0.005	<0.001	<0.001	<0.002	0.015	0.002

5.1 LPBF manufacturing of MAD542

To search the LPBF processing window of the MAD542 superalloy, a set of printing parameters (laser powder, P ; scan speed, V_s ; hatching distance, H ; layer thickness, L) with 9 different combinations were used. The detailed printing parameters are listed in Table 5.2., where the energy density derived by $E_v = P/V_s \cdot H \cdot L$, is included as well. The LPBF is conducted using an EOS M100 system at the Centre for Additive Manufacture – Metal, CAM² (in the Chalmers University of Technology).

Table 5.2. Laser powder bed fusion processing parameters used in this study (layer thickness: 20 μm)

Exp	Laser power, P (W)	Scan speed, V_s (mm/s)	Hatching distance, H (μm)	Energy density, E_v (J/mm ³)
#1	100	1000	50	100
#2	170	1000	50	170
#3	100	1300	50	77
#4	170	1300	50	131
#5	100	1000	70	71
#6	170	1000	70	121
#7	100	1300	70	55
#8	170	1300	70	93
#9	135	1150	60	98

After the cubes (10 mm $\times$ 10 mm $\times$ 10 mm) being printed, a metallographic observation of the well-polished samples was applied to identify the as-built defect level. Fig. 5.1. shows the results of 9 cubes by using different printing parameters. As plotted in the chart, the minimum defect level (e.g., see micrograph of #3) is achieved around 0.06% at the valley of the 'defect area fraction vs. energy density' curve, of which the suitable energy density is between 70-80 J/mm³. The suggestion raising from this processing window searching experiments is to LPBF the MAD542 superalloy with #3 printing parameters in Table 5.2., thus the combination of laser power of 100 W, a scan speed of 1300 mm/s, hatching distance of 50 μm , and layer thickness of 20 μm . In this work, if it is not specially stated, these printing parameters were used for the fabrication of the MAD542 superalloy for microstructural investigations and mechanical testing.

Fig. 5.1. Laser powder bed fusion (LPBF) processing window investigation of MAD542 superalloy on 10 mm × 10 mm × 10 mm cubes. With lower energy density input, the major defects are dominated by lack of fusion, while higher energy density inputs result in micro-cracks. The crack-free part is provided by #3 printing parameters, which has a suitable energy density input for MAD542.

5.2 As-built microstructures

Fig. 5.2. Microstructural characterization of multiple length scales for as-built MAD542 superalloy, (a) EBSD inverse pole figure coloring map showing the columnar grains parallel to the building direction, (b) OM micrograph of the chemical-etched sample showing the melt pool and melt pool boundary, (c) SEM SE imaging the cellular structure and the HAGB, (d) DF-STEM micrograph of the as-built MAD542 microstructure in detail, (e) enlarged view of the cellular/dendritic structure. (f) EDS mapping results of the cellular/dendritic structure and its surrounding region including high-angle annular dark-field (HAADF) imaging, Co-K map, Al-K map, Cr-K map, W-L map, Nb-, Mo-, Ta-overlapping map, Nb-L map, Mo-L map, Ta-M map, and Ti-K map.

The as-built microstructure of the MAD542 superalloy at multiple length scales is characterized by using different methods as presented in Fig. 5.2. In Fig. 5.2.(a), the grain orientation, and HAGB morphology were measured by EBSD scanning. Typical columnar grain shapes are obviously obtained in the as-built condition. The optical micrograph in Fig. 5.2.(b) on the etched as-built sample reveals the traces of melt pool morphology with the melt pool boundary (MPB) indicated by the arrow. It worth mentioning that the laser scanning strategy used for the LPBF process is 67° rot-scan, which means that the scan vector rotates 67° between each layer. If one compares the length scale of columnar grains and the melt pool, no half-ellipse melt pool-like features remains at the HAGB, indicating that the grain growth direction is barely obstructed by the MPB [217]. The secondary electron SEM imaging on a slightly etched sample in Fig. 5.2.(c) shows the fine cellular structures. Generally, the longitudinal direction of the cellular structure is closely parallel to the grain growth direction. In this sense, the HAGB could be distinguished from the distinct directions of alignment of cellular structures. Within the grain interior region, low angle misorientations sometimes present at the intercellular boundaries [164]. The dark-field (DF) scanning-TEM (STEM) micrographs in Fig. 5.2.(d-e) show the characteristics of cellular structure in higher magnification. The cellular boundaries are decorated with dense dislocations, compared to the sparsely distributed dislocations within the cellular core region. The average intercellular arm spacing in this sample is measured to be 420 nm. In addition, the overall dislocation density is estimated to be $7.3 \times 10^{14} \text{ m}^{-2}$. The elemental

distribution via STEM-EDS composition mapping was conducted in a cellular structure and its surrounding area (Fig. 5.2(f)). Consistent with the abovementioned elemental segregation behavior, it is evident in the EDS maps that the segregations of alloying elements across the cellular core and boundary are not fully suppressed by the LPBF solidification process. According to this finding, the cellular structure simultaneously plays the role of solidification dendritic structure, in which segregation necessarily occurs.

5.3 Solutioning heat treatment of the MAD542 superalloy

One of the most important variables for solutioning heat treatment is the target temperature. The γ' -solvus, solidus, and liquidus temperatures for MAD542 superalloy have been assessed by thermodynamic calculations (TCNI10 database) as 1180 °C, 1328 °C, and 1378 °C, respectively. In this work, super-solvus solutioning temperature was used as 1230 °C. Various holding time of 10 min, 30 min, 60 min, and 120 min were used. The cooling method is air cooling after the target holding time is achieved.

Fig. 5.3. The twin boundary (TB) and recrystallization (RX) fraction evolution as a function of annealing time at 1230 °C, indicating a combination of rapid RX and TB formation processes. The EBSD scans cover 870 μm × 1266 μm area with a 2-μm step size. In the GB+TB maps, the grain boundaries (GB) are plotted in black lines while TBs in red lines. In the RX maps, RXed grains are colored in blue. All the scale bars are 125 μm.

The LPBF MAD542 superalloy shows good recrystallization (RX) response. In Fig. 5.3., the RX area fraction and twin boundary (TB) evolution as a function of holding time at 1230 °C is presented. By the EBSD scanning, the RX grains are defined as the grains with grain orientation spread (GOS) values less than 1°. Greater than 90% of RX grains are promoted after 30-min solutioning heat treatment, which corresponds with the rapid formation of TBs. More than 55% of TBs are retained in the full RX sample. As discussed in the appended manuscript, the LPBF superalloys are considered as hard to RX owing to the interdendritic trapping effect on the grain boundary migration. While, in the MAD542 superalloy, extensive TB formed assists the finish of RX, because of the reduced stacking fault energy by the addition of the alloying elements, which is discussed in the appended paper III.

The solutioning heat treatment temperature was set as 1230 °C, which is higher than the γ' solvus temperature and where the alloy is in the single γ phase region. Therefore, the formation of the γ' phase occurs during the cooling process. Another purpose of conducting solutioning heat treatment is to develop a more homogeneously distributed γ' phase and then for the following ageing process to tune the morphology and volume fraction.

Fig. 5.4. Secondary electron SEM imaging of solutioning heat-treated MAD542 superalloy for 10 min, 60 min, and 120 min. Sample preparation: metallographic polishing plus chemical etching which dissolved the γ' but γ retained. All the scale bars indicate 1 μm .

As Fig. 5.4. shows, both 10-min and 60-min solutioning heat treatments failed to promote the homogeneously distributed γ' phase. It indicates that the chemical homogenization is not accomplished within 60 min. As the red arrows indicate, the cellular pattern like features are still obtained. In the enlarged view, these cellular patterns comprise the aligned coarse and fine γ' precipitates. At the cellular boundary regions, the γ' shows a larger size than the ones at the cellular core regions. As widely reported in the investigation of single-crystal superalloy, in the as-cast condition, the γ' precipitates at the interdendrite are coarser than those at the dendritic core [218,219]. It represents that more γ' phase formers (like Al and Ti) are enriched at the interdendrite. In this work, to solutioning heat treat the LPBF MAD542 superalloy, 1230 °C for 2 h is suggested.

5.4 γ' precipitates characteristics after post-process heat treatment

Based on the argument that super- γ' -solvus solutioning temperature is the premise, different cooling methods and ageing scenarios are used for promoting the γ' phase. The as-built MAD542 superalloy was firstly solutioning heat-treated at 1230 °C for 2 h followed by 1) air cooling (AC), and 2) furnace cooling (FC). The cooling rates for AC and FC were assessed by an external thermocouple as 300 °C/min and 5-15 °C/min, respectively. After that, two

ageing steps were applied: 1) ageing #1 at 1080 °C for 4 h and 2) ageing #2 at 900 °C for 24 h. Then 4 different heat treatment cycles are introduced for each cooling methods: 1) 1230-AC/FC, 2) 1230-AC/FC-900-24h (solution + ageing #2), 3) 1230-AC/FC-1080-4h (solution + ageing #1), and 4) 1230-AC/FC-1080-4h-900-24h (solution + ageing #1 + #2).

Fig. 5.5. SEM secondary electron imaging of the γ/γ' morphologies. All the scale bars indicate 1 μm .

The morphologies of the γ' phase after different heat treatment conditions are presented in Fig. 5.5. Compared with the as-solutioning heat treated conditions, the AC results in much finer γ' than FC. After the ageing heat treatments of AC samples, the size and volume fraction of the γ' increase. Importantly, the morphologies of γ' is tuned as well. Semi-cuboidal γ' is presented in ageing #2 sample, while ageing #1 provides more cuboidal shaped γ' . After the full ageing steps #1 + #2, 'cuboidal γ' with rounded corners' [220] is developed with a very thin γ matrix channel. The volume fraction of γ' reaches up to 65% in this case. In contrast, in the FC group, the as-solutioning sample provides degraded shaped γ' owing to its slow cooling rate. After the ageing step at 900 °C, irregularly shaped γ' developed. Increasing the ageing temperature to 1080 °C, as the micrograph of 1230-FC-1080-4h sample, the circularity increased. In the sample which underwent the full 2-step ageing processes, the semi-spherical γ' formed at the ageing #1, then ageing #2 continuously promoted the formation of very fine γ' phases at the existing broad γ matrix channel. Therefore, bi-modal γ' distribution is promoted in the 1230 °C furnace cooled sample with two steps of ageing processes.

5.5 Microhardness response of post-process heat treatment

Microhardness tests were applied to the as-built and heat-treated samples, as shown in Fig. 5.6. A matrix of 3×3 indentations was used for determining the average microhardness of the sample. Owing to the excellent strengthening effect of dislocations, the as-built sample shows the mean value of 448 HV0.3, which is only less than the 1230-AC (472 HV0.3) and 1230-AC-900-24h (491 HV0.3) samples. According to the full recrystallization microstructure achieved after 2 h at 1230 °C, the dislocation strengthening could assume no longer operatively influence the hardness of the heat-treated samples. The EBSD HAGB (in black) +TB (in red) plots of the tested condition are provided close to the microhardness results,

6 Mechanical properties of MAD542

In this chapter, the results of uniaxial tensile and creep tests of LPBF MAD542 superalloy at high temperature is provided and discussed. Before the testing, the MAD542 bars were printed horizontally, thus the loading direction was perpendicular to the building direction. The as-built bars are provided in the hexagonal dimension of a side-to-side diameter of 9 mm with a length of 70 mm. The heat treatment condition was: solutioning treatment at 1230 °C for 2 h following with air cooling plus a subsequent ageing treatment at 900 °C for 24 h. It should be highlighted here that no HIP cycle was used because of the excellent post-processing crack-resist feature of this alloy.

6.1 High-temperature slow strain rate tensile property

Slow strain rate tensile (SSRT) testing at the elevated temperature was used for assessing the short-term creep performance of additively manufactured nickel-based superalloy. The nominal slow strain rates are set to be 10^{-5} and 10^{-7} /s. To assess the high-temperature strength, a uniaxial tensile test at 10^{-3} /s is conducted as well. In Fig. 6.1., the comparison of stress-strain curves of the MAD542 and IN738LC superalloys at 850 °C under various strain rate conditions are presented. The tensile curves of IN738LC are re-plotted from the appended paper I and IN738LC* results are from the authors' unpublished work. All the MAD542, IN738LC, and IN738LC* bars are LPBF processed horizontally, indicating the loading direction of the test is perpendicular to the building direction (BD), which is generally parallel to the columnar grain growth direction. The gauge diameter for the MAD542 test bars is 4 mm, while for IN738LC and IN738LC* it is 5 mm. The measured composition of IN738LC and IN738LC* is listed in Table 6.1. It should be well mentioned that the HIP was applied at 1210 °C for 4 h for both IN738LC and IN738LC* samples following with the standard heat treatment including 1120 °C solutioning for 2 h and 850 °C ageing for 24 h.

Table 6.1. Chemical composition of IN738LC and IN738LC* superalloys used for SSRT tests.

wt. %	Cr	Co	Mo	W	Al	Ti	Ta	Nb	C	B	Ni
IN738LC	15.7	8.3	1.79	2.63	3.4	3.3	1.8	0.91	0.11	0.01	Bal.
IN738LC*	15.9	8.5	1.69	2.64	3.6	3.4	1.7	0.92	0.12	<0.001	Bal.

Fig. 6.1. Engineering stress-strain curves for LPBF MAD542, IN738LC, and IN738LC* at 850 °C at nominal strain rates 10^{-3} , 10^{-5} , and 10^{-7} /s.

For all the samples, the strain rate or time-dependent mechanical responses are shown. With decreasing the tensile strain rate, the strength decreases. At 850 °C, the MAD542 superalloy shows a superior strength limit owing to its higher volume fraction of γ' precipitates. However, the lack of ductility of the MAD542 superalloy is found to be the 'Achilles' heel' for the high-temperature failure. First, the low ductility results from the strength-toughness trade-off relation [221]. Second, more importantly, intergranular cracking at this temperature takes over the dominated failure mode via grain boundary sliding. The RX of MAD542 occurs with the assistance of the promotion of twin boundary formation, rather than the common GB migration process. As the comparison of RXed grain structures between LPBF MAD542, IN738LC, and CM247LC shown in the appended paper III, fine grains (grain diameter of 16 μm) are retained in the as-solutioning-treated condition, which dramatically increases the grain boundary density. In addition, the horizontally built sample exposes the vulnerable side against the high-temperature deformation, where a higher amount of grain boundaries are transverse to the loading.

6.2 Creep property

Besides the SSRT tests by the constant displacement controlling, creep tests with constantly applied loading at 300, 200, and 150 MPa were conducted on MAD542. All the creep tests were carried out at a constant temperature of 850 °C. The creep curves are provided in Fig. 6.2. Like the SSRT test, the creep bars show very limited ductility. With increasing the applied stress from 150 to 200 to 300 MPa, the creep rupture life decreases from 51.5 to 5.3 to 0.2 h.

Fig. 6.2. (a) Creep curves for MAD542 superalloy at 300, 200, and 150 MPa conditions at 850 °C, (b) the magnified curves in (a) at the lower creep strain region.

7 Conclusion

Based on the results described above, the following conclusions could be drawn, which calls back to the research objectives in section 1.2.

1. To propose a new alloy design criterion regarding the additive manufacturability of nickel-based superalloys.

In this work, a two-parameters model for predicting the additive manufacturability of nickel-based superalloys was proposed. The fundamental of this model originally comes from the segregation behaviors of the alloying elements in superalloys. The assumption is that the as-built microstructure could be separated into the dendritic and interdendritic parts, where the composition differs from each other. In the AM processed alloys, the interdendritic region is considered as the vulnerable point which is the primary cracking (in-process cracking: solidification cracking and liquation cracking) source. On this basis, this additive manufacturability model focuses on the comparison of deformation resistance (strength) and heat resistance differences (melting temperature) between interdendritic and dendritic regions. Thus, if the interdendrite of one alloy shows close or even higher deformation and heat resistant capacity than the dendrite, the cracking susceptibility of this alloy is supposed to be lower. To plot the legacy superalloys into the additive manufacturability diagram, the predicted additive manufacturabilities between different alloys show good agreement with the experimental results.

2. To design a novel chemical composition of γ' strengthened superalloy for the LPBF process.

Based on the additive manufacturability diagram, the composition of a novel γ' strengthened superalloy, MAD542, was selected from an alloy space containing 921,600 candidates. Besides the consideration of the additive manufacturability, the undesired phase formation propensity is validated by the New PHACOMP method, and the γ' volume fraction is validated by the CALPHAD method. The LPBF processing window of MAD542 is explored by a design of the experiment matrix including 9 different printing parameters. Crack-free MAD542 parts could be LPBF processed by using the optimized parameters. Additionally, the MAD542 superalloy shows excellent recrystallization response by promoting the twin boundary formation during the solutioning heat treatment, which helps to mitigate the cracking susceptibility during post-processing treatments. After the ageing heat treatment, the volume fraction of γ' could go up to 60-65%. Different morphologies of γ' are then achieved by various heat treatment scenarios.

3. To examine the microstructure and high-temperature mechanical properties of the new alloy

By examining the high-temperature tensile properties of the heat-treated MAD542 superalloy, it shows superior strength comparing with the hot isostatic pressed and heat-treated IN738LC. The creep rupture lives of MAD542 superalloy decrease with increasing the applied load at the same temperature. However, both the results from high-temperature tensile and creep tests show that the MAD542 is lacking of ductility. On one hand, the higher amount γ' intermetallic phase embrittles the material. On the other hand, the fine-grain

microstructure of MAD542 is not the optimal form for the high-temperature mechanical properties.

8 Future work

As shown in the present work, for the MAD542 superalloy, the design approach is rational and bold, the suggested alloy is highly cracking resistant during printing and the microstructure is of great potentiality for high-temperature properties. However, the mechanical properties, especially the low ductility, is disappointing at this stage and needs further improvements.

Three directions of the future work that are worth to considering are:

1. Post-processing treatment optimization. To improve the mechanical properties, post-processing acts as a key role in controlling the microstructure.
2. Evaluate the creep performance of vertically built specimens rather than the horizontal ones. The grain boundary is vulnerable during high-temperature deformation. With the assistance of columnar grain, the vertically built specimen is expected to have better creep resistance.
3. Comparing the oxidation resistance of MAD542 with other superalloys. Oxidation resistance is another important property of superalloys for the assessment of high-temperature performance.

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Appended Papers

Paper I

Short-term creep behavior of an additive manufactured non-weldable Nickel-base superalloy evaluated by slow strain rate testing

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Acta Materialia, vol. 179, pp. 142-157, 2019

Contents lists available at ScienceDirect

Acta Materialia

journal homepage: www.elsevier.com/locate/actamat

Full length article

Short-term creep behavior of an additive manufactured non-weldable Nickel-base superalloy evaluated by slow strain rate testing

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ARTICLE INFO

Article history:

Received 1 July 2019

Received in revised form

18 August 2019

Accepted 19 August 2019

Available online 20 August 2019

Keywords:

Nickel-base superalloy

Laser processing

Creep

Grain boundary sliding

Dislocations

ABSTRACT

Additive manufacturing (AM) of high γ' strengthened Nickel-base superalloys, such as IN738LC, is of high interest for applications in hot section components for gas turbines. The creep property acts as the critical indicator of component performance under load at elevated temperature. However, it has been widely suggested that the suitable service condition of AM processed IN738LC is not yet fully clear. In order to evaluate the short-term creep behavior, slow strain rate tensile (SSRT) tests were performed. IN738LC bars were built by laser powder-bed-fusion (L-PBF) and then subjected to hot isostatic pressing (HIP) followed by the standard two-step heat treatment. The samples were subjected to SSRT testing at 850 °C under strain rates of 1×10^{-5} /s, 1×10^{-6} /s, and 1×10^{-7} /s. In this research, the underlying creep deformation mechanism of AM processed IN738LC is investigated using the serial sectioning technique, electron backscatter diffraction (EBSD), transmission electron microscopy (TEM). On the creep mechanism of AM polycrystalline IN738LC, grain boundary sliding is predominant. However, due to the interlock feature of grain boundaries in AM processed IN738LC, the grain structure retains its integrity after deformation. The dislocation motion acts as the major accommodation process of grain boundary sliding. Dislocations bypass the γ' precipitates by Orowan looping and wavy slip. The rearrangement of screw dislocations is responsible for the formation of subgrains within the grain interior. This research elucidates the short-creep behavior of AM processed IN738LC. It also shed new light on the creep deformation mechanism of additive manufactured γ' strengthened polycrystalline Nickel-base superalloys.

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1. Introduction

Nickel-base superalloys have been one of the most important alloy systems owing to its significant role in fuel-efficient turbine engines [1]. Through the past two decades, metallic additive manufacturing (AM), also known as three-dimensional (3D) printing technique has been developed rapidly [2]. This novel process promotes localized melting and solidification of a power bed to build up a part in the manner of layer by layer. It provides advanced design flexibility for net-shaped components, e.g. turbine blades with complicated internal cooling channels. This advanced cooling configuration potentially opens up the possibility for turbine blades to operate at even higher service temperatures.

However, how the AM processed components can be suitably implemented in the hot-section condition requires significant consideration from both the materials science and engineering side. Since each component in a turbine engine has its own critical service environment and been adopted to the corresponding mature material systems, and the high-temperature mechanical behavior has attracted plenty of investigations on those conventionally processed Nickel-base superalloys. Among the wide family of manufacturing techniques available, different processes e.g. conventional casting [3], directional solidification [4], cast and wrought [5], and powder metallurgy [6], can be used to produce the Nickel-base superalloy components. Correspondingly, tailored compositions have been developed to improve the critical high-temperature mechanical properties.

So far, the AM community has strongly focused on weldable superalloys, such as IN718 [7], IN625 [8,9] and Hastelloy X [10], where they share the similarity that the composition of these

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superalloys have limited content of the γ' forming elements Al and Ti. Therefore, driven by more demanding applications, the investigation of non-weldable superalloys fabricated by AM is of huge interest. In order to have sufficient creep resistance, the superalloys are expected to have a high γ' volume fraction. Some studies related AM processes for non-weldable superalloy have been reported, which revealed the printability of those superalloys by refining the AM printing strategy [11] or tune the composition [12]. While the high-temperature mechanical properties of γ' containing Nickel-base superalloy processed by AM have not received much attention, the major studies are limited to the cracking susceptibility [13], powder characteristics [14], microstructures [15] or post-process effects [16].

Among several mechanical properties, the creep resistance acts as the critical indicator of component performance under load at elevated temperatures. There were plenty of work aiming at the creep performance, creep mechanisms, and dislocation dynamics in creep of single-crystal superalloys [17–19] under constant load condition. For the γ' strengthened polycrystalline Nickel-base superalloy, the interaction between γ' and dislocation has been unveiled by characterization of substructures in depth [20,21]. The dislocation activity is highly dependent on the creep deformation conditions. Unocic et al. [22] found that microtwinning was the prevalent deformation mechanism of a disk superalloy ME3 applied on 677 °C and 690 MPa creep condition. When crept at a higher temperature (760 °C) and lower stress (345 MPa), the dislocation activity revealed a distinctly different shearing configuration, which indicates partial dislocations present stacking faults with the γ channel [23]. Instead of microtwinning and stacking fault, at high-temperature regime (above 800 °C) the dislocations bypass the γ' precipitates in a manner of thermally activated climb mechanism. Those studies majorly focus on dislocation activities, which lacks the consideration of grain microstructures. In polycrystalline materials, the grain boundaries serve as the weak points which are associated with the environmental attack (i.e. oxidation) resulting in the intergranular cracked fracture after high-temperature testing. Meanwhile, the grain boundaries of AM processed superalloy yield a zig-zag morphology [24]. These grain boundary serrations would prolong the creep life significantly [25,26]. Yet inferior creep resistance of AM processed γ' strengthened polycrystalline Nickel-base superalloy has been reported and claimed to be a consequence of the smaller grain size [27]. This raises the question of how the AM processed polycrystalline superalloys respond to creep deformation. Further investigation is required for a better understanding of the creep behavior of AM processed superalloy by comprehensive consideration on both grain structure and secondary precipitates.

Unfortunately, indiscriminately applying constant load creep experiments on AM processed superalloys makes little sense since the relationship between creep life, temperature and load is unknown and can be supposed to be far from that of conventionally processed superalloys. Thus, in this study, we use slow strain rate tensile test (SSRT) [28] to evaluate the creep performance of an AM superalloy at 850 °C, which is a typical operating temperature for components in turbine engines.

The outline of this study is to elucidate the high-temperature short-term creep behavior of the AM processed γ' strengthened Nickel-base superalloy IN738LC. Extending these studies, work has also been addressed on the tensile deformation mechanisms which are active in the plasticity and creep regime. Such studies also may shed light on the dislocation arrangement evolution during short-term creep deformation.

2. Experiment

The prealloyed IN738LC powder was gas atomized under Ar

atmosphere and supplied by Höganäs AB (Sweden). The nominal composition is given in Table 1. The virgin state powder morphology and grain microstructure were characterized using a Hitachi SU70 field emission scanning electron microscope (FE-SEM) equipped with an Oxford EBSD detector. EBSD data analysis was performed using an open-source MATLAB toolbox MTEX [29]. For the reconstruction of grain microstructure in EBSD, all the high angle grain boundaries are defined as larger than 10° misorientation. As shown in Fig. 1(a), the as-received powder has a spherical particle morphology with the diameter ranging from 5 to 80 μm . According to the inverse pole figure (IPF) map from EBSD measurements (Fig. 1(b)), every individual powder particle has a polycrystalline structure. Columnar dendritic structures formed during the solidification process in atomization can be observed in Fig. 1(c). Grain boundaries with different dendrite orientation on the powder particle surface are highlighted by white dotted lines. As reported by Duflos et al. [30], the cooling rate during gas atomization is up to 10^6 K/s to form powder particles with a diameter down to 10 μm . Taking the Scheil solidification freezing range 239 K of IN738LC (ThermoCalc, TTNi8 database) as an example, the solidification process is supposed to be accomplished within 3×10^{-4} s. Internal defects occur inside a powder particle are not surprising owing to the nature of rapid cooling. The major internal defects of the powder particles in this study are porosities, see the cross-section viewed in Fig. 1(d).

The as-received prealloyed IN738LC powder was then loaded into an EOS M290 AM printing system, equipped with a Yb fiber laser. All the test samples were built in the horizontal direction. It made the tensile bar longitudinal direction perpendicular to the building direction. As the principle directions used in this study illustrate in Fig. 2(a), the test loading direction is parallel to the powder bed build platform but perpendicular to the building direction.

After the L-PBF building process, the as-built samples were cut off from the base plate and subjected to hot isostatic pressing (HIP). The HIP has been served as an effective way to eliminate the casting defects in cast Nickel-base superalloys [31] before the development of additive manufacturing. Furthermore, for the application of AM processed components, HIP also acts as the important post-process to heal the internal defects [32], such as voids, and internal microcracks. In this study, the HIP is applied at 1210 °C for 4 h accompanied by 100–200 MPa HIP pressure. Then, a standard two-step heat treatment of IN738LC follows the HIP process. The first solution heat treatment is 1120 °C for 2 h, then cool down to 850 °C for 24 h for aging.

The microstructure of the heat treated specimen is shown in Fig. 2(b). As shown in the IPF map, the columnar grain morphology is related to the building direction, where the grain growth direction is parallel to the building direction. The IPF coloring is according to the loading direction of the test bar. In the pristine state of materials before testing, the misorientation distribution between each grain boundary (GB) is according to the inset of Fig. 2(b). The GB misorientation angle follows the axisymmetric Gaussian distribution profile, which has the mean misorientation angle to 30°. It should be noted that only a few misorientation angles lower than 10° are present, indicating that a fully recrystallized structure is formed after HIP and HT. In addition, annealing twins are barely overserved both in the IPF map and from misorientation

Table 1
The nominal composition of IN738LC used in this study (in wt. %).

Alloy	Ni	Cr	Co	Mo	W	Nb	Al	Ti	Ta	C	B
IN738LC	Bal.	15.7	8.3	1.8	2.6	0.9	3.4	3.3	1.8	0.11	0.01

Fig. 1. (a) Typical characteristics of the gas-atomized IN738LC powder, (b) EBSD IPF map indicating the polycrystalline microstructure within the powder particles, (c) surface morphology of a representative powder particle, (d) SEM back-scatter micrograph illustrating the internal defects within a virgin powder particle from a cross-sectional view.

distribution.

The heat treated samples were then machined to SSRT test bars, in which the gauge diameter is 5 mm and the gauge length 24.5 mm. Slow strain rate tensile tests were performed at 850 °C in lab air under the equivalent strain rate of 10^{-5} /s, 10^{-6} /s, and 10^{-7} /s, using an Instron 5982 testing system with 100 kN load capacity. An extensometer with two ceramic rods attached the gauge length surface was used for the engineering strain measurement. The gauge length of the extensometer was 12.5 mm.

Fractography observations were conducted using an optical microscope and SEM. Transmission electron microscopy (TEM) analysis was employed to investigate the interactions of dislocations with precipitates as well as the subgrain boundary configurations. TEM foils were cut from failure samples close to the fracture surface. Final polishing was performed using twin-jet electropolishing on a Struers apparatus. The electrolyte solution was 10% perchloric acid and 90% ethanol. The polishing temperature was -25 °C, and polishing voltage was 20 V. High-resolution (HR) TEM and scanning TEM (STEM) investigations were carried out on a FEI Tecnai G2 microscope operating at 200 kV accelerating voltage.

3. Results

The SSRT tests are performed under isothermal test condition

with a constant temperature of 850 °C. The temperature change due to the deformation is negligible, which can be assessed by:

$$\Delta T = \frac{\beta}{\rho C_p} \int_{\epsilon_1}^{\epsilon_2} \sigma d\epsilon \quad (1)$$

Where $\beta = 0.9$ by assuming 90% mechanical deformation work was converted to heat, ρ is the density of the specimen and C_p is the specific heat capacity, taken as $\rho = 7840$ kg/m³ and $C_p = 675$ J/kg for IN738LC superalloy at 1200 K [33]. As a result, the temperature rise is less than 2 K, which can be reasonably ignored. Engineering stress-strain curves of the SSRT tests are shown in Fig. 3. Three different strain rate regimes are obviously distinguished with different yield strengths (YS), ultimate tensile strength (UTS) and tensile ductility. First, for the strength part, both the YS and UTS are affected by the strain rate, in which slowest strain rate results in most reduced YS and UTS. Second, all tests showed relatively low tensile ductility, with values less than 3%. Since the tensile ductility is limited to a low value and no necking was found in the following fracture observation (Fig. 4), the strain rate is supposed to be constant beyond the elastic region. Third, the measured Young's modulus appears to have a strain-rate dependence, since Young's modulus decreases with decreasing strain rate. Since the SSRT experiments are conducted with constant displacement control, the

Fig. 2. (a) Schematic depicting the relation between building direction and loading direction, (b) grain structure characterized by EBSD, distribution of grain boundary misorientation angles shown in the inset, IPF coloring reference axis: Z (SSRT loading direction), EBSD step size: 1 μm .

Fig. 3. Engineering stress-strain curves for AM processed IN738LC at 850 °C at nominal strain rates $10^{-5}/\text{s}$, $10^{-6}/\text{s}$, and $10^{-7}/\text{s}$.

strain varies slightly during the whole tensile procedure. By calculating the strain rate at the UTS point, the creep rate can be reflected by the combination of applied stress (UTS) and strain rate (minimum strain rate at UTS). The SSRT test results are summarised in Table 2.

The fracture surfaces of the AM IN738LC superalloy after SSRT are visible in Fig. 4. All the fracture surfaces appear to have environmentally damage features, which can be seen from the darker

color. Notably, the fracture surface size remained the same comparing to the as-machined test bars, indicating the absence of necking or localized necking. The red line in Fig. 4(a1), (b1) and (c1) indicate the cross-section plane cutting direction for the following characterization. The fracture surface topography is illustrated using an optical microscope Z-direction stacking. According to the fracture surface measurement in Fig. 4(a3), (b3) and (c3), a faceted grain morphology can be observed from the obvious height differences.

More fractography observations are conducted under SEM as shown in Fig. 5. It is generally believed that the dark color shown on the fracture surface is associated with an environmentally assisted damage attack during deformation. Time-dependent oxidation-assisted cracking is the major environmental damage occurring in this study. Then, as shown in Fig. 5(a), the area of the environmental damage region increases as the tensile strain rate decreases. Furthermore, as shown in secondary electron imaging in Fig. 5, the intergranular cracks dominate the fracture surface for the specimens tested at 850 °C for all the strain rates. It should be noted that, from the top view of the fracture surface, the building direction can be one of each direction parallel to the surface plane. It infers that the building direction can be deduced by the morphology of intergranular cracks, as the arrow marked in Fig. 5(b1-3). The morphology and size of the grain microstructure are consistent with the pristine state microstructure before testing. Moreover, an oxidized layer was also observed covering the decohesive grain facets, see Fig. 5(c1-3). Although the specimens have different size of the dark blue region on the fracture surface, they all show the same high-temperature intergranular fracture mechanism.

Fig. 4. Optical microscope images showing fracture surfaces of specimen tested at (a) $10^{-7}/s$, (b) $10^{-6}/s$, and (c) $10^{-5}/s$. Higher magnification optical microscope tomography can be correlated to the intergranular crack features with the corresponding height contour coloring map. The scale bar, 50 μm .

Table 2
The SSRT results at 850 °C.

Equivalent strain rate (/s)	YS (MPa)	UTS (MPa)	Tensile ductility (%)	Young's modulus (GPa)	Minimum strain rate (/s)
10^{-5}	376	460	1.63	106	8.0×10^{-6}
10^{-6}	267	313	1.51	89	8.2×10^{-7}
10^{-7}	148	188	2.63	76	8.3×10^{-8}

Besides the fracture surface characterized by the top view, cross-sectional observation reveals the interaction between grain boundaries and internal deformation defects. In general, for creep rupture occurrence, it's caused by the growth and coalescence of voids on grain boundaries. In this study, the minimum strain rates are in the range from $8.0 \times 10^{-6}/s$ to $8.3 \times 10^{-8}/s$, in combination with high temperature ($\sim 0.7T_m$, where T_m is the melting temperature in Kelvin). As shown in Fig. 6 from the back-scattered images,

internal voids are frequently observed. Those voids form at grain boundaries and then coalesce to get linked with each and form microcracks. It is clear that the size of the voids is larger as the strain rate applied decreases. Cross-sectional internal defects were characterized by serial-sectioned images reconstruction. It provides a three-dimensional observation of voids and microcracks. An open-source software ImageJ [34] was used to reconstruct the image slices. It is not evident from serial sections tomography

Fig. 5. Detailed fracture surface observation from SEM imaging, (a) fracture overviews (b) appearance of intergranular cracks, (c) fracture surface oxidation under higher magnification SEM observations.

observations that the voids or microcracks are very localized. The voids are particularly distributed in the horizontal direction, which is transverse to the applied tensile stress (the north-south direction in Fig. 6). The morphology of those voids is observed in an olive-like shape. Basically, it is widely accepted that the void nucleation at grain boundaries is caused by condensation of vacancies under the stress [35]. After the nucleation of voids, the vacancies agglomerate and grow controlled by the micromechanics of matter transport, either by diffusion or by plasticity [36].

Of critical importance is the different strain rates applied to the IN738LC superalloy during SSRT testing, while the temperature is set constant at 850 °C. Strain rate sensitivity (m) and flow stress activation volume (V^*) serve as the two primary signatures of the deformation process. Thermally activated mechanisms contributing to plastic flow processes in metals can be evaluated using these two factors. The strain rate sensitivity can be expressed as the ratio of the incremental change in $\log(\sigma)$ to the resultant change in $\log(\dot{\epsilon})$:

$$m = \frac{\partial \log(\sigma)}{\partial \log(\dot{\epsilon})} = \frac{1}{\sigma} \cdot \frac{\partial \sigma}{\partial \ln(\dot{\epsilon})} \quad (2)$$

Based on Eq. (2), the strain rate sensitivity, m , is determined from the flow stress versus strain rate in double-log plots. From the experiment tests, m is fitted to be 0.2 with R^2 (coefficient of determination) of 99.4%.

The activation volume, V^* , provides significant information to distinguish different deformation mechanism, and can be expressed as [37]:

$$V^* = \sqrt{3}kT \left(\frac{\partial \ln(\dot{\epsilon})}{\partial \sigma} \right) \quad (3)$$

Where k is Boltzmann's constant. Substitute Eq. (2) in Eq. (3), V^* can be calculated using the determined m as:

$$V^* = \frac{\sqrt{3}kT}{m\sigma} \quad (4)$$

The apparent activation volume was determined to be $V^* = 21 b^3$, $30 b^3$, and $53 b^3$ for the $10^{-5}/s$, $10^{-6}/s$, and $10^{-7}/s$ tests, respectively, where b is the magnitude of the Burgers vector (0.257 nm at 850 °C for Nickel-base superalloy, referenced from [38]).

By considering the grain boundaries to be the major sources and sinks for vacancies, the diffusional flow rate controlling processes can be described by Nabarro-Herring [39,40], and Coble [41] creep theories. The N-H creep mechanism only considers the lattice diffusion rather than Coble creep for GB diffusion only. Hence, in fine grain materials, e.g. Ni with grain size down to the nanometer scale [42], the dislocation motion is reduced by the grain boundaries mobility. These two creep mechanisms are included in the diffusional creep regime and do not require dislocation motion [43]. By comparing the activation volume, it is widely accepted that diffusion mediated creep has extreme small activation volume in the order of the atomic spacing, e.g., less than b^3 [44], which is far much lower than the activation volume calculated by Eq. (4). This analysis indicates that the SSRT deformation at 850 °C of AM processed IN738LC is not purely attributed to lattice diffusive creep or

Fig. 6. Post-mortem serial-section tomography of internal deformation defects from a cross-sectional view. (a) SSRT tested at 10^{-5} /s, (b) at 10^{-6} /s and (c) at 10^{-7} /s.

Coble creep.

On the other hand, larger activation volume is expected for pure dislocation-mediated plastic deformation, e.g. coarse-grained Cu and Ni leading to an activation volume of about $100\text{--}1000b^3$ [45,46]. According to the following TEM observations in section 4.3, the interaction of dislocations played a significant role in the creep deformation, but in the intermediate-to-high temperature regime, grain boundary sliding is also activated. Considering the deformation mechanism map for IN738LC blades [47], the test results match the regime of grain boundary sliding (GBS) dominated creep mechanism.

4. Discussion

It is demonstrated that the L-PBF IN738LC superalloy exhibit a creep deformation behavior during slow strain rate testing at 850°C . Intergranular cracks play a vital role in the rupture process. However, these findings require further rationalization in order to better understand the physical mechanism and the corresponding substructure response. More detailed information for understanding the deformation mechanisms can be achieved by analysis of the thermally activated deformation processes.

4.1. Stored energy

As the results show in Fig. 6, creep voids nucleate on grain boundaries and then act as stress concentrations. Grain boundary sliding needs be released by an accommodative mechanism in order to impede extensive void coalescence. On the grain scale, to generate good strain compatibility and low stress concentration caused by GBS, the grain structures needs to be rearranged. Recrystallization (RX) and grain-boundary migration serve as two

major accommodative mechanisms to modify the grain size and grain morphology. First, the driving energy for RX is here calculated from the stored energy. Consequently, for the deformed specimens, the stored energy is approximated by considering the contribution from dislocation term and an interfacial term. Based on the EBSD characterization of the cross-section from the post-mortem samples, no deformation twins features were observed, which results in grain boundaries (GBs) as the major boundaries formed. Thus, the stored energy (E) can be expressed as [48]:

$$E = E_D + E_{GB} \quad (5)$$

$$E_{GB} = \gamma_{GB} S_v \quad (6)$$

Where E_D is the stored energy contribution from dislocations, and E_{GB} is the GB part. Then E_{GB} can be expressed as GB energy per unit area of the grain boundary γ_{GB} and the GB area per unit volume S_v . The γ_{GB} can be estimated using the Read-Shockley equation [49], and that the average misorientation angle θ is determined to be 30° by EBSD (Fig. 2). For the high-angle grain boundary case, the empirical extension of the Read-Shockley equation by Wolf [50], substituting θ as $\sin \theta$, was used instead:

$$\gamma_{GB} = \sin(\theta) \cdot \frac{1}{b} \cdot [E_c - E_s \cdot \ln(\sin \theta)] \quad (7)$$

Where E_c and E_s are the dislocation-core and strain field energies, when taken dislocation core radius equals the magnitude of the Burgers vector, which can be written as:

$$E_c = \frac{G \cdot b^2}{2\pi} \quad (8)$$

$$E_s = \frac{G \cdot b^2}{4\pi \cdot (1 - \nu)} \quad (\text{for tilt boundaries}) \text{ or } E_s = \frac{G \cdot b^2}{4\pi} \quad (\text{for twist boundaries}) \quad (9)$$

Where G is the shear modulus and ν is the Poisson's ratio (0.3), and it is assumed that half of the grain boundaries are tilt and half are twist. Combining these equations, γ_{GB} is calculated as 849 mJ/m², which is reasonably consistent with the reported high-angle GB energy calculated by Sangid et al. [51] for the Nickel-base superalloy U720. Moreover, the GB energy per unit volume, E_{GB} is calculated to be 0.053 MJ/m³, by using the grain shape factor S_v ($S_v = \frac{\pi}{2d}$), which is evaluated with grain size $d = 25 \mu\text{m}$ (see inset in Fig. 7(a) [52]).

The stored energy contribution from dislocations is positively correlated to the dislocation density, $E_D = \frac{1}{2}Gb^2\rho^{\frac{1}{2}}$, where $\rho^{\frac{1}{2}}$ is the dislocation density within the grain/cell interiors. Here, we can estimate the dislocation density from Taylor's equation [53]:

$$\sigma = M\alpha Gb\sqrt{\rho^{\frac{1}{2}}} \quad (10)$$

Where M is the Taylor factor (3.06), α is an empirical constant as 0.47 for non-cell forming dislocations [54]. The $\rho^{\frac{1}{2}}$ is determined to

be $9.3 \times 10^{14}/\text{m}^2$ (calculated from the SSRT results tested at $10^{-5}/\text{s}$), and E_D is calculated to be 1.25 MJ/m³. The total stored energy is then 1.3 MJ/m³, compared to the barrier to the growth of a recrystallized nucleus in γ' containing Nickel-base superalloys, which is three orders of magnitude larger than the stored energy [55]. From both the stored energy consideration and grain size observation (Fig. 7), recrystallization has barely happened during SSRT for the tested specimens.

After deformation, the grain size in post-mortem samples have similar value compared to the samples before testing, see Fig. 7. In order to reduce the uncertainty induced by the EBSD measurement, the fine grains with grain size lower than $5 \mu\text{m}$, which value is comparable to step size $1 \mu\text{m}$ in this map, were excluded from the calculation. It is worth noting that the deformed grain size distribution is also in good agreement with its counterpart before testing. It supports the calculation of store energy, which indicates that dynamic recrystallization did not appear during testing in the grains larger than $5 \mu\text{m}$. Thus, the mechanism of RX during SSRT testing can be ruled out for this study.

As mentioned above, grain-boundary migration is another possible mechanism for the accommodation of deformation. Despite the complex grain boundary micro-mechanism, the characteristic of migrated grain boundaries can be generally tracked by the grain boundaries morphology. The EBSD grain boundary maps are illustrated in Fig. 7(a) and (b). The AM processed superalloys in this study appear to have a serrated GB morphology. To normalize the GB morphology, the grain shape factor, F , can be defined as the

Fig. 7. High angle grain boundaries map measured by EBSD: (a) sample before testing, (b) after testing at $10^{-7}/\text{s}$. Insets indicate the grain size distribution for each sample. Step size: $1 \mu\text{m}$, scale bar: 0.1 mm . And grain shape factor distribution in (c) sample before testing, (d) after testing at $10^{-7}/\text{s}$.

grain boundary perimeter P_{GB} divided by the equivalent perimeter P_E , as $F = \frac{P_{GB}}{P_E}$.

The grain shape factor distribution is shown in Fig. 7(c) and (d). The F value before and after SSRT is larger than 1, due to the serrated GBs. The mean F value is 1.81 and 1.77 for the grains before and after testing, respectively, and thus very similar for the two conditions. Additionally, by comparing the post-mortem GB morphology in EBSD map with the counterpart in the pristine state, no evidence of GB migration was found. In other words, it supports that GB sliding is not accommodated by GB migration to any large degree. Although in other metallic materials system during creep, such as Titanium alloys [56], the migration of GB can be one of the most significant accommodating GB sliding, which leads to an obvious grain structure change. However, in this study, the GB migration is effectively hindered by the serration shaped GB.

4.2. On the role of dislocation motion in SSRT deformation mechanism

Based on the discussion in section 4.2, the grain structure of the AM processed IN738LC superalloy is stable during SSRT, giving no clear indication that recrystallization or grain boundary migration occur.

Micrographs representative of the deformation substructure after testing at 850 °C are presented in Fig. 8. It worth mentioning

that, before SSRT testing, 1210 °C HIP was performed for 4 h and followed by standard heat treatment. These post-processing treatments are believed to highly reduce the dislocation density to a lower level [57,58]. We expect that the dislocations observed in Fig. 8 are responded to the SSRT deformation process. In the regime of strain rate at $10^{-5}/s$, the dislocations appear in the channels between γ/γ' as in Fig. 8(a). Note that dislocation loops are left around the γ' particles. It shows relatively lower deformation activity than the samples after testing at $10^{-6}/s$ and $10^{-7}/s$. According to the substructures in Fig. 8, few shearing dislocations were found left within γ' . When ordinary dislocations shear ordered γ' precipitates, they must travel in the manner of dislocation pairs to keep the order. When the size of γ' reaches a critical size, e.g., approximately 10–20 nm in planar diameter for Nickel-base superalloys, the resistance to dislocation shearing decrease. On the other hand, compared with dislocations penetrating γ' precipitates, the necessary stress for a dislocation to bow around these particles is lower. The required resolved shear stress for dislocation bowing was proposed by Orowan [59] as:

$$\tau_{Or} = \frac{Gb}{L_s} \quad (11)$$

Where L_s is the spacing between precipitates. For spherical particles, the L_s is determined by γ' volume fraction and the mean planar diameter d_s as [60]:

Fig. 8. BF-STEM images showing the dislocation substructure after SSRT at (a) $10^{-5}/s$, (b) $10^{-6}/s$, and (c) $10^{-7}/s$, the scale bar is 500 nm.

$$L_s = \sqrt{\frac{8}{3\pi f}} d_s - d_s \quad (12)$$

The volume fraction of γ' is determined to be 45% at 850 °C by ThermoCalc® calculations (TCNi8 database) and the mean γ' diameter is estimated to be 300 nm based on image analysis of TEM images. It results in a value for τ_{or} of 94, 79, and 67 MPa for strain rates of 1×10^{-5} , 1×10^{-6} , and 1×10^{-7} /s, respectively. By estimating the relationship between shear stress and ultimate tensile strength (UTS) [61], the shear stress can be considered as UTS divided by Taylor's factor. It indicates that the applied uniaxial tensile stress can drive dislocation looping around γ' particles. It supports the dislocation configuration morphology observed in Fig. 8.

As shown in Fig. 8(b), with the strain rate decreasing to 10^{-6} /s, the dislocation density reaches the highest value among the three test conditions. The dislocation density is reflected by the plastic deformation level at this strain rate condition, but no effective dislocation recovery process is operative that resulting in the embrittlement of this sample, which is agreed with the lowest ductility in the stress-strain curves in Fig. 3. It can be found that the dislocations are highly tangled within the γ channel. Besides the dislocation loops surrounding the γ' precipitates, the stair-like dislocation configuration crossing the γ' particles is attributed to wavy slip caused by dislocation cross slipping within the γ' obstacles. Similar substructures are reported for other Nickel-base superalloys crept above 700 °C [62].

For the Nickel-base superalloy strengthened by large γ' precipitates (~300 nm) [60], the thermally activated cross-slip of mobile dislocations could occur. Based on the postulation of Bonneville and Escaig [63], the activation energy and activation volume for cross-slip in FCC materials can be approximated using Escaig stress model.

In short, the activation volume for cross-slip in FCC materials can be expressed as [64]:

$$V^* = Ab\lambda_\sigma d_\sigma \quad (13)$$

Here A is a constant derived as $1.55 \times \frac{\sqrt{3}}{12}$, λ_σ is a typical length of the partial dislocations bending towards the constriction point under Escaig stress σ_{Esc} , and d_σ is the width between the pair of dissociated partial dislocation under σ_{Esc} . Then λ_σ and d_σ can be written by multiplying the stress-related factor β to equilibrium partial dislocation bending length λ_0 and equilibrium partial dissociation width d_0 as:

$$\lambda_\sigma = \beta\lambda_0 \text{ and } d_\sigma = \beta d_0 \quad (14)$$

Where:

$$\beta = 1 + \frac{\sqrt{3}b}{6\gamma} \sigma_{Esc} \quad (15)$$

The Escaig stress here is estimated as $\sigma_{Esc} = 2\gamma/b$ [65], here γ is the stacking fault energy (taken as 20 mJ/m² for highly alloyed Nickel-base superalloys [66]).

$$\lambda_0 = 1.5d_0 \quad (16)$$

$$d_0 = \frac{Gb^2}{24\pi\gamma} \frac{2-3\nu}{1-\nu} \quad (17)$$

Then, the activation volume induced by the cross-slip is calculated to be ~16 b^3 , which is within the same order of magnitude as the activation volume derived in section 4.1 ($V^* \sim 20\text{--}50 b^3$).

This kind of dislocation configuration supports our activation volume calculation for cross-slip from substructure characterization. It has been suggested that the dislocation loop segments are driven into the narrow γ channels and then the permeating dislocation deposit segments at the γ/γ' interfaces [67]. On the other hand, the cross-slip features can be observed from non-planar deformation bands i.e. wavy slip, which is associated with cross-slipping screw dislocations. In the investigation of Phillips et al. [68] on a polycrystalline precipitation-strengthened superalloy, the wavy slip shows non-planar features which are believed to be caused by the unequal length of cross-slipping dislocations being in conjugate slip planes. The TEM images from their work [69] also provide solid evidence for the cross-slipping behavior.

Besides the Orowan loops and wavy slip lines, some subgrain boundaries are formed and can be distinguished from the array of dislocation through the continuous γ channel at the slowest strain rate regime of 10^{-7} /s. In Fig. 8(c), the morphology, configuration and arrangement of dislocations are revealed in specimen tested under 10^{-7} /s at 850 °C. Based on the figure, the dislocations have the following characteristics: (i) they are relatively long with the length in the scale of hundreds of nanometers; (ii) several dislocations loops appear over γ' ; (iii) jogged dislocations are formed; (iv) there is a lack of tangled dislocation; (v) there are grown-in subgrain boundaries formed through the γ matrix channel. We discussed the effect of forming the subgrains in detailed in the next section.

4.3. On the influence of subgrain formation on SSRT

After testing at 10^{-6} /s, it can be seen that highly tangled dislocations have begun to form and filled the matrix channel, as shown in Fig. 9(a). Subgrains here is defined as cells consisting of well-organized boundaries rather than tangled wall structures or dislocation networks. These square-like dislocation networks sit close to subgrain boundaries since two sets of dislocations with orthogonal Burgers vectors do not strongly react. The formation of dislocation networks can effectively cause softening, which is consistent with the lack of strain hardening behavior shown in the stress-strain curves for the specimen tested at 10^{-6} /s and 10^{-7} /s. The rearrangement of dislocation substructures into lower-energy dislocation network configurations decrease the resistance to dislocation motion. Carroll et al. [70] also reported a similar softening behavior of a Nickel-base superalloy in the regime of creep-fatigue interaction deformation.

It's an interesting comparison of the dislocation density and distribution between the substructure after testing with strain rates of 10^{-6} /s and 10^{-7} /s. In general, the lower creep rate results in further refinement of the dislocation arrays around subgrains boundaries and a decreased dislocation density within the subgrain interiors. Moreover, subgrain boundaries also emerge. Although the dislocations underwent a rearrangement to form subgrain boundaries as shown in Fig. 9(b), the dislocation density is still relatively high in the boundary regions. A representative section of a subgrain boundary is highlighted by the white dash-line overlapped with dislocation lines marked in red in Fig. 9(b). The dislocation density along this subgrain boundary section ρ_{SGB} can be estimated using the following equation introduced by Bailey and Hirsch [71] as:

$$\rho_{SGB} = \frac{4}{\pi} \frac{R_p}{A_r h} \quad (18)$$

Where R_p is the total projected length of dislocation line in the area A_r (the white dash-line area in Fig. 9(b)), which can be measured from STEM images and h is the transparent area thickness of the TEM thin foil (taken as 50 nm). The ρ_{SGB} is determined to be

Fig. 9. BF-STEM images showing dislocation morphology after testing at (a) 10^{-6} /s with dislocation networks shown in the inset, and (b) 10^{-7} /s with highlighted subgrain boundaries within the white dash-line. The scale bar is 200 nm.

$2.8 \times 10^{15}/\text{m}^2$ in this case. It indicates that the SGB region has around one order of magnitude higher density of dislocations than the dislocation density within the interior of the grains as calculated before.

These results are consistent with the experimental observation that the slowest strain rate specimen shows a strain softening behavior according to the stress-strain curve. The rearrangement of dislocation to form subgrains during the relatively longer test duration reduces the corresponding stress.

For SSRT tests with the nominal strain rate of 10^{-7} /s, the damage sites close to the fracture surface are illustrated in Fig. 10(a). As shown in Fig. 10(b), according to the IPF map of an individual grain, the crystallographic orientations vary from one location to another. The intragranular misorientation distribution within a single high angle grain boundary is shown in Fig. 10(c). Taking the mean crystallographic orientation as the reference, the intragranular misorientation angle can be expressed as:

$$\text{mis}(\mathbf{o}_i, \mathbf{o}_0) = \mathbf{o}_i^{-1} \mathbf{o}_0 \quad (19)$$

Where $\mathbf{o}_i$ is the crystal orientation for i^{th} hit point, and $\mathbf{o}_0$ is the mean orientation from every hit point in a grain. From Fig. 10(c), one can see that the misorientation map divides into several subgrains with similar misorientation angles. Meanwhile, the orientation data is used for the local misorientations analysis to highlight subgrain boundaries. The Kernel Average Misorientation (KAM) mapping is illustrated in Fig. 10(d), in which each scan point has been assigned to a value equal to the average of the misorientation calculated between that point and its nearest 8 neighbors [72]. Different from intragranular misorientation, KAM reveals the local misorientation distribution. It clearly shows that higher KAM values are formed along the subgrain boundaries. The KAM in a subgrain interior is close to 0° , however at subgrain boundaries up to 8° . It is also found in Fig. 10(d) that the interception points between subgrain boundaries and high angle grain boundaries are often consistent with the small curvature positions along the serrated grain boundaries. The KAM can be reflected as the boundaries of

subgrains, where geometrically necessary dislocations (GND) are arranged in arrays. Under the assumption that the misorientation angle θ is caused by a series of twist subgrain boundaries, the GND density ρ_{GND} is related to θ as [73]:

$$\rho_{\text{GND}} = \frac{2\theta}{ub} \quad (20)$$

Where u is the unit length of step size and b is the magnitude of the Burgers vector as usual. As shown in Fig. 10(d), the first order neighbor KAM, which is calculated from the average misorientation of nearest 8 EBSD data spots, was chosen as the measure for the local misorientations. The mean KAM value of those subgrain boundaries is around $3\text{--}5^\circ$, from which the ρ_{GND} is approximated to be $2.0\text{--}3.4 \times 10^{15} \text{ m}^{-2}$. This result is consistent with the dislocation density measured from subgrain boundaries in the BF-STEM image (Fig. 9(b)). Within a single grain, it has been suggested that subgrain boundaries with GNDs can occur from dislocation reactions to accommodate differences in slip or cross-slip. Furthermore, the morphology of the subgrains is typically elongated in one direction, which means that the growth of the subgrains is direction dependent.

Fig. 10(e) shows an example of a subgrain boundary analysis derived from the information in Fig. 10(d). In the pole figure in Fig. 10(e), three low indexed crystallographic planes $\{100\}$, $\{110\}$ and $\{111\}$ are illustrated. The inferred subgrain boundary is oriented normal to $[001]$ or parallel to (001) plane in the example. In other FCC polycrystalline alloy systems deformed at elevated temperature, e.g. Al alloys, non-octahedral slip can happen, leading to the (001) type cube texture [74]. For SSRT in the 10^{-7} /s regime, the movement of dislocations composes cross-slip, non-octahedral slip as well as dislocation climb, rendering the elongated subgrains.

Based on the EBSD observation of subgrain in Fig. 10, further investigation can be done in order to reveal the dislocation configurations. HR-TEM images of the subgrain boundary region are illustrated in Fig. 11. As shown in Fig. 11(a), the FCC matrix is highlighted on the upper right corner, and the subgrain boundary is

Fig. 10. (a) EBSD IPF map from the cross-sectional view close to the fracture surface, the highlighted grain is shown in (b), the IPF map of an individual grain at the damage sites with the IPF color bar, reference axis: Z, (c) the misorientation map indicate the subgrains within the same grain, and (d) KAM distribution map with the subgrains boundaries marked out, and (e) the stereographic projection of some of the subgrains in (d). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

in the lower left region. The FCC atomic structure is shown in Fig. 11(c1), the d-spacing of (010) lattice planes is measured to be 0.35 nm, which is consistent with the corresponding d-spacing in a Nickel matrix. The FFT pattern from the same region in Fig. 11(c1) is shown in Fig. 11(c2). It shows one set of fundamental reflections from the γ matrix without any other reflections from the overlapping phases. For the subgrain boundary part in Fig. 11(a), the presence of washed out stripe features indicates that the periodic contrast is associated with screw dislocations. Enlarged details are shown in Fig. 11(b1) and the corresponding FFT diffraction patterns can be seen in Fig. 11(b2). The intensity of crystal planes including eight peaks along the 1.61 nm length is found in the inset in Fig. 11(b1) lower left corner. The d-spacing between each plane is calculated to be approximately 0.2 nm, which is in good agreement with the d-spacing of {111} plane in Nickel-base superalloys. The two sets of {111} spots in Fig. 11(b2) have a 12° rotation angle caused by arrays of screw dislocations. Such an arrangement of screw dislocations leads to a change in the grain boundary angle θ , between neighboring grains, as estimated by the Frank-Bilby

equation [75]:

$$\frac{b}{d} = 2\sin \frac{\theta}{2} \quad (21)$$

Here b is the magnitude of the Burgers vectors as usual, and d is the average dislocation spacing. Based on Eq. (20), d is calculated to ~ 1.22 nm. Here, the dislocation spacing measured from Fig. 11(d) is 1.2 nm. Meanwhile, as schematic two arrays of rotated planes (red and blue lines) with an angle 12° shown in Fig. 11(d), the black dot-lines match the position of faded screw dislocations.

To summarize, the short-term creep deformation of the AM processed IN738LC superalloy is combined with environmentally-assisted grain boundary damage and dislocation-precipitate interaction, as illustrated in Fig. 12. When the temperature reaches the high-temperature regime, this is 850°C in this study, grain boundary sliding (GBS) act as the most dominant deformation process. Owing to the nature of serrated grain boundaries introduced by the AM process and following post-treatment,

Fig. 11. HR TEM image of a representative subgrain region in the specimen after 10^{-7} /s SSRT testing, (a) location of γ channel, (b1) enlarged image in the red box in (a), (b2) the corresponding FFT pattern in (b1), (c1) enlarged image in the blue box in (a), (c2) the corresponding FFT pattern in (c1), (d) enlarged image shows the repeated washed-out stripe feature. Zone axis is close to $[10\bar{1}]$. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

intergranular voids homogeneously nucleate at GBs comparing with well-recrystallized equiaxed grain structure which has relative straight GB lines. Consequently, these intergranular voids coalesce and get linked to form microcracks which cause final failure. Thus, grain boundary sliding plays a significant role in controlling the creep deformation. In general, GBS is accommodated by the rearrangement of the grain structure, such as GB migration or even recrystallization. However, the grain boundary structures before testing remain unchanged in the post-mortem specimen which is not consistent with of GB migration. By calculating the stored energy, recrystallization can also be ruled out when comparing with the driving energy. Dislocation activities act as the operative GBS accommodation process, which is associated with the interaction between dislocations and precipitates. As a precipitate strengthened Nickel-base superalloy, the γ' phase provides AM processed IN738LC strength at high temperature. In this study, the dislocations loop around γ' phase during deforming. Dislocations also bypass γ' by cross slipping with the assistance of screw dislocation segments. With the deformation becoming severer, subgrain boundaries form in γ matrix by rearrangement of arrays of dislocations in order to lower the energy from heavily tangled dislocations.

5. Summary and conclusions

By using the slow strain rate tensile testing approach with different strain rates corresponding to 10^{-5} /s to 10^{-7} /s, we systematically investigated the short-term creep behavior as well as creep deformation mechanism of a laser powder-bed-fused IN738LC superalloy. The following specific conclusions can be drawn:

- (i) Intergranular cracks have been observed in the AM IN738LC specimen after SSRT failure. Environmental damage during testing at 850 °C is expected to occur along the fracture surface. As revealed by 3D reconstruction from serial section cross-sectional SEM images, the voids and microcracks along grain boundaries are greatly affected by the strain rate condition. Growth of grain boundary voids leads to microcracks and final fracture.
- (ii) Grain boundary sliding is shown to be the dominant process for the creep deformation in the present study. However, the grain boundary of AM IN738LC provides stable signature which maintained its integrity after testing. The grain boundary sliding is not accommodated by the evolution of

• SSRT deformation mechanism

• GBS accommodation mechanism

Fig. 12. Schematic illustration of the AM processed IN738LC SSRT deformation mechanism. Intergranular voids and microcracks happen in the SSRT deformation process, which is caused by grain boundary sliding (GBS). Dislocation motion assists GBS in the manners of cross-slipping, Orowan looping and forming subgrain boundaries by screw dislocation segments.

grains structure, which is convinced by both microstructure characterization and stored energy calculations.

- (iii) Dislocation activity accommodates grain boundary sliding in the manner of interaction between γ' precipitates. By comparing the substructure observation and calculation of shear stress and activation volume, dislocations bypass γ' particles by Orowan looping and cross slipping.
- (iv) At the slowest strain rate 10^{-7} /s used in this study, subgrain boundary formed in the γ channels by localized high density of dislocations up to $2.8 \times 10^{15}/\text{m}^2$. These subgrains have a {011} preferred orientation. These subgrain boundaries are composed of arrays of rearranged screw dislocation segments. The formation of subgrain boundaries results in the lack of work hardening.

Acknowledgments

This work has been performed with support from the Swedish Governmental Agency for Innovation Systems, (Vinnova grant 2016-05175 and 2018-00804). Also, the faculty grant SFO-MAT-LIU#2009-00971 from Linköping University is acknowledged.

Centre for Additive Manufacture - Metal (CAM2) is acknowledged. The authors acknowledge Prof. E. Hryha from Chalmers University of Technology, Dr. H. Brodin from Siemens Industrial Turbomachinery AB, Dr. S. Bengtsson from Höganas AB, Dr. A. Eklund from Quintus Technologies AB and K. Minet from EOS Finland Oy for fruitful discussions. J. Xu and D. Deng acknowledge Dr. R. Boyd for TEM assistance. J. Xu acknowledges the suggestions from X. Wang of Central South University.

All data included in this study are available from the corresponding author on reasonable request.

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On the strengthening and embrittlement mechanisms of an additively manufactured Nickel-base superalloy

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Materialia, vol. 10, 2020

Full Length Article

On the strengthening and embrittlement mechanisms of an additively manufactured Nickel-base superalloy

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ARTICLE INFO

Keywords:

Laser powder-bed-fusion
 Nickel-base superalloy
 Mechanical property
 Cellular structure
 γ' phase

ABSTRACT

The γ' phase strengthened Nickel-base superalloy is one of the most significant dual-phase alloy systems for high-temperature engineering applications. The tensile properties of laser powder-bed-fused IN738LC superalloy in the as-built state have been shown to have both good strength and ductility compared with its post-thermal treated state. A microstructural hierarchy composed of weak texture, sub-micron cellular structures and dislocation cellular walls was promoted in the as-built sample. After post-thermal treatment, the secondary phase γ' precipitated with various size and fraction depending on heat treatment process. For room-temperature tensile tests, the dominated deformation mechanism is planar slip of dislocations in the as-built sample while dislocations bypassing the precipitates via Orowan looping in the γ' strengthened samples. The extraordinary strengthening effect due to the dislocation substructure in the as-built sample provides an addition of 372 MPa in yield strength. The results of our calculation are in agreement with experimental yield strength for all the three different conditions investigated. Strikingly, the γ' strengthened samples have higher work hardening rate than as-built sample but encounter premature failure. Experimental evidence shows that the embrittlement mechanism in the γ' strengthened samples is caused by the high dislocation hardening of the grain interior region, which reduces the ability to accommodate further plastic strain and leads to premature intergranular cracking. On the basis of these results, the strengthening micromechanism and double-edge effect of strength and ductility of Nickel-base superalloy is discussed in detail.

1. Introduction

Acting as some of the most significant engineering alloys for high-temperature applications, e.g. hot section components in turbine engines, the Nickel-base superalloys are well-performed under cyclic [1] and constant [2] loading condition at elevated temperatures. Nickel-base superalloys are primarily reinforced by a secondary phase, the ordered $L1_2$ γ' intermetallic phase embedded in the continuous disordered FCC austenite γ matrix phase [3]. In the γ - γ' Nickel-base superalloys, the volume fraction of γ' phase could be as high as 50% for polycrystalline superalloys [4] and single crystal superalloys used for power generation [5] and even up to 70% for desired creep-resistance in single crystal superalloys for aero engine applications [6]. However, due to the dual-phase microstructure configuration, the γ' strengthened superalloys face the conflicting nature of the strength-ductility paradigm, i.e. the precipitation hardening benefit is based on the cost of ductility. In many respects, the γ - γ' Nickel-base superalloys act as the “classical” two-phase alloy systems.

Recently developed additive manufacturing (AM, known as three-dimensional printing as well) techniques, e.g. laser powder-bed-fusion (L-PBF) [7], open up new opportunities for the fabrication of Nickel-base superalloys, with almost no design limitations. Owing to the net-shape forming nature, the AM techniques attracts a large amount of interest with regard to component geometrical complexity which permits the use of complicated internal structures for enhanced engineering reliability and energy efficiency in high-temperature applications [8]. Indeed, plenty of research has been conducted on well-known Nickel-base superalloys, such as Inconel 718, Inconel 625 and Hastelloy X, to investigate their printing strategies [9], microstructural evolutions [7], anisotropic mechanical behavior [10] and high-temperature performance [11]. However, the above-mentioned Nickel-base superalloys have limited amount of strengthening phase, e.g. the volume fraction of γ'' strengthening phase in forged Inconel 718 is normally less than 20% with the grain size smaller than 100 nm [12], or majorly strengthened by solid solution atoms, e.g. the Inconel 625 [13] and Hastelloy X [14] Nickel-base superalloys.

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Received 5 March 2020; Accepted 11 March 2020

Available online 14 March 2020

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Importantly, L-PBF can provide an almost γ' -free microstructure in γ - γ' Nickel-base superalloys, compared with its post-processing condition [15,16] or the as-manufactured counterparts by the conventional metallurgical routes [17,18]. As reported by Kunze et al. [19], the as-built IN738LC superalloy (γ' volume fraction up to 43% after solution treatment [20]) by selective laser melting does not show any γ' under the observation by scanning electron microscopy. Even in the case of high γ' fraction Nickel-base alloys, e.g. CM247LC (γ' volume fraction up to 65% [21]), the as-built CM247LC only got 1.5 vol% nano-sized γ' secondary phase [22]. Alongside this net-shape or near-net-shape processing benefit from manufacturing prospects, L-PBF provides large thermal gradient and rapid cooling rates (up to hundreds of thousand K/s [23]) owing to the localized melting [24]. Several desired microstructural features can be achieved, solidification dendrites are refined [25] and dislocations are favored to form [26].

Inspired by the unique hierarchical microstructure promoted by L-PBF and the dual-phase configuration nature of γ' strengthened Nickel-base superalloys, the microstructural characteristics within the L-PBF material potentially holds the key to overcome the strength and ductility dilemma. We aim to propose a mechanical performance enhancement of the metallic L-PBF built components. In addition, this study will also shed new lights on the strengthening mechanism of the conventional Nickel-base superalloys regarding the heterogeneous microstructural aspects, which may be further implemented to design more suitable post-process treatment after 3D printing of high strength Ni-based superalloys.

2. Experiment

The studied Nickel-base superalloy was designated as IN738LC with a modified composition for L-PBF (Ni–16.2Cr–8.5Co–3.5Al–3.5Ti–2.4W–1.8Mo–1.7Ta–1.1Nb–0.1C–0.01B), which is a commercial alloy commonly used for turbine blades and vanes. The IN738LC powder was supplied by Electro Optical Systems Finland Oy. Samples were horizontally built by laser powder-bed-fusion using an EOS M 100 (EOS GmbH) 3D printing system. The processing parameters of L-PBF were modified to reduce the microcracks as much as possible according to the basis of a design of experiments [27]. The laser power was set to 135-watt with a laser spot size of 40 μm and scanning speed of 1150 mm/s. A powder layer of 20 μm thickness and 60 μm hatch distance has been used. All the test samples were horizontally built in a stripe pattern. Between each layer, the scanning direction was rotated 67°. The longitudinal direction of the tensile bar was perpendicular to the building direction. For a fair comparison, the tensile properties of the as-built samples, denoted as AB, were compared to post-processing samples from the same batch. The following two post-processing scenarios were implemented: (1) hot isostatic pressing (HIP) at 1000 °C and standard heat treatment (HT) for IN738LC, denoted as 1000HIP; (2) HIP at 1210 °C and standard HT, denoted as 1210HIP. The necessary HIP after additive manufacturing effectively heal the microcracks and protects the component from post-processing induced cracking [28]. The internal structure of the three conditions was near-crack-free in the AB sample (crack density: $93 \pm 33 \mu\text{m}/\text{mm}^2$ with microcrack length: $33 \pm 10 \mu\text{m}$) and crack-free in the HIPed samples with only some remaining isolated porosities (see Fig. S1 in Supplemental material). In order to introduce γ' phase and grain size differences, we intentionally set the HIP temperature at 1000 °C and 1210 °C, which are lower and higher, respectively, than the γ' solvus temperature (~ 1150 °C for IN738LC). The IN738LC standard HT combines solution at 1120 °C for 2 h and aging at 850 °C for 24 h.

The tensile testing was performed at a nominal strain rate of $10^{-3}/\text{s}$ using an Instron 5582 testing system at room temperature. Round tensile bars with a gauge length of 25 mm and a gauge diameter of 5 mm were prepared by machining from $\Phi 13 \times 80$ mm AM cylinder bars. An extensometer was used to measure strains in the elastic and elastoplastic regime (till 5%). The detailed pristine microstructures and fracture surfaces were characterized using a Hitachi SU70 field emission

scanning electron microscope (FE-SEM) equipped with an Oxford electron backscatter diffraction (EBSD) detector. EBSD data was analyzed using an open-source MATLAB package MTEX [29]. Metallographic etching was performed on 1000HIP and 1210HIP samples to enhance the observation of γ' phase. The Marble's reagent was used to dissolve γ' phase by immersion etching for 10–15 s.

Deformation substructures were observed by scanning transmission electron microscopy (STEM) on thin foils prepared from the gauge section of tested tensile bars. Suitable samples were initially ground to $\sim 60 \mu\text{m}$, and then punched into $\Phi 3$ mm circular sheets. The twin-jet electro-polishing was conducted at the polishing temperature of -25 °C under 10% perchloric acid and 90% ethanol electrolyte solution. The STEM investigation was performed on a FEI Tecnai G2 microscope operated at 200 kV. Images were taken using an annular detector operated at various camera lengths, high angle annular dark field images with a camera length of 140 mm, dark field 350 mm and bright field 2100 mm.

The nanoindentation hardness tests were carried out at room temperature on the UMIS Nanoindentation system with a Berkovich tip. The surface of nanoindentation test samples were carefully polished using Struers OP-U colloidal silica suspension to reduce the effect of surface hardening layer. The nanohardness test was performed on the load-controlled mode. The loading rate was 1 mN/s and the peak load was 20 mN. The nanoindentation interval spacing was 10 μm for AB and 1000HIP samples which have fine grain structure but 20 μm for coarse grain structured 1210HIP sample.

3. Results

3.1. Microstructure of L-PBF IN738LC

The pristine microstructures of the undeformed samples under the three different post-treatment conditions are illustrated in Fig. 1. The grain microstructure of the AB sample is columnar shaped (Fig. 1(a)), in which the fine grains are generally oriented along the building direction. In the post-thermal treated samples, the grain structures are distinctly different. Owing to the applied HIP temperature, the 1000HIP sample (Fig. 1(b)) has similar grain structures and grain morphology as the AB sample (Fig. 1(a)), while the 1210HIP sample has a totally different grain configuration. Strong grain growth during super-solvus HIP treatment resulted in a relatively faceted grain morphology (Fig. 1(c)). The average grain size of the as-built sample is 44 μm , and after HIP at 1000 °C and HT, the average grain size slightly grows to 50 μm . After HIP at 1210 °C and HT, the average grain size obviously grows to 154 μm . Here, the grain size is derived from the square root of grain area which surrounded by high angle grain boundaries (GBs) with misorientation higher than 10° , from EBSD measurements.

Beyond the grain structures, the high magnification SEM backscattered electron image shows that within the grains of the AB sample (Fig. 1(d)), the interior microstructure can be identified as a sub-micron sized cellular structure with a measured average size $d_c = 423$ nm. These cellular structures share the comparable size with the primary dendrite arm spacing λ_1 , which is negatively correlated with the cooling rate, $\dot{T}$, as $\lambda_1 \propto \dot{T}^{-0.3}$ [30]. Due to the rapid solidification condition of L-PBF, i.e. up to 10^6 K/s [31], these cellular structures are restricted to sub-micron size. Meanwhile, these cellular structures induced by L-PBF can be commonly found in different alloy systems in the as-built state. For example, in this study IN738LC has similar cellular size to a selective laser melted CoCrFeNiMn high entropy alloy [26] and 316 L stainless steel [32]. Messé et al. [33] reported that the cellular boundaries are composed by high density of dislocations as a feature of the L-PBF process in as-built IN738LC superalloys. Similarly, Qiu et al. [34] reported the cellular band with large amount of dislocation in L-PBF IN738LC.

The γ - γ' dual phase microstructural configuration of 1000HIP and 1210HIP are shown in Fig. 1(e) and Fig. 1(f) by SEM secondary electron imaging, respectively. Both 1000HIP and 1210HIP have γ' phase of divergent sizes and morphologies. Obviously, the characteristics

Fig. 1. Microstructural images of pristine microstructures of the undeformed samples in this study, EBSD-IPF coloring maps (reference axis parallel to loading direction) and their corresponding pole figures of (a) AB sample, (b) 1000HIP sample, (c) 1210HIP sample, (d) SEM backscattered electron (BSE) image of AB sample showing the sub-micron size cellular structure, (e) SEM secondary electron (SE) image of 1000HIP sample showing the spherical γ' precipitates and (f) SE image of 1210HIP sample showing the cuboidal γ' precipitates.

of γ' phase are easily distinguished, as the sub-solvus HIP treatment (1000HIP) results in moderate-size γ' but the super-solvus HIP treatment (1210HIP) renders coarser γ' . By image analysis, it is observed that the 1000HIP sample is composed of γ' phase with a spherical shape ($d_{\gamma'}=180$ nm and an estimation volume fraction of $f_{\gamma'}=35\%$), as in Fig. 1(e). In contrast, under the super-solvus HIP temperature, the cuboidal γ' ($d_{\gamma'}=400$ nm and volume fraction of $f_{\gamma'}=45\%$) are formed in the 1210HIP sample, as shown in Fig. 1(f). Besides the γ' phases, carbides are observed in post-thermal treated samples. In 1000HIP sample, Cr- and Mo- enriched $M_{23}C_6$ carbides are occasionally found at grain boundaries (Fig. S2 in Supplemental information), while Ti-, Nb- and Ta- enriched MC carbides were observed at both grain boundaries and grain interior in 1210HIP sample (Fig. S3).

In addition to the coarse grain structure in the 1210HIP sample, the crystallographic characteristics of the cuboidal γ' are further illustrated by EBSD in Fig. 2. Here, two sub-areas with the orientation close to [001] (Fig. 2(b)) and [011] (Fig. 2(c)) are selected from the inverse pole figure (IPF) coloring map. The morphology of these coarse γ' phases are shown in Fig. 2(d and e) with the corresponding pole figures of the sub-areas. It can be seen that the edge of the cuboidal γ' are aligned with the trace of {100} crystallographic planes, leading to the {111} crystallographic plane traces to appear in the diagonal direction of the γ' precipitates. Potentially affecting dislocations movement with respect to the specified γ' phase morphology along specific crystallographical planes, which will be further discussed in Section 4.1.

3.2. Uniaxial tensile response at room temperature

The mechanical response of the L-PBF manufactured IN738LC samples are compared in Fig. 3, depicting the strengthening influence of the different microstructures. The mechanical properties including 0.2% offset yield strength (YS), ultimate tensile strength (UTS) and elongation (EL) -to-fracture are summarized in Table 1. All the tested engineering stress-strain curves are available in Fig. S4 in the Supplementary information. As shown in the engineering stress-strain curves of the representative specimens from different treatment scenarios (Fig. 3(a)), a distinctive difference in mechanical behavior can be observed. Firstly, the 1000HIP sample exhibits the highest yield strength, up to approxi-

Table 1
The mechanical properties of AB, 1000HIP and 1210HIP L-PBF IN738LC superalloy.

Alloys	0.2% YS (MPa)	UTS (MPa)	EL (%)
AB	1075.5	1360.5	18.9
	1093.0	1367.8	18.9
1000HIP	1339.1	1472.1	4.5
	1296.5	1449.5	4.0
	1285.2	1462.5	4.6
	1300.6	1383.0	3.0
	1309.7	1484.6	4.9
1210HIP	1315.4	1496.1	5.1
	887.5	1270.0	10.6
	882.0	1361.5	14.9
	919.8	1398.3	16.2
	915.4	1375.7	14.5

mate 1300 MPa, but limited ductility with a tensile elongation of $\sim 4.5\%$. It is also clearly shown that the post-processing conditions play a significant role for the tensile properties, the higher HIP temperature at 1210 °C results in the lowest yield strength (~ 882 MPa) but better elongation ($\sim 14.9\%$) for the 1210HIP sample. More strikingly, the AB sample displays a good combination of both yield strength (~ 1093 MPa) and ductility ($\sim 18.9\%$).

To demonstrate the synergic strength-ductility improvement of the AB sample, the test results in this study and from literature (open triangle and square mark) are put together in Fig. 3(b) for comparison [35–37], where other traditional γ' hardened cast Nickel-base superalloys are included as well (open diamond mark). Compared with the γ - γ' two-phase structure of Nickel-base superalloys, it can be seen that the AB sample has relatively high yield strength and at the same time exhibits extremely good ductility, suggesting that the effective strengthening was achieved without compromising the ability for plastic mediation. In contrast, owing to the similar two-phase microstructural configuration, the 1000HIP and 1210HIP γ - γ' superalloys are trapped in the strength-ductility dilemma (left-lower corner in Fig. 3(b)).

Fig. 2. (a) EBSD IPF coloring map of 1210HIP sample from observation plane perpendicular to the loading direction, (b) selected sub-area #1 with orientation close to [001], (c) selected sub-area #2 with orientation close to [011], (d) the γ' phase morphology in sub-area #1 with its corresponding {100} and {111} pole figure, (e) the γ' phase morphology in sub-area #2 with its corresponding {100} and {111} pole figures.

3.3. Fractography observations

In this study, fractography was used to identify the differences between the fracture modes for the different microstructures. Post-mortem fractography of the three samples were carefully examined and presented in Fig. 4(a)–(c) for AB, 1000HIP, and 1210HIP samples, respectively. Crystallographic cracks dominate the fracture surface of the AB sample (Fig. 4(a1)) caused by the failure response to its single-phase structure. The evidence of intergranular cracks is shown in the 1000HIP sample (Fig. 4(b1)), and 1210HIP sample (Fig. 4(c1)). The size and morphology of the intergranular cracks are in good agreement with the corresponding pristine grain structure in Fig. 1. Non-fatal intergranular

cracks can be observed, as the white arrows show in Fig. 4(b1) and (c1), resulting from the decohesion of grain boundaries. These intergranular cracks for the 1000HIP and 1210HIP samples are consistent with the room temperature tensile fracture of cast IN738LC superalloy with fine γ' (~70 nm) and coarse γ' (~700 nm) microstructures [37].

Interestingly, a ductile fracture mode through dimple formation by voids nucleation and growth could be found in all samples. As shown in Fig. 4(a2)–(c2), all the tested samples have different scales of ductile dimples, even though the 1000HIP sample which has limited tensile elongation. The sizes of the dimples are well matched with the corresponding microstructure within the grain interior (cellular structure ~423 nm in AB and γ' secondary phase ~180 nm and ~400 nm in

Fig. 3. (a) Representative engineering stress-strain curves of the AB, 1000HIP and 1210HIP specimens. (b) Yield strength versus the tensile elongation of the AB, 1000HIP and 1210HIP specimens compared with those of other cast IN738LC, CM247LC and GTD111 Nickel-base superalloys.

Fig. 4. Typical fractography of the room temperature tensioned samples from SEM secondary electron images, (a1), (b1), (c1) overall view of the fracture surface of AB, 1000HIP, and 1210HIP, respectively, (a2), (b2), and (c2) high-magnification micrographs show the dimple ruptures of AB, 1000HIP, and 1210HIP, respectively.

1000HIP and 1210HIP, respectively). For the post-thermal treated samples, the dimples are postulated to be formed from the debonding of the γ' precipitates and γ matrix interface. The primary strengtheners for AB, 1000HIP, and 1210HIP samples can be deduced as the cellular structure, the fine γ' phase, and coarse γ' phase, respectively. As reported from Balikci et al. [37], the size of dimples is equivalent to the size of γ' .

The cross-sectional fractography of 1000HIP and 1210HIP samples can be found in Fig. S5 and Fig. S6, respectively. The intergranular cracking of these two samples could be attributed to the interaction between GBs and GB carbides. In Nickel-base superalloys, the GB carbides play an important role in inhibiting the GB sliding during high-temperature deformation. The cause of uncommon GB sliding at room temperature is discussed in Section 4.3 in detail.

4. Discussion

4.1. On the strengthening mechanisms

In this section, the strengthening mechanisms of all the three samples will be discussed in detail by combination of microstructural evidence and mathematic interpretation.

Firstly, by considering the contribution of grain boundaries to the yield strength, the well-known Hall–Petch relation is used and the increment of yield strength is quantified as:

$$\Delta\sigma_{GB} = \frac{k_y}{\sqrt{d_m}} \quad (1)$$

Where k_y is the Hall–Petch coefficient, which is 710 MPa/ $\mu\text{m}^{1/2}$ for general Nickel-base superalloys [38] and d_m is the average grain size. The calculated $\Delta\sigma_{GB}$ is 107 MPa, 100 MPa, and 57 MPa for the AB, 1000HIP, and 1210HIP specimens, respectively.

4.1.1. As-built sample

To further unravel the deformation micro-mechanism of the three samples, detailed scanning transmission electron microscopy (STEM) investigations were carried out. Fig. 5 shows the deformation substructures of the AB sample from both top view and side view of cellular structures. It is clearly shown in Fig. 5(a1) and (b1) that the cellular walls are composed of highly tangled dislocations. Owing to the observed different features of the cellular bulk and the cellular wall with a regular distribution pattern, the cellular structure is best described as a “composite” deformation substructure [39]. Cellular wall thickness, h , is measured to approximate 30 nm in the “clean” cellular wall region, as shown in the inset of Fig. 5(b1), with limited deformation activities avoiding the contrast influence from dislocation tangles. Comparing with the cellular size d_c , h is far less than d_c . Therefore, the volume fraction f_w of cellular wall can be calculated as [39]:

$$f_w \approx \frac{\kappa h}{d_c} \quad (2)$$

Where f_w , h , and d_c are defined previously, and κ is a geometric constant set as 3 for a regular cellular structure. This results in a cellular volume fraction around 21%.

Fig. 5. Bright field STEM micrographs of the deformed AB specimen, demonstrating the major deformation mechanism and cellular walls interaction, (a) top view and (b) side view of cellular structure.

Owing to its single-phase structure, the glide of dislocations is the main operative deformation mode. As indicated by the black arrows in Fig. 5(a1) and (a2), slip bands are parallelly arrayed. By further increasing the imaging magnification, the interaction between slip bands and dislocation cellular walls is shown in Fig. 5(a2). As shown in the section between the paired dashed lines, the slip bands are mainly restricted within the dislocation cell interior. Thus, the cell walls with an extremely high density of dislocations effectively block the motion of gliding dislocations.

More dislocation substructures are illustrated in Fig. 6 to show the planar slip character of the deformed AB samples. The nature of the dislocation substructure is characterized by the planar slip bands, as shown as classical planar slip band fingerprints in Fig. 6(b). During the deformation process, the carpet-like dislocation substructure formed due to the activation of double or multiple slip systems. The planar slip planes follow the traces of the {111} planes, which are shown as the yellow cross in Fig. 6(a). It is commonly observed in low stacking fault energy materials that after the onset of extensive planar dislocation bands in the stage I work hardening state, secondary slip system could be activated to keep a certain amount of work hardening. This double or even multiple planar slip lead to the formation of the “carpet-like” dislocation substructure configuration [40], as shown in Fig. 6(a1) and (a2).

It is believed that the nature of rapid cooling ($\sim 10^6$ K/s) to ambient temperature involved in the L-PBF process leaves a large amount of dislocations behind. Due to the dislocation heterogeneity, the AB samples are hardened. Other processes commonly involving several steps of cold working and tempering also introduce high dislocation density [41], however the L-PBF process can provide this cellular character in a net-shape or near-net-shape manufactured condition. As analyzed from the mechanical performance and deformation mechanisms, the disloca-

tion cellular strengthening has a big impact on the AB sample. It is well accepted that the strengthening effect of dislocation substructures can be estimated by the Taylor relation using the corresponding dislocation density [42,43].

For strengthening by a huge amount of heterogeneously distributed dislocations as in the AB sample shown in Figs. 5 and 6, it is inaccurate to measure the overall dislocation density across the cell walls and cell interiors. In addition, due to the large amount of dislocations squeezed in the cellular wall region, it is almost impossible to directly measure the dislocation density in these areas. Several relationships between the cellular size and dislocation density have been proposed. For example, as proposed by Holt [44], the cellular size is comparable to the wavelength of dislocation density modulation, caused by the energetic unstable significance of the uniformly distributed distribution to cluster. It is commonly expressed as [45]:

$$\rho = \frac{c}{d_c^2} \quad (3)$$

Where ρ is dislocation density, d_c is the average cellular size as 423 nm in this study, and c is a constant for a given materials. The generally used value for c is 1, as reported in [26,46]. Based on this assumption, the resulted ρ is determined as $5.6 \times 10^{12}/\text{m}^2$, which is 1–2 order less than the reasonable value for L-PBF alloys such as selective laser melted high entropy alloy [47].

Therefore, instead we determined the dislocation density within the cells using the intersection measurement method [48] from TEM images to be $7.14 \times 10^{14}/\text{m}^2$ (Std. Dev.: $0.58 \times 10^{14}/\text{m}^2$). By inserting the measured dislocation density result and cellular size value back into Eq. (3), it gives the material dependent constant $c=128$. This fitted value is consistent with other empirical results as c has been reported to be in the

Fig. 6. Deformation substructure of the AB specimen, (a) double slip activities between cell walls, (b) detail feature of planar slip. ((a1-2) and (b1-2) are taken from dark field STEM imaging and (a3) from bright field STEM imaging).

range of 80–170 [49]. When replacing the bulk dislocation density with the cell interior dislocation density, the dislocation walls are assumed undeformed and no hardening effect should be added. Then the Taylor's equation is rewritten as:

$$\Delta\sigma_{Dis.} = f_c \alpha \bar{M} G b \sqrt{\rho} \quad (4)$$

Here f_c is the cell fraction (79%), α is a constant. The average $\bar{M}$ value is given to be 3.19, 3.09, and 3.10 for AB, 1000HIP, and 1210HIP, respectively based on EBSD measurement. Owing to the nature of dislocation heterogeneity in this study, using an α value for homogeneously distributed dislocations $\alpha_{Hom.}$ (0.3) will result in higher strengthening values. Herein, we use a modified α value for cell-containing dislocation structures as proposed in [49]:

$$\alpha = 2\alpha_{Hom.} \sqrt{f_c f_w} \quad (5)$$

Where f_w is the cell wall fraction (21%) and f_c is the cell fraction (79%). The calculated contribution $\Delta\sigma_{Dis.}$ is then 372 MPa, which ensures the AB sample's high-strength performance in spite of its single-phase structure.

4.1.2. 1000HIP and 1210HIP samples

In the post-thermal treated samples, 1000HIP and 1210HIP, the yield strength is greatly enhanced due to the precipitation of spherical γ' precipitates in 1000HIP sample but reduced while the coarse γ' phase appear in 1210HIP sample. Distinctly, after post-processing, secondary γ' precipitated, as shown in Fig. 7(a) and (b). The γ' phase has a L1₂ crystal structure, with the stoichiometry Ni₃Al, which is near-coherent with the FCC γ matrix. This L1₂ γ' phase acts as the effective strengthening source for the commercial Nickel-base superalloys and other austenite-based alloys [50]. Fig. 7(a1) shows the representative deformation substructure of the 1000HIP sample. Two sorts of dislocation activities are observed:

(1) dislocation lines occupied the continuous γ channel with the length up to micron-scale (as shown in parallel dotted-lines in Fig. 7(a1)); (2) other dislocations loop around the γ' phase (e.g. γ' within blue circled area in Fig. 7(a1)). It is clearly demonstrated that the soft domain (γ matrix) provides the dislocation accommodation area, which is fully squeezed with dislocations (Fig. 7(a2)). For the coarse γ' in the 1210HIP sample (Fig. 7(b1)), the strengthening mechanism is similar: dislocations loop around γ' (shown as the red ellipses). The cuboidal γ' phase has specific crystallographic planes as the phase outer edges are aligned with the {100} crystal planes of the FCC matrix, as determined by EBSD in Fig. 2. The red ellipses indicated in Fig. 7(b) match the trace of {111} slip systems in the corresponding matrix. However, the coarse γ' has less efficiency in strengthening, which results in the more undeformed γ matrix (Fig. 7(b2)), where the 1210HIP sample has less dense dislocations than the 1000HIP counterpart in Fig. 7(a2). As a consequence, the 1210HIP sample can accommodate the deformation easier and a better tensile elongation is achieved compared to the 1000HIP sample.

Confirmed by the deformation substructure analysis in the two post-process treated samples (Fig. 7(a) and (b)), the dislocations interact with γ' in the manner of Orowan looping. Then, the strength given by the γ' phase can be written as Orowan stress τ_{Or} as [51]:

$$\Delta\sigma_{\gamma'} = \bar{M} \tau_{Or} = \bar{M} \frac{Gb}{L_s} \quad (6)$$

Where L_s is the spacing between the precipitates. For spherical particles, L_s is determined by the γ' volume fraction, $f_{\gamma'}$, and the size of γ' , $d_{\gamma'}$ as [52]:

$$L_s = \sqrt{\frac{8}{3\pi f_{\gamma'}} d_{\gamma'} - d_{\gamma'}} \quad (7)$$

Fig. 7. Dark field STEM micrographs of typical deformation substructure of post-thermal treated specimens, (a) 1000HIP, (b) 1210HIP.

Here, L_s is calculated to be 100 nm and 149 nm for 1000HIP and 1210HIP, respectively. The contribution of γ' to strength is then calculated to be 696 MPa and 469 MPa for 1000HIP and 1210HIP sample, respectively. It should be noted that the L_s value in Eq. (6) is modified for spherical shaped particles, but the 1210HIP sample has cuboidal shaped γ' . Then we calculated the $\Delta\sigma_{\gamma'}$ for this sample directly using the γ channel spacing L as [38]:

$$\Delta\sigma_{\gamma'} = \frac{3}{2} \bar{M} \frac{Gb}{L} \quad (8)$$

Owing to the orientation dependence of the γ' in 1210HIP sample, the γ channel spacing L is measured through the diagonal intersects in the γ phase, as measured to be 225 nm on average. It gives the close value of 467 MPa as compared to 469 MPa calculated from Eqs. (6) to (7). By combining the micrograph analysis and mathematical calculations, it is found that the ordered precipitates effectively harden the material by hindering the dislocation movements. A high density of dislocations was generated as a response to the precipitate blocking effect. In addition, in the regime of the Orowan loop mechanism, the strengthening effect is highly dependent on the precipitate spacing with respect to the precipitate size.

Therefore, based on the discussion above, we aim to quantify the yield strength of the three different samples. For the γ' strengthened and highly alloyed polycrystalline Nickel-base superalloys, the increase in yield strength $\Delta\sigma_y$ can be expressed using several separate strengthening factors, on the assumptions that these mechanisms operate independently, the addition law can be used [52]:

$$\Delta\sigma_y = \Delta\sigma_{SS} + \Delta\sigma_{GB} + \Delta\sigma_{\gamma'} + \Delta\sigma_{Dis}. \quad (9)$$

Where $\Delta\sigma_{SS}$ is from solid-solution strengthening, $\Delta\sigma_{GB}$ is the strength contributed by the grain boundaries, $\Delta\sigma_{\gamma'}$ is the strength contributed by the γ' precipitates, which is highly dependent on the size of γ' , and $\Delta\sigma_{Dis}$ is the dislocation strengthening part.

The solid-solution hardening of the Nickel-base superalloy matrix contribute to the overall strength by the effect from each alloying element, which is proportional to the square root of individual alloying concentration $\sqrt{C_i}$, as:

$$\Delta\sigma_{SS} = f_\gamma \sum_i \left(\frac{d\sigma}{\sqrt{dC_i}} \sqrt{C_i} \right) \quad (10)$$

Where f_γ is the fraction of the γ matrix (for AB sample f_γ is assumed to be equal to the fraction of cell interior) and $\frac{d\sigma}{\sqrt{dC_i}}$ is a strengthening coefficient for each element in the unit of MPa/(at%)^{1/2}, the values are listed in detail in Roth's et al. work [53]. It gives the result of $\Delta\sigma_{SS}$ to be 586 MPa, 443 MPa, and 342 MPa for AB, 1000HIP, and 1210HIP, respectively. Nominal composition of IN738LC was used for calculating the $\Delta\sigma_{SS}$ of AB sample, while γ phase compositions derived from thermodynamic calculations (ThermoCalc TCNI8 database) were used for 1000HIP and 1210HIP.

Additionally, the total yield strength is the sum of Peierls stress (crystal lattice resistance), σ_0 , and yield strength increment $\Delta\sigma_y$. We take $\sigma_0=37$ MPa [53] for pure Nickel at room temperature to conclude the calculation. According to the analysis, the yield strength is determined as 1101 MPa, 1276 MPa, and 905 MPa for the AB, 1000HIP, and 1210HIP, respectively, with the corresponding microstructural parameters. Meanwhile, the average measured yield strength value is 1084 MPa, 1307 ± 19 MPa, and 901 ± 19 MPa for the AB, 1000HIP,

Fig. 8. (a) Work hardening rate and true stress curves as a function of true strain. (b) dynamic evolution of the work hardening exponent as a function of true strain, (c) schematic illustration of the typical work-hardening curves for AM processed IN738LC alloys with different microstructures.

and 1210HIP, respectively, as shown in Table 1. The experimental and calculated yield strength values are thus in a very good agreement with each other.

4.2. On the work hardening response

Fig. 8(a) combine the work hardening rate, θ , and true stress curves as a function of true strain for all of the AB, 1000HIP and 1210HIP specimens. By analyzing the work hardening behavior of the three samples, multiple-stage work hardening behaviors are distinguishable. At the work hardening stage I, i.e. the ‘easy glide’ stage [46], the work hardening rate (assessed at true stress over true strain, $d\sigma/d\epsilon$) of 1000HIP sample dramatically drops to the lowest value among the three samples, where the AB sample has the intermediate value and 1210HIP keeps the highest value. At the small strain level in work hardening stage I, the work hardening rate value is reflected by the difficulty of dislocation activity, i.e., the dislocation mean free path, Λ . Specifically, the 1000HIP sample presents the lowest work-hardening rate due to its largest Λ , which is approximately equal to the continuous γ channel length (>1000 nm) between the spherical γ' , as inferred of micrographs in Fig. 7(a1). In the AB sample, the dislocation mean free path is mainly determined by the size of dislocation cells (~ 423 nm for the average cellular size), resulting in the intermediate work hardening value. Moreover, for the 1210HIP sample, owing to the restricted slip plane direction, the Λ has the shortest value equals to its average γ channel spacing around 225 nm, leading to the highest work hardening value.

At around 1.8% true strain, the stage II work hardening, i.e. the linear work hardening rate region, occurs, which has the biggest contribution to the strength. At stage II, the 1000HIP sample shows rapid increase in work hardening rate until reaching $\sim 3.9\%$ of true strain. The other post-thermal treated sample 1210HIP displays a work hardening rate plateau at ~ 5100 MPa till $\sim 5\%$ of true strain. On the other hand, the AB sample have a smooth evolution of the work hardening rate up to $\sim 7.4\%$ of true strain and similar behavior in the following work-hardening stage.

Furthermore, the instantaneous work hardening exponent, n , (derived from Hollomon equation, $\sigma = K\epsilon^n$) as a function of true strain (Fig. 8(b)) is used to assess the work hardening behavior with multiple hardening mechanism [50]. It can be noted that the higher n value gives the higher work hardening behavior. At identical true strain levels, the 1000HIP and 1210HIP samples present similar increase of the work-hardening exponent because of the similar hardening effects by the secondary γ' phase precipitation strengthening.

Here we introduce a dimensionless index, W , to qualitatively describe the work hardening degree, which can be written as:

$$W = \int_{\epsilon_{II}}^{\epsilon_{frac}} n d\epsilon \quad (11)$$

Where, ϵ_{II} and ϵ_{frac} are the true strain at the start of work hardening stage II and true strain at the fracture, respectively. n is the work hardening exponent. Then, by integrating n over ϵ in the dynamic evolution

of the work hardening exponent curve, the W is calculated to be 2.16%, 0.28% and 3.02% for AB, 1000HIP and 1210HIP specimen, respectively.

It should be mentioned that both post-thermal treated samples underwent premature failures. As shown in the work hardening curves in Fig. 8(a), the 1000HIP and 1210HIP samples fractured within its uniform plastic regime, before the θ reaches to the equal amount as true stress, as defined by the Considère instability criterion [54]. Interestingly, in general, higher work hardening rate would keep the deformation proceeding and thus ensure a higher tensile elongation, or more uniform plasticity before necking. As reported by Yang et al. [50], good ductility was achieved by sustaining higher work hardening rate during the plastic deformation process in a multicomponent intermetallic nanoparticle enhanced alloy system. Moreover, in twinning-induced plasticity steels, higher work hardening rate caused by twinning interaction also results in the higher ductility [55]. As well as in the medium- or high- entropy alloy systems, the high work hardening capacity induced higher ductility is well used for the interpretation of temperature dependence elongation differences [56]. On the other hand, the intermetallic precipitates also have a strong effect on the embrittlement. The double-edge effect of precipitate strengthening is discussed in details in Section 4.3.

To summarize, we analyzed the work-hardening evolution and coupled it with the microstructural parameters for the three specimens as presented in the schematic illustration in Fig. 8(c). At work-hardening stage I, easy glide starts by dislocation motion on the slip systems. The work hardening rate value here is reflected by the difficulty of dislocation activity. In the AB specimen, the work hardening rate curve (black-dashed curve) keeps decaying within the deformation process. The continuous drop of the work hardening rate represents that dislocation planar slip dominates the plastic deformation. Coming to work hardening stage II, in contrast, the 1000HIP and 1210HIP specimens underwent a recovery of work hardening rate after the sharp drop of θ in work hardening stage I, owing to the significant strengthening effect of the γ' phase. Beyond Nickel-base superalloy, more specifically, the recovery of work hardening rate is widely found in twinning-induced plasticity (TWIP) and/or transformation-induced plasticity (TRIP) alloys. Briefly, these different categories of work hardening rate recovery is caused by the reduction of dislocation mean free path, Λ , during plastic deformation [57,58]. In TWIP alloys, the newly formed twin boundaries decrease the Λ , while it is newly formed phase boundaries in TRIP alloys. However, in this study the reason for the recovery of work hardening rate in the 1000HIP sample is due to the dynamic evolution of dislocation motion with respect to the multi-scale deformation places. With the deformation preceding, the Λ is reduced by the consumption of the long-chain continuous γ channels for gliding, then the dislocations bypass the obstacles via dislocation looping in the space between the precipitates.

4.3. On the conflicting nature of strengthening and ductility reduction

The tensile ductility of the tested L-PBF IN738LC is profoundly influenced by the strengthening mechanisms in the aforementioned

Fig. 9. Illustration of nanoindentation locations and the corresponding IPF coloring maps showing the distance between the center of indents respect to the closest grain boundary. The EBSD-IPF coloring mapping is overlapped on the corresponding nanoindents area after the nanoindentation measurements.

discussions. Moreover, the grain boundaries play a signification role on the plastic deformation. As the results shown from fractography, intergranular cracking characteristics are observed in the two post-thermal treated samples. To further reveal the role played by the grain boundaries and bulk grains, we used nanoindentation to identify the mechanical response differences within the localized micron-scale microstructure, as shown in Fig. 9. To fairly compare the evolution of microstructure under the plastic deformation, “undeformed” and “deformed” nanoindentation samples were extracted from the grip section and gauge section, respectively from the identical tested tensile bars for each of the AB, 1000HIP, and 1210HIP conditions. Owing to the high load-displacement sensitivity of the nanoindentation test, the local indentation mechanical behavior can be illustrated, which has enabled studies of the grain boundaries mechanical properties [59,60] and local slip resistances [61]. By systematically studying the nanoindentation hardness changes as a function of the distance from the closest grain boundary, the mechanical characteristics of the grain boundary and grain interior regions are reasonably revealed. However, in particular, these kind of investigations have previously focused on mainly simple alloy systems, e.g. Fe-Si steel [62] or pure metals [63]. Furthermore, the studied polycrystalline materials in these investigations [62–64] are all coarse grain with the grain size in the millimeter scale. However, according to the large-scale uncertainty of the complex alloy system and the anomalous fine grain morphology of the L-PBF IN738LC in this study, an indentation matrix was used for a better statistical meaning, where the indentation matrix map is shown in Fig. 9. With the imposed orientation imaging mapping from the EBSD measurement on the nanoindentation area, the grain boundaries with grain boundary misorientation higher than 10° were marked in color white. To create the distance profile, the distance from the center of each individual indent to its closest grain boundary was measured. As shown in Fig. 9, the round mark indicates the indent and cross mark indicates the corresponding closest grain boundary positions.

Observed from the TEM micrographs in Section 4.1, successive dislocations are nucleated and moved, which controls the plasticity behavior of polycrystalline materials. Furthermore, the operative space of dislocation motion is restricted to certain areas, e.g. mainly the cellular interior for the AB sample and the γ channels for the 1000HIP and 1210HIP samples. The cellular boundaries and γ' phases act as the main strengthen-

ing source for the corresponding specimen. By comparing the hardness profile along the distance from GBs in both deformed and undeformed microstructures, the deformation process evolution can be unveiled, as shown in Fig. 10. As depicted in the hardness profile curves, the overall hardness in the deformed microstructure is increased comparing with the undeformed ones. The incremental hardness increase between undeformed and deformed microstructures are consistent with the estimated work hardening degree as calculated by Eq. (11), i.e., the 1210HIP has the largest work hardening degree (3.02%), AB is in the middle (2.16%) and less work hardening occur in 1000HIP (0.28%).

From one hand, to achieve the stronger mechanical response, more effective strengthening microstructures are desired. On the other hand, to achieve the ductile properties, more space to accommodate the plasticity is required. For the AB sample, the undeformed microstructure exhibits stronger (higher hardness value) grain boundaries but weaker grain interior (lower hardness). After the deformation process, although the overall hardness response increased, the deformed hardness profile along distance from GBs has the similar trend compared with the undeformed one. According to the comparison between undeformed and deformed microstructural hardness profiles, the deformation is homogeneously distributed across GB and grain interior in AB samples. Additionally, the microstructure of the grain interior of the AB sample is mainly a cellular structure, where the cellular interior has the higher fraction (21% cellular walls but 79% cellular interior). The large proportion of cellular interior area ensure the higher potential for AB sample to accommodate the plasticity.

In contrast, the mechanical response of the grain boundaries and the grain interior appear different for the 1000HIP and 1210HIP samples, as shown in Fig. 10(b) and (c). Even though the overall hardness value of the deformed microstructure has increase compared to the undeformed state, heterogeneous deformation occur between the grain boundary (GB) and grain interior. In the undeformed microstructure, both 1000HIP and 1210HIP samples has a stronger GB region than the grain interior region, demonstrating a similar hardness profile as in the AB undeformed microstructure. With the deformation proceeds, the movement of dislocations in the grain bulk encounters the γ' phase, which has an effective hinderance effect on the mobile dislocations. These mobile dislocations are restricted to the γ matrix, resulting in the difficulty to push the dislocations to the grain boundaries. Conse-

Fig. 10. The plots of distance from grain boundaries versus the nanoindentation hardness, H , for both deformed and undeformed regions, (a) AB sample, (b) 1000HIP sample, and (c) 1210HIP sample.

quently, the grain interior region shows a higher degree of hardening owing to the larger amount of stored dislocations. This heterogeneous deformation process leads to a different hardness distribution across GB and grain interior in the deformed microstructures, i.e. the hardness value in grain interior region is close to or greater than the GB region, as shown in Fig. 10(b) and (c). Once the space for the dislocation motion in the grain interior is limited by the stored dislocations, the grain boundaries have to act as the sites for mediating plasticity and ductility is reduced.

In general, the mechanisms for GB-mediated plasticity are GB sliding and grain rotation [65]. Indeed, in our previous study [66], GB sliding could substitute as the dominant deformation accommodation mechanism in L-PBF IN738LC superalloys at the elevated temperature and under slow strain rate conditions. However, it has been proposed that the GB-mediated plasticity at relatively low temperature requires that the grain size is reduced to a critical value, e.g. 11–22 nm for Nickel [67]. Based on the discussion, under the test condition in study, the coarse GBs (comparing with nanograins) of L-PBF IN738LC superalloys have poor ability for plasticity mediation. It means that in the 1000HIP and 1210HIP sample, once the γ matrix in the grain interior is highly occupied by the impeded dislocations, to maintain the plastic flow, the grain boundaries debones, which leads to the intergranular failure as proofed in Fig. 4. By comparison between 1000HIP and 1210HIP sample, the 1000HIP has lower tensile elongation. It can be well interpreted by the higher strengthening effect of finer γ' in 1000HIP than 1210HIP, according to the mechanical evidence of recovery of work hardening rate curve in Fig. 9, and deformation substructure evidence of higher dislocation density in γ channel than 1210HIP in Fig. 7.

4. Conclusions

We successfully demonstrated that the Nickel-base superalloy IN738LC produced by L-PBF yields simultaneously enhanced strength and ductility compared to its conventional cast counterparts reported in literature, while post AM-processes combining HIP and standard heat treatment result in the typical strength-ductility trade-off for γ - γ' alloys. The following conclusion can be drawn:

1. The as-built microstructure is composed of weakly textured polycrystalline grains with heterogeneous dislocations, i.e., a high density of cellular dislocation structures. The cellular wall structures are confirmed to effectively hinder the dislocation movements, which highly strengthened the alloy. While in the γ' strengthened samples, the major strengthening effect comes from the precipitation hardening. By taking grain boundary, solid solution, precipitation and dislocation hardening into consideration, the calculated yield strength is 1101 MPa, 1276 MPa, and 905 MPa for AB, 1000HIP, and 1210HIP samples respectively. The results agree well with the experimentally determined yield strength.
2. Under the room temperature deformation process, the primary deformation mechanism is dislocation planar slip within the cellular

interior in the as-built sample while dislocation looping around the γ' precipitates in post-thermal treated samples.

3. Work hardening is correlated to the dislocation mean free paths, where the recovery of work hardening rate in γ - γ' Nickel-base superalloys is caused by an evolution of the multi-scale deformation volume. When the dislocation mean free paths are reduced after the easy glide within the continuous γ channels, a recovery of the work hardening rate occurs.
4. Under the room temperature tensile condition, the plastic deformation is mediated by local dislocation activities. The suitable size of the precipitates leads to an obvious positive increase of yield strength by impeding the dislocation motion. This results in a larger degree of hardening in the grain bulk area, where the precipitates in the grain interior region barely allow the dislocation to be pushed to the grain boundaries. Once the grain interior γ channel being rapidly occupied by stored dislocations, the early stage embrittlement occurs.

Declaration of Competing Interest

No potential conflict of interest was reported by the authors.

Acknowledgment

This work was supported by the Swedish Agency for Innovation Systems, (Vinnova grant 2016-05175 and 2018-00804); faculty grant from Linköping University (SFO-MAT-LiU#2009-00971); and center for Additive Manufacture – Metal (CAM2). The authors acknowledge K. Minet and A. Shaikh from EOS Finland Oy, Dr. A. Eklund from Quintus Technologies AB, Dr. H. Brodin from Siemens Industrial Turbomachinery AB, Prof. E. Hryha from Chalmers University of Technology, and Dr. S. Bengtsson from Höganäs AB for fruitful discussions. JX would like to thank Dr. D. Deng for the helpful discussions.

All data included in this study are available from the corresponding author on reasonable request.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.mtla.2020.100657.

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A Novel γ' -Strengthened Nickel-Based Superalloy for Laser Powder Bed Fusion

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Materials, vol. 13, issue 21, 2020

Communication

A Novel γ' -Strengthened Nickel-Based Superalloy for Laser Powder Bed Fusion

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Received: 7 October 2020; Accepted: 30 October 2020; Published: 2 November 2020

Abstract: An experimental printable γ' -strengthened nickel-based superalloy, MAD542, is proposed. By process optimization, a crack-free component with less than 0.06% defect was achieved by laser powder bed fusion (LPBF). After post-processing by solution heat treatment, a recrystallized structure was revealed, which was also associated with the formation of annealing twins. After the aging treatment, 60–65% γ' precipitates were obtained with a cuboidal morphology. The success of printing and post-processing the new MAD542 superalloy may give new insights into alloy design approaches for additive manufacturing.

Keywords: nickel-based superalloy; γ' phase; laser powder bed fusion; alloy development

1. Introduction

To improve the high-temperature mechanical and chemical properties, the nickel-based superalloy family has been developed significantly over the past several decades by chemical composition optimization. Therefore, the γ' -strengthened nickel-based superalloys are highly alloyed material systems. With the nickel acting as the austenitic matrix, it is doped with up to 10 or more alloying elements [1,2]. The addition of these alloying elements primarily serves the purpose of improving high-temperature performance. Generally, the mechanical performance is associated with the combination of the precipitation hardening effect from the ordered L1₂ γ' intermetallic phase and the solid solution strengthening effect from refractory elements slowly diffusing at elevated temperature. For the chemical properties, it is strongly related to the formation of protective oxide layers during high-temperature applications. Owing to the excellent high-temperature properties and wide engineering application of nickel-based superalloys, the fabrication of superalloy parts by the promising additive manufacturing (AM) techniques is of great interest. Extensive investigations have been done regarding the AM process tailoring, the post-process treatments, and characterization of high-temperature mechanical and chemical properties of a group of γ' precipitate-strengthened nickel-based superalloys, such as IN939 [3], IN738LC [4–6], and CM247LC [7,8]. The compositions of these superalloys were proposed decades ago but, unfortunately, they were not developed with the intention of being adopted for AM processes.

Based on this, the need for novel chemical compositions of nickel-based superalloys ready for AM processing is urgent. However, the AM processing of precipitation-strengthened nickel-based superalloys is a great challenge, owing to its intrinsic cracking susceptibility during the AM process and/or the associated post-processing treatment. Four critical cracking mechanisms of precipitate strengthened nickel-based superalloys summarized from the welding literature below are generally accepted:

1. Solidification cracking (SC). During the last stage of solidification, the residual tensile stress caused by the shrinkage strain may tear apart the remaining liquid at the interdendritic region [9].
2. Liquation cracking (LC). During the intrinsic re-heating [10] of the heat-affected zone, the (sub)grain boundaries or interdendritic regions, where the solidus temperatures are reduced by the elemental segregation during solidification, get liquified and pulled apart [11,12].
3. Strain-age cracking (SAC). During the post-processing thermal treatment, while the material is exposed to an aging temperature, the formation of precipitates will reduce the ductility. Simultaneously, the un-released residual stress plus the precipitation stress could induce cracking when the strain exceeds the ductility limit [13].
4. Ductility-dip cracking (DDC). During the post-processing thermal treatment of precipitate-strengthened nickel-based superalloys, a certain temperature range is critical because the ductility is highly reduced (ductility dip). Similar to SAC, a high enough strain leads to cracking in the low-ductility region [14].

In a simplistic sense, SC and LC could be attributed to the poor stress resisting capacity of the interdendritic spaces. One of the natures of the AM microstructure is the cellular-dendritic structure, whose size is around a few hundred nanometers to micrometers, depending on the specific AM process. On the other hand, these cellular structures are fine dendritic structures in terms of the elemental distribution, since, even though the cooling rate for the AM process is significantly high, the micro-segregation between the dendrite/interdendritic region cannot be fully inhibited. In the highly alloyed metallic material systems, it is widely reported that some of the elements segregate to the dendritic core region in the as-fabricated condition, such as W (in a selective electron beam melted (SEBM) CMSX-4 superalloy [15] and a laser powder bed fused (LPBF) CM247LC superalloy [16]) and Fe (in a laser beam welded (LBW) IN718 superalloy [17] and LPBF 316L steel [18]). In contrast, some other elements partitioned at the interdendritic region, such as Mo (LPBF 316L [18], LPBF IN718 [19]), Al, Ta (SEBM CMSX-4 [15], LPBF CM247LC [16]), Ti (LPBF CM247LC [16]), and Nb (LPBF IN718 [19]). Among these important major alloying elements, Al and Ti primarily act as the γ' phase formers, while W, Ta, Mo, and Nb are usually considered the solid solution strengtheners. On this basis, we considered Mo, Nb, and Ta as the key elements that may reduce the cracking susceptibility, because (1) they are prone to segregating at the interdendritic region and could compensate for the solidification shrinkage, (2) they will enhance the strength of the interdendritic region in the solidified condition and thereby increase the cracking resistance by solid solutioning, and (3) they do not serve as the major γ' formers.

In addition, the SAC and DDC mechanisms could simply be described as having a lack of stress releasing capacity during the post-processing thermal treatment. A sluggish recrystallization behavior is commonly found in the LPBF alloys, partially because that dislocation recovery barely happens in nickel-based superalloy systems [20,21]. These facts indicate that the stored energy is barely accommodated by the recovery-recrystallization-grain growth process. On this basis, to handle the stored energy by alternative approaches, such as tuning the composition, remains desirable in order to resist the post-processing cracking. Despite the reduction of stored energy by the conventional grain boundary (GB) migration process, the formation of annealing twins could also be an effective way to decrease the stored energy. Once the annealing twin boundary (TB) develops during the post-processing thermal treatment, these TBs provide adequate interfaces for accommodating dislocations for increasing ductility [22], thus the SAC and DDC susceptibility could be reduced. From the alloy composition modification perspective, lowering the stacking fault energy (SFE) of the alloy is usually an operative way to promote annealing twins. In the Re-free nickel-based superalloys, the Mo and Nb are the most effective interdendritic partitioning elements for reducing the SFE [23].

To this end, we developed a novel nickel-based superalloy, MAD542, for the LPBF process and its corresponding post-processing treatment. By adding appropriate levels of interdendritic segregating elements, i.e., 5 wt.% Mo and 2 wt.% Nb, crack-free parts could be fabricated in the as-built condition. Meanwhile, the addition of Mo and Nb decreased the SFE, which lowered the stored energy by

TB formation. Extending this, the LPBF processing window of this novel superalloy was explored. Subsequently, the microstructures of as-built and post-processing heat-treated samples were validated by different characterization methods.

2. Materials and Methods

The chemical composition of the MAD542 superalloy is listed in Table 1. The thermodynamic equilibrium diagram was evaluated by a thermodynamic calculation software (version 2020b, Thermo-Calc Software, Stockholm, Sweden) with a TCNI10 database (see Figure A1 in the Appendix A). The raw powders (particle size 15–45 μm) for the LPBF process were supplied by Höganäs AB, Höganäs, Sweden. The micrographs of the powders used in this study are available in Figure A2 in the Appendix A. The LPBF process was conducted using an EOS M 100 system (EOS GmbH, Krailling, Germany) equipped with a 200 W ytterbium fiber laser source. The printing was carried out under argon atmosphere protection. To explore the LPBF processing window of MAD542, we used 9 sets of processing parameters, including 2 different laser powers, P (100 and 170 W) $\times$ 2 different scan speeds, V (1000 and 1300 mm/s) $\times$ 2 different hatching distances, and H (50 and 70 μm) + the #9 parameters with the middle values of P (135 W)/ V (1150 mm/s)/ H (60 μm). An identical layer thickness, L , of 20 μm was used for all the prints. The processing parameters are listed in Table 2. To compare the various processing parameters, the volume energy density, E (J/mm^3), was calculated as $E = P/(V \cdot H \cdot L)$ and is listed in Table 2. Nine cubes with the size of 10 mm $\times$ 10 mm $\times$ 10 mm were fabricated according to the 9 different printing parameters and with a 67° scanning vector rotation between each layer.

Table 1. The chemical composition of the MAD542 nickel-based superalloy investigated in this study.

Element	Cr	Co	Mo	W	Al	Ti	Ta	Nb
wt. %	8	8	5	4	5	1	3	2
Element	C	B	Si	P	S	Zr	O	Ni
wt. %	0.1	<0.001	<0.005	<0.001	<0.001	<0.002	0.015	Bal.

Table 2. Laser powder bed fusion processing parameters used in this study (layer thickness: 20 μm).

Exp	Laser Power, P (W)	Scan Speed, V (mm/s)	Hatching Distance, H (μm)	Energy Density, E (J/mm^3)
#1	100	1000	50	100
#2	170	1000	50	170
#3	100	1300	50	77
#4	170	1300	50	131
#5	100	1000	70	71
#6	170	1000	70	121
#7	100	1300	70	55
#8	170	1300	70	93
#9	135	1150	60	98

Metallographic sample preparation, including grinding and polishing routines, was performed and a Leica DM6 optical microscope (OM) (Leica Microsystems GmbH, Wetzlar, Germany) was used for evaluation of AM defects. The final finish of the metallographic sample preparation was polishing with 0.04 μm colloidal silica suspension for 2 min. The defects were analyzed using the open-source image analysis software, ImageJ (1.53c, National Institutes of Health, Bethesda, MD, USA) [24]. Scanning transmission electron microscopy (STEM) was used for characterizing the as-built microstructure using a high-angle annular dark field (HAADF) detector on an FEI Tecnai G2 microscope (FEI Company, Hillsboro, OR, USA) operated at 200 kV. The thin foil was prepared by conventional twin-jet electro-polishing at -25°C in a 10% perchloric acid and 90% ethanol electrolyte solution. The γ' morphology was observed using a Hitachi SU70 field emission scanning electron microscope (FE-SEM) (Hitachi, Ltd., Tokyo, Japan). Electron backscatter diffraction (EBSD) measurements were conducted on the SEM, equipped with an Oxford EBSD detector (Oxford Instruments, Oxfordshire, UK).

3. Results and Discussion

3.1. LPBF Processing Window of the MAD542 Superalloy

Figure 1 shows the results from the design of experiments (DoE) to find the LPBF processing window. Owing to the various processing parameters applied for printing, an energy density study is well adapted to understand the parametric influence and reduce the complexity of the parameters [25]. By metallographic observation of the well-polished samples via OM, the level of defects could be quantitatively measured with the assistance of image analysis, e.g., threshold adjustment of binary images to identify defects. In the present study, the total level of defects was presented as the area fraction, including all cracks, porosities, and other defects. As plotted in the chart, the minimum defect level (e.g., see micrograph of #3) was achieved around 0.06% at the valley of the ‘defect area fraction vs. energy density’ curve. It suggests that the optimal energy density for printing MAD542 was between 70–80 J/mm³. The MAD542 superalloy printed by the optimized process parameters had good quality with no microcrack presence in the mm-scale (see Figure A3 in the Appendix A). Similar to other studies [26,27], lower energy density resulted in defects, such as porosities or ‘lack-of-fusion’ (e.g., see micrograph of #7), while higher energy density lead to cracking (e.g., see micrograph of #2). To perform the microstructural validation of the LPBF MAD542 superalloy, the #3 printing parameters, with the combination of laser power of 100 W, scan speed of 1300 mm/s, hatching distance of 50 µm, and layer thickness of 20 µm, was used for fabricating the as-built MAD542 sample.

Figure 1. Laser powder bed fusion (LPBF) processing window investigation of MAD542 superalloy on 10 mm × 10 mm × 10 mm cubes. With lower energy density input, the major defects are dominated by lack of fusion, while higher energy density inputs result in micro-cracks. The crack-free part is provided by #3 printing parameters, which has a suitable energy density input for MAD542.

3.2. As-Built Microstructure

Figure 2 shows the as-built microstructure (printed with #3 parameters in Table 2), imaged via dark-field STEM (DF-STEM) micrographs, and the elemental distribution was imaged via STEM-energy dispersive x-ray spectroscopy (EDS) composition mapping. It is well known that the cellular structure is one of the core features of the as-AM-fabricated microstructure. By measuring the center-to-center spacing (shown as the superposed networks in Figure 2a) of neighboring cells, the average cellular size was determined as 420 nm. An enlarged view of the cellular structure is provided in Figure 2b. The cellular walls were composed of dense, entangled dislocations (as indicated by the red arrow), while in the interior region of the cell, less and more sparsely distributed dislocations were observed (as indicated by the blue arrow). It should be noted that these cellular structures still represented the features of the solidification dendrites without the development of secondary dendrites. In fact, it can be supposed that the microsegregation of elements could not be fully suppressed in the LPBF process. Here, we applied STEM-EDS composition mapping of a dendrite and its surrounding region, as illustrated by the dashed box drawn in Figure 2b. Among the major alloying elements, Nb, Mo, Ta, and Ti strongly partitioned to the interdendritic region. The segregation behaviors of these elements follow the same tendencies as other LPBF nickel-based superalloys [8,28–30] and their conventional cast counterparts [31–33].

Figure 2. (a) Dark-field scanning transmission electron microscopy (DF-STEM) micrograph of the as-built MAD542 microstructure overlapped with cellular/dendritic arm spacing measurements in sub-micron size. (b) Enlarged view of the cellular/dendritic structure. (c–l) EDS mapping results of the scanning area as shown as the box in (b): (c) High-angle annular dark-field (HAADF) imaging, (d) Co-K map, (e) Al-K map, (f) Cr-K map, (g) W-L map, (h) Nb-, Mo-, Ta-overlapping map, (i) Nb-L map, (j) Mo-L map, (k) Ta-M map, and (l) Ti-K map.

3.3. Heat Treatment of MAD542 Superalloy

Figure 3a–c depicts the microstructure of the LPBF MAD542 superalloy after post-processing heat treatment. For comparison, the microstructures of the heat-treated LPBF-processed γ' -strengthened superalloys IN738LC (Ni–16.2Cr–8.5Co–3.5Al–3.5Ti–2.4W–1.8Mo–1.7Ta–1Nb–0.1C–0.01B, wt.%) and

CM247LC (Ni–8Cr–9.3Co–5.6Al–0.7Ti–9.5W–0.5Mo–3.2Ta–1.4Hf–0.07C–0.015B, wt.%) are illustrated in Figure 3d–i, respectively. It should be noted that IN738LC and CM247LC are two common superalloys of good interest for the LPBF process. In this study, the MAD542 was solutioning treated at 1230 °C for 2 h, the IN738LC was hot isostatic pressed at 1210 °C for 4 h (for healing the cracks), followed by solutioning heat treatment at 1120 °C for 2 h and aging at 850 °C for 24 h [34], and CM247LC was solutioning treated at 1260 °C for 2 h. It should be noted that all the three superalloys were thermal treated at the super-solvus temperature, which indicate that single γ phase region was achieved. The grains with a grain orientation spread (GOS) value less than 1° were defined as the recrystallized grains. All three samples were recrystallized (RX) according to the GOS maps shown in Figure 3a,d,g. The inverse pole figure (IPF) coloring maps, with GBs highlighted in black lines, shown in Figure 3b,e,h, revealed the grain size (GS) of the RX samples. The GBs and TBs maps are plotted in Figure 3c,f,i. It is worth noting that, compared with other LPBF precipitation-strengthened nickel-based superalloys, the MAD542 alloy shows excellent RX response during post-processing heat treatment, even though the LPBF superalloys are considered difficult to thermally treat into the recrystallized condition.

Figure 3. Post-processing heat treated microstructures of LPBF MAD542 (a) grain orientation spread (GOS) map, (b) inverse pole figure (IPF) coloring map, (c) grain- and twin-boundary map; LPBF IN738LC [34] (d) grain orientation spread (GOS) map, (e) inverse pole figure (IPF) coloring map, (f) grain- and twin-boundary map; LPBF CM247LC (g) grain orientation spread (GOS) map, (h) inverse pole figure (IPF) coloring map, (i) grain- and twin-boundary map. Electron backscatter diffraction (EBSD) step size: 2 μm .

Owing to the greater amount of Mo and Nb added, annealing twins were easily promoted. We found that the TB fraction of MAD542 increased from almost null (0.3%) in the as-built condition to 40% after 10 min annealing and to 57% after 30 min annealing at 1230 °C. Meanwhile, 95% RX fraction could be achieved by 60 min annealing. See Figure A4 in the Appendix A for details regarding the RX and TB fraction evolution. As introduced above, the precipitation-strengthened nickel-based superalloys not only faced the challenging cracking issues during AM-processing, but also during the post-processing heat treatment. With the assistance of twin formation, the developed

TB broke the parent GBs into finer interfacial networks. Consequently, the grain size was finer and the GS distribution was more uniform in MAD542 (Figure 3b) compared to IN738LC (Figure 3e) and CM247LC (Figure 3h). Furthermore, these interfacial boundaries effectively accommodated either the internal strains caused by residual stresses or the precipitation strains from the γ' formation during the post-processing heat treatment. For verification, the resultant sample of MAD542 after heat treatment was still in good quality with no microcrack presence (micrograph available in Figure A5 in the Appendix A).

3.4. γ' Precipitate Characterization

Figure 4 shows the micrographs of γ' precipitates after solutioning plus aging heat treatment. In the γ' strengthened nickel-based superalloy, the volume fraction and morphology of γ' precipitates were well associated with the critical mechanical properties at the elevated temperature, such as creep resistance and yield strength. To reveal the grain boundary γ' (Figure 4a,b), deep etching was conducted using electro-etching at 5 V in a 10% phosphoric acid solution. Stereo-images were generated by image pairs from $\pm 10^\circ$ angle of reproduction to illustrate the depth information, along with GB networks. In Figure 4b, high density of γ' phases decorated the GB. The morphology and fraction of γ' at GBs were very similar to those in the bulk grains, indicating a uniform distribution of precipitation throughout the whole sample. The γ' precipitates in the grain interior are shown in Figure 4c,d. Cuboidal shaped γ' were obviously identified, and the average length was measured as 372 (± 76) nm. By applying image analysis, the volume fraction of γ' in this heat treatment condition was measured to be between 60–65%. It is worth noting that after the successful precipitation of γ' , no apparent defects like cracks were introduced (see Figure A6 in the Appendix A).

Figure 4. The γ' precipitate morphology of MAD542 superalloy after post-processing heat treatment. (a) Stereo-image from SEM-secondary electron (SE) micrographs on a deep etched sample, showing a high amount of γ' precipitate decorating the grain boundary region with an enlarged view in (b); (c) SEM-SE imaging of high density of γ' precipitates observed in the grain interior region; (d) the enlarged view of cuboidal γ' morphology.

4. Conclusions

To summarize, in this work, a novel chemical recipe of a precipitation-strengthened nickel-based superalloy, MAD542, for AM processes was proposed. By searching the processing window

using a DoE matrix containing nine different printing parameters, the MAD542 superalloy was successfully fabricated in a crack-free condition with limited defects by LPBF. Beyond the excellent manufacturability, this superalloy was successfully heat-treated without any cracking occurrence. The key insight of developing the ‘non-weldable’ nickel-based superalloy in this study was to add a higher amount of Mo, Nb, and Ta. These elements segregated to the interdendritic region and helped to mitigate the interdendritic-like cracking (solidification and liquation cracking) during processing. Meanwhile, the elements Mo and Nb acted as effective SFE reducers, initiating the formation of annealing twins, which decreased the cracking susceptibility (SAC and DDC) during the post-processing treatment. The results from this study will hopefully contribute to a new paradigm for alloy design and lead to more precipitation-strengthened superalloys specifically tailored for AM processes in the future.

Author Contributions: Conceptualization, J.X., R.L.P., and J.M.; methodology, J.X. and H.G.; validation, J.X. and H.G.; formal analysis, J.X., R.L.P., and J.M.; investigation, J.X.; resources, H.G.; data curation, J.X.; writing—original draft preparation, J.X.; writing—review and editing, J.X., H.G., R.L.P., and J.M.; visualization, J.X.; supervision, R.L.P. and J.M.; project administration, J.M.; funding acquisition, J.M. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by the Swedish Agency for Innovation Systems, (Vinnova grant 2016-05175 and 2018-00804); faculty grant from Linköping University (SFO-MAT-LiU#2009-00971); and center for Additive Manufacture–Metal (CAM2).

Acknowledgments: The authors acknowledge K. Minet and A. Shaikh from EOS Finland Oy, J. Gårdstam from Quintus Technologies AB, H. Brodin from Siemens Industrial Turbomachinery AB, E. Hryha from Chalmers University of Technology, and S. Bengtsson from Höganäs AB for helpful and fruitful discussions and efforts, which made the MAD542 superalloy come true.

Conflicts of Interest: The authors declare no conflict of interest.

Appendix A

Figure A1. The thermodynamic equilibrium step diagram of MAD542 using the TCNI10 database in the Thermo-Calc software.

Figure A2. Secondary electron SEM micrographs of the virgin powders of the MAD542 superalloy for laser powder bed fusion. (a) at low magnification with an overall view and (b) at high magnification with a detailed view.

Figure A3. The optical micrographs of the as-built MAD542 processed by #3 printing parameters (laser power: 100 w; scan speed: 1300 mm/s; hatching distance: 50 μm ; layer thickness: 20 μm). (a) The overview of the as-built cube and (b) the enlarged view with higher magnification (sample preparation: metallographic polishing).

Figure A4. The twin boundary (TB) and recrystallization (RX) fraction evolution as a function of annealing time at 1230 $^{\circ}\text{C}$, indicating a combination of rapid RX and TB formation processes. The EBSD scans cover an area of $870 \mu\text{m} \times 1266 \mu\text{m}$ with a 2- μm step size. In the GB + TB maps, the grain boundaries (GB) are plotted in black lines, while TBs are plotted in red lines. In the RX maps, RXed grains are colored in blue. All the scale bars are 125 μm .

Figure A5. Large-scale (around 3.3 mm × 3.3 mm square) optical micrograph of the MAD542 superalloy heat treated at 1230 °C for 2 h (sample preparation: metallographic polishing).

Figure A6. Large-scale (around 3.3 mm × 3.3 mm square) optical micrograph of the MAD542 superalloy heat treated at 1230 °C for 2 h and 900 °C for 24 h (sample preparation: metallographic polishing).

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