

DEVELOPMENT AND PROCESSING OF Ti-Ni-BASED SHAPE MEMORY ALLOYS USING LASER MELTING TECHNIQUES

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**UNIVERSITY OF
BIRMINGHAM**

A thesis submitted to

The University of Birmingham

for the degree of

Doctor of Philosophy

School of Metallurgy and Materials

College of Engineering and Physical Sciences

The University of Birmingham

September 2016

UNIVERSITY OF
BIRMINGHAM

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Abstract

This thesis focused on the development of Ti-Ni-based shape memory alloys (SMA) using a novel alloy development process based on laser melting technique, suspended droplet alloying (SDA), and on development of a manufacturing route for Ti-Ni-based structures using selective laser melting (SLM), specifically for negative Poisson's ratio (NPR) auxetic structures.

To assess the SDA process, a series of Ti-Ni-based binary, ternary and quaternary shape memory alloys (SMA) have been built to analyse the chemical and microstructural homogeneity of the builds produced by the SDA process. The shape memory performance in terms of the transformation temperature, thermal stability and thermo-mechanical stability was also investigated and compared with commercial SMA and literatures. It proved that the SDA built sample was comparable to the bulk SMA prepared by other alloy development processes.

To assess the processability of Ti-Ni-based alloys, SLM process parameters were optimised for Ti-Ni SMA and the SMA NPR structure was built for mechanical testing. It was found that the SLM process parameters can severely alter the microstructure and

shape memory properties due to different cooling rate and Ni vaporisation.

Finally, TiNiCuNb and TiNiHfCuNb alloys were developed using SDA to improve the shape memory properties by altering the precipitates. The analysis of these alloys indicated that the addition of Cu, Hf and Nb altered the precipitate types and morphology altogether, resulting in a unique shape memory behaviour during thermal cycling.

Acknowledgements

I would like to express my sincere gratitude and thanks to those who have supported me both personally and academically. Without them, the completion of this dissertation could not have been possible.

First and foremost, my heartfelt thanks go to my supervisors Prof. Moataz M. Attallah and Dr. Nicholas J. Adkins, whose scientific and financial input helped me improve and finish this work. Their excellent advice on research and career have kept me motivated and enriched my research skills. In addition, I am grateful to Prof. Mike H. Loretto who kindly helped to correct my grammatical errors and minimised the influence of Chinese in this thesis.

I would also like to express my profound gratitude to Dr. Jian Yang, Dr. Hany Hassanin, Dr. Khamis Essa, Mr. Jan White, Mr. Minshi Wang and all other staffs and students in the School of Metallurgy and Materials. I thank you all for the supportive help in my experiment, TEM sample preparation and giving me advice all the time.

I acknowledge Dr. Wayne Voice in ESA and DMPA for financial support and providing me this opportunity to carry on shape memory alloys development on suspended droplet

alloying machine.

Last but not least, I am so grateful to my parents for their love, and continuous support in my scientific research and study in University of Birmingham. A special thanks goes to my fiancée Yangyang Li for her tirelessly support and taking good care of my life.

Preface

This dissertation is submitted for the degree of the Doctor of Philosophy at the University

of Birmingham. It describes research carried out in the School of Metallurgy and Materials between October 2010 and September 2016, under the supervision of Prof. Moataz Attallah and Dr. Nicholas J. Adkins.

Except where appropriately referenced, this work is original and has not been submitted for any other degree, diploma and other qualification. It does not exceed 50,000 words in length.

Parts of this dissertation were published in:

S Li*, S Liu, NJ Adkins, MM Attallah: *Analysis of Microstructural Inhomogeneities of Ti-Based Alloys Produced Via Laser-Based Combinatorial Synthesis*: Proceedings of the TMS Annual Meeting, San Diego, USA, February 2014.

S Li*, H Hassanin, MM Attallah, NJE Adkins, K Essa: *The development of TiNi-based negative Poisson's ratio structure using selective laser melting*, Acta Materialia 105, 75-83, 2016.

(1): The author did the experimental work and fully wrote the paper.

(2): The author did the entire experimental work. Dr. Hany Hassanin and Dr. Khamis Essa did the simulation work in the paper.

Table of Contents

DEVELOPMENT AND PROCESSING OF Ti-Ni-BASED SHAPE MEMORY ALLOYS USING LASER MELTING TECHNIQUES	1
Abstract	2
Acknowledgements	4
Preface	6
Table of Contents	7
Table of figures	10
1. Chapter 1. Introduction, aims and objectives	18
1.1. Ti-Ni-based Shape memory alloys	18
1.2. Aims and objectives	21
2. Chapter 2. Literature Review	25
2.1. Metallurgy of Ti-Ni-based shape memory alloys	25
2.1.1. Phases and crystal structure of Ti-Ni-based shape memory alloys	25
2.1.2. Influence of the alloying elements on the transformation temperatures Ti-Ni-based SMAs	32
2.1.3. Ternary Ti-Ni-based shape memory alloys	37
2.1.4. Other factors affecting the TTs in Ti-Ni-based SMA	48
2.2. Theoretical analysis of the martensitic transformation	51
2.3. Applications of Ti-Ni-based Shape memory alloys	55
2.4. Combinatorial metallurgy	61
2.5. Selective laser melting	71
2.6. Negative Poisson's ratio materials	74
2.7. Summary	79
2.8. Reference	80
3. Chapter 3. Materials and experimental method	100
3.1. Metals and alloyed wires	100
3.2. Ti-Ni pre-alloyed powder	101
3.3. List of samples	101
3.4. Selective Laser Melting	104
3.5. Sample preparation	104
3.6. Microstructural and phases characterisation	106

3.7.	Heat treatment	107
3.8.	Shape memory properties characterisation.....	108
3.9.	Thermo-mechanical testing on shape memory alloys	110
3.10.	Reference	115
4.	Chapter 4. Suspended Droplet Alloying process and shape memory alloys	117
4.1.	Introduction	117
4.2.	Microstructural investigation and phase determine.....	117
4.3.	Temperature measurement and temperature field calculation.....	128
4.3.1.	Temperature measurement and temperature calculation during deposition.....	128
4.3.2.	Temperature measurement and temperature calculation during deposition.....	133
4.4.	Chemical composition	140
4.5.	Gradient composition samples	147
4.6.	Shape memory properties	149
4.7.	Heat treatment	151
4.8.	Conclusions and further work	156
4.9.	Reference.....	157
5.	Chapter 5. Mechanical testing	159
5.1.	Introduction	159
5.2.	Tensile testing at austenite temperature.....	159
5.3.	Thermo-mechanical testing at the austenite temperature	164
5.4.	Fracture surface analysis	169
5.5.	Conclusions and further work	173
5.6.	Reference.....	173
6.	Chapter 6. Selective Laser Melting of Negative Poisson's Ratio Shape Memory Alloy.....	175
6.1.	Introduction	175
6.2.	Design of negative poisson's ratio structure.....	176
6.3.	Material and Experiment Methods	178
6.4.	Results and Discussion	179
6.4.1.	Microstructural assessment of the powder and of SLMed samples	179
6.4.2.	Process Optimisation.....	180
6.4.3.	Build Microstructure	184
6.4.4.	Post SLM Heat Treatments	189

6.4.5.	The Phase Transformation Behaviour.....	191
6.4.6.	NPR Structure Morphology and Performance	195
6.5.	Conclusions and further works.....	199
6.6.	Reference	200
7.	Chapter 7. Development of TiNiHfCuNb shape memory alloys.....	203
7.1.	Introduction	203
7.2.	Influence of Hf and Cu content on transformation temperature of TiNi-based shape memory alloys.....	203
1.1.	Improving stability of quaternary and quinary shape memory alloys.....	210
7.3.	Precipitates controlled by chemical composition in TiNiHfCuNb alloys	220
7.3.1.	Different performance in TiNiHfCuNb SMAs with similar composition	220
7.3.2.	Microstructure of TiNiHfCuNb SMAs	222
7.3.3.	X-ray diffraction analysis of TiNiHfCuNb alloys	231
7.3.4.	Heat treatment on TiNiHfCuNb samples.....	232
7.4.	Conclusions and further work	242
7.5.	Reference.....	244
8.	Chapter 8. Conclusions and Future Work	258
8.1.	The SDA process for alloy development.....	258
8.2.	Thermo-Mechanical fatigue testing on SDA built Ti-Ni-based alloys.....	260
8.3.	Ti-Ni shape memory alloy negative Poisson's ratio structure built by selective laser melting	261
8.4.	The development of TiNiCuNb and TiNiHfCuNb shape memory alloys	262

Table of figures

Figure 1.1. Typical Differential Scanning Calorimetry curve of shape memory alloys showing thermal parameters of transformation including A_s , A_p , A_f , M_s , M_p , M_f and hysteresis. 19

Figure 1.2. A stress-strain-temperature curve for two-way SME observed in Ti-Ni-based SMAs [6]. 20

Figure 2.1. The crystal structures of the phases observed in Ti-Ni-based SMAs (a) B2 austenite phase with cubic structure, (b) martensite orthorhombic B19 phase, (c) martensite monoclinic B19' phase, and (d) rhombohedral R phase. 27

Figure 2.2. Shearing elements in martensite twinning (a) and sketch of martensite twinning deformed from parent phase (b). 30

Figure 2.3. A Time Temperature Transformation (TTT) diagram of $Ti_{48}Ni_{52}$ alloys, showing the evolution of Ni-rich precipitations in Ni-rich SMAs [2]. 35

Figure 2.4. Influence of Ni-concentration on the M_s temperature in Ti-Ni-based SMAs, with the M_s dropping significantly on the Ni-rich side [19]. 36

Figure 2.5. Phase diagram of Ti-Ni alloys [2]. 37

Figure 2.6. Effect of Cu-content on the transformation behaviour of TiNiCu SMAs. One-step B2-B19' transformation occurs at Cu-content lower than 7.5 at. %, while a two-step B2-B19-B19' transformation happens at higher copper content [30]. 39

Figure 2.7. Schematic diagram illustrating the influence of Nb particles on the transformation hysteresis in TiNiNb alloys: (a) Nb-content < 3 at. %; (b) Nb-content from 3 at.% to 20 at. %; (c) Nb-content 20 at.%; (d) Nb content >20 at. % [32]. 40

Figure 2.8. The thermal stability of TiNiHfCu alloys, showing that Cu does not significantly improve the thermal stability of TiNiHf alloys [41]. 44

Figure 2.9. Influence of different alloying elements the M_s of Ti-Ni-based SMAs [2]. 45

Figure 2.10. The Free Energy as a function of lattice distortion at different temperatures for a first order martensitic transformation. Martensite is marked as "M" and "P" for parent phase. Shear strain is presented as order parameter η which indicates the shear distortion of the lattice [2]. 53

Figure 2.11. Model wing with SMA torque tube in in a wind tunnel (developed by Northrop Grumman) [76].60

Figure 2.12. Variable geometry chevron nozzle of a high-bypass jet engine during a flight test by Boeing [76]. 60

Figure 2.13. Schematic illustration of a sputter deposition system to create Ti-Ni-Hf thin

film libraries [84]. 62

Figure 2.14. (a) Schematic illustration of parallel nanoscanning calorimeter, and (b) layout of the calorimeter cell [84]. 63

Figure 2.15. Schematic drawing of the LENS process with coaxial nozzle feeders. 65

Figure 2.16. Ti-Ni-Fe ternary materials library deposited by powder-based LENS combinatorial synthesis [87]. 66

Figure 2.17. Laser absorption of different metals under different wavelengths. Most metals show decreasing absorption as the wave length increases [91]. 70

Figure 2.18. A schematic diagram for SLM process with building chamber, powder chamber, laser system, scanning system and wiper [97]. 73

Figure 2.19. Negative Poisson's ratio or auxetic materials, which shrinkage during compress, act contrarily to convention materials can be applied for many structural and functional applications [119]. 77

Figure 3.1. TiNi sample built by suspend droplet alloying process. The diameter of steel disk substrate is 20mm. The different color on sample surface is due to different oxidation thickness of Ti oxide. 103

Figure 3.2. Schematic drawing of electrical discharge machining used for sample cutting {Jameson, 2001 #185}. 105

Figure 3.3. DSC testing result of hot-rolled Ti-Ni reference sample with different sample dimension. The result shows that the larger size sample has a higher transformation temperature as well as higher amount of heat in transformaiton. 109

Figure 3.4. Schematic diagram of dog bone shape shape memory alloys sample used for thermal mechanical testing. The sample surface with gauge area was ground by P1200 SiC paper. 112

Figure 3.5. ESH hydraulic mechanical testing machine with vertical tube furnace was applied for thermal mechanical testing 114

Figure 4.1. (a) Optical micrograph for the cross-section of etched $\text{Ti}_{50}\text{Ni}_{50}$ sample, showing the three microstructural zones, and (b) showing the distribution of Ti_2Ni (dark spots). (c) XRD pattern for the same sample showing the phases (B19' and Ti_2Ni). 120

Figure 4.2. The SDA $\text{Ti}_{52}\text{Ni}_{48}$ sample, showing (a) the columnar grain structure oriented towards the central zone, (b) backscattered electron micrograph of the remelted zone in XY plane, (c) secondary image showing the remelted zone in XZ plane and (d) dendrites surrounded by Ti_2Ni 122

Figure 4.3. A schematic drawing of SDA process. The temperature range in the figure is not measured temperature but estimated to introduce the concept. The time is measured during actual building with slow feed rate. 124

Figure 4.4 Ti-Ni phase diagram [1]126

Figure 4.5. The EBSD map of the XY section of $\text{Ti}_{48}\text{Ni}_{52}$ sample (a) and $\{100\}$ pole figure of the whole sample (b) shows strong texture in the $\{100\}$ direction in XY section. 127

Figure 4.6. Substrate temperature variation in SDA process according drops during heating (a) and time during cooling (b). The black line with square spots is the substrate temperature of 516W deposition, the red line with round spots is for 813W deposition and the green line with triangle spots is for 1312W. 130

Figure 4.7. Temperature field in the SDA samples during cooling against time with (a) 516 W deposition power, (b) 813 W deposition power and (c) 1312 W deposition power. Temperature field in the sample is linear but the cooling rate is exponential. The fastest cooling rate of these sample is about 5 K/s (300 K/min) at the top of 516 W deposited sample. 139

Figure 4.8. Ti-content contour for the XY section of $\text{Ti}_{50}\text{Ni}_{50}$ sample (a) shows the ring structure and the total composition is close to target, the contour for XY section of $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ sample (b) shows the composition variation in ternary sample, and (c) shows XZ section of TiNi_{48} sample with the remelt pattern in the centre. 142

Figure 4.9. A schematic illustration for the interaction of the wires and the droplet during melting in SDA process. The Ti wire melts slower than the Ni wire due to the higher melting point of Ti. In some extreme situations, the high melting point wire may penetrate the droplet during melting. 143

Figure 4.10. EDS mapping of TiNi_{40} droplet in different sections, showing the chemical composition distribution within the droplet. The Ti content varied from 55 at. % to 71 at.% in the droplet. The position of section is labelled at the top left corner of image as Z position, the sample started from 6 mm to 14 mm in Z axis (section position can be found in Figure 4.8). 147

Figure 4.11 Chemical composition in the compositional gradient samples made by SDA process. The EDS results in the vertical section (a) showing the Hf-content varying from 0 at.% to 25 at.% within the $\text{Ti}_{52-x}\text{Ni}_{48}\text{Hf}_x$ sample and (b) showing the Cu-content varying from 0 at.% to 20 at.% within the $\text{Ti}_{52}\text{Ni}_{48-x}\text{Cu}_x$ sample. 148

Figure 4.12. DSC trace for hot-rolled reference sample (blue solid), as-built $\text{Ti}_{50}\text{Ni}_{50}$ (green dash dot dot), $\text{Ti}_{52}\text{Ni}_{48}$ (orange dot) SDA samples and heat treated $\text{Ti}_{52}\text{Ni}_{48}$ (black dash), heat treated $\text{Ti}_{50}\text{Ni}_{50}$ (red dash dot). 150

Figure 4.13. DSC trace for hot-rolled $\text{Ti}_{50.4}\text{Ni}_{39.6}\text{Cu}_{10}$ reference sample (black line) and SDA built $\text{Ti}_{52}\text{Ni}_{38}\text{Cu}_{10}$ sample shows the same transformation behavior. 151

Figure 4.14. Composition contour of XZ section of heat treated $\text{Ti}_{52}\text{Ni}_{48}$ sample with homogeneous composition in the centre. 152

Figure 4.15. DSC curves of reference hot rolled $\text{Ti}_{50.4}\text{Ni}_{49.6}$ sample (golden line marked as reference), As built $\text{Ti}_{50}\text{Ni}_{50}$ sample (dark blue line marked as As-built TiNi_{50}) and 3 h (pink line marked as HT3 Ni_{50}Ti), 6 h (green line marked as HT6 Ni_{50}Ti), 24 h (blue line marked as HT24 Ni_{50}Ti), 48 h (red line marked as HT48 Ni_{50}Ti), 100 h (black line marked as HT100 Ni_{50}Ti) heat treated Ni_{50}Ti samples. The as-built sample has lower transformation temperature while the heat treated samples have the sample transformation behaviour as the reference sample. 155

Figure 5.1. Tensile testing curve of $\text{Ti}_{50.4}\text{Ni}_{49.6}$ reference SMA sample at 573 K (austenite phase). The maximum stress was 757 MPa and the permanent strain after testing was 0.7 %. 161

Figure 5.2. Tensile testing curve of $\text{Ti}_{50.5}\text{Ni}_{49.5}$ SDA built SMA sample at 573 K (austenite condition). The maximum stress was 780 MPa and the permanent strain after testing was 1.1 %. 162

Figure 5.3. Tensile testing curve of $\text{Ti}_{54}\text{Ni}_{34}\text{Cu}_{12}$ SDA built SMA sample at 573 K (austenite condition). The maximum stress was 651 MPa and the permanent strain after testing was 0.013%. 163

Figure 5.4. TMF testing result of $\text{Ti}_{50.4}\text{Ni}_{49.6}$ reference sample. The testing temperature was 573K, maximum stress was 800MPa and the sample was broken after 40 test cycles. The starting strain and residual strain are the strain before and after each cycle loading. 166

Figure 5.5. TMF testing result of $\text{Ti}_{50.5}\text{Ni}_{49.5}$ SDA sample. The testing condition is the same as the reference sample and the sample was also broken after 40 cycles. 167

Figure 5.6. TMF testing on $\text{Ti}_{54}\text{Ni}_{34}\text{Cu}_{12}$ SDA sample at 573K, 600MPa. Due to the starting strain in this testing were all the same as residual strain, the starting strain was not plotted here. 168

Figure 5.7. Low stress (400MPa) TMF testing on $\text{Ti}_{50.5}\text{Ni}_{49.5}$ SDA sample. The residual strain became stable after 30 cycles. 169

Figure 5.8. BSE image of fracture of bottom-right corner of $\text{Ti}_{50.4}\text{Ni}_{49.6}$ reference sample showed a crack around the corner. 171

Figure 5.9. Fracture surface of $\text{Ti}_{50.4}\text{Ni}_{49.6}$ reference sample showed dimpled structure and the holes were Ti-rich precipitates. 171

Figure 5.10. Fracture surface of $\text{Ti}_{50.5}\text{Ni}_{49.5}$ SDA sample showed larger dimpled structure and cleavage facets comparing to reference sample. 172

Figure 5.11. Fracture surface of $\text{Ti}_{54}\text{Ni}_{34}\text{Cu}_{12}$ SDA built SMA shows a generally brittle fracture surface, with large amount of mirco-cracks along the cell boundary. 172

Figure 6.1: (a) Influence of re-entrant angle on Poisson's ratio in two different model, (b) 3D construction of AM modified re-entrant design [144]. 177

Figure 6.2. The Ti-Ni powder in as-received condition; a) morphology of powder, b) dendritic microstructure and an entrapped gas pore in particles section and c) powder size distribution [144]. 180

Figure 6.3. The plot of energy density vs porosity, showing the porosity fraction variation in Ti-Ni SLM [144]. 181

Figure 6.4. Lack of structural integrity in the samples built using energy density < 350 J/mm³ [144]. 183

Figure 6.5. The correlation of the EL and cracking density with the (a) porosity fraction and (b) crack density, showing representative builds from the extremes of the investigated window; (c) low cracking only (90 W, 115 mm/s, 0.0675 mm, high E_L), (d) low cracking and low porosity (70W, 105mm/s, 0.0675mm), and (e) low porosity only (60 W, 120 mm/s, 0.056 mm, low E_L) [144]. 183

Figure 6.6. BSE micrographs taken along the X-Z plane showing (a) the residual porosity in high E_L samples (90 W, 115 mm/s, 0.0675 mm), (b) the dendritic structure and the melt pool beads in the low E_L condition (60 W, 120 mm/s, 0.056 mm), and (c) high magnification micrograph for the low E_L condition [144] 185

Figure 6.7. Ti₂Ni area fraction around the pores in high E_L sample. Most pores show decreasing Ti₂Ni area fraction as the distance increasing but some of them show different variation. 187

Figure 6.8. Horizontal thermal cracks shown by white arrows at the edge of near fully dense sample and vertical cracks appeared after sectioning in (a) optical microscope image, cracks grow through the cell and Ti₂Ni (b) and cracks are initiated on Ti₂Ni in (c) back-scatter images of XZ section [144]. 188

Figure 6.9. XRD result for SLM built Ti-Ni and powders reveal the presence of B19' and Ti₂Ni. The high E_L sample has larger amount of Ti₂Ni than the low E_L sample), while the powder (blue) has random orientations [144]. 189

Figure 6.10. DSC trace of the low E_L AF condition shows Ti₂Ni melts around 1000°C and solidified about 980°C during cooling [144]. 190

Figure 6.11. Back-scatter images of 1000°C 2h solution treated (HT2) sample in (a) XY plane and (b) ZX plane show the precipitations separated into small spot or short bar after heat treatment [144]. 191

Figure 6.12. DSC traces for the as-built low E_L, as-built high E_L and heat-treated low E_L samples. The low E_L sample (noted as Low E_L with dash line) has the widest martensitic transformation peak from 56 to 30°C, the high E_L sample (note as Low Energy with solid line) has narrower peak than low E_L sample with the 4°C lower martensite start temperature (M_s), while the heat-treated sample (dot line) has the narrowest peak with M_s at 56°C [144]. 193

Figure 6.13. Dark field TEM image of low E_L sample showing Ti_2Ni and $TiNi$ matrix. The EDS result shows the martensite area indicated by black arrow is Ti-riched (51 at.% Ti), while the area near Ti_2Ni indicated by white arrow is Ni-riched (49 at.% Ti) [144]. 195

Figure 6.14. The morphology of NPR cells investigated by SEM (a) conventional re-entrant design, (b) modified AM re-entrant design [144]. 196

Figure 6.15. Force-displacement curve shows the as-fabricated sample (blue) has higher strength but lower ductility than the heat treated sample (red) [144]. 198

Figure 6.16. The Poisson's ratio $\nu_{\tau z}$ (-2.01) was calculated as the negative ratio between the transverse and vertical deformation from the best fit of force-displacement data of heat treated sample [144]. 199

Figure 7.1. Improvement of Martensitic transformation start temperature (ΔM_s) of $TiNiHf$ SMA according to the Hf content. 204

Figure 7.2. Decreasing of martensitic transformation start temperature (M_s) of some $TiNi$ based SMA as the increasing of thermal cycles. The $TiNiCu$ alloys have very good thermal cycle stability and the $TiNiHf-Cu$ alloy has higher M_s and better thermal cycle stability than $TiNi$ alloy. 206

Figure 7.3. Influence of Cu content on martensite transformation temperature (M_s) of Ti-Ni shape memory alloys shows linear M_s decreasing as the Cu content increase. 208

Figure 7.4. Both $Ti_{36}Ni_{49-x}Hf_{15}Cu_x$ (labelled as Ti-Ni-Hf15-Cux) and $Ti_{41}Ni_{49-x}Hf_{10}Cu_x$ (labelled as Ti-Ni-Hf10-Cux) alloys shows linear decreasing M_s as the Cu content increase in $TiNiHfCuNb$ alloys. The influence of Cu become stronger in higher Hf content alloys. 210

Figure 7.5. Nb decreases the M_s of Ti-Ni SMA and slightly increases the A_s , which leading large temperature hysteresis in $TiNiNb$ SMA. The Nb content and M_s shows near linear relation in $TiNiNb$ alloys [33]. 211

Figure 7.6. $Ti_{51-0.5x}Ni_{39-0.5x}Cu_{10}Nb_x$ produced by SDA process shows Nb decreases the M_s but the hysteresis remains the same level as Ti-Ni alloys and the thermal stability is as good as $TiNiCu$ SMA. 212

Figure 7.7. Backscatter image of $Ti_{51-0.5x}Ni_{39-0.5x}Cu_{10}Nb_x$ samples produced by SDA. The sample with 1 at. % Nb (a) has a few Nb-rich particles (white) around the $Ti_2(Ni,Cu)$ precipitates. The sample with 2 at. % Nb (b) has larger Nb-rich particles around the precipitates. The sample with 3 at. % Nb (c) shows more Nb-rich particles with 2 to 3 μm size around the $Ti_2(Ni,Cu)$. (d) shows low magnification backscatter image of $Ti_{49.5}Ni_{37.5}Cu_{10}Nb_3$ SMA. 214

Figure 7.8. Transformation temperature and thermal cycle stability of $Ti_{41-x}Ni_{44-x}Cu_5Hf_{10}Nb_{2x}$ SMA. 216

Figure 7.9. Transformation temperature and thermal cycle stability of $\text{Ti}_{41-x}\text{Ni}_{39-x}\text{Cu}_5\text{Hf}_{10}\text{Nb}_{2x}$ SMA. The alloys with 1 at.% Nb has higher Ms than the others but the thermal stability is the worst. 217

Figure 7.10. Influence of Nb content on thermal cycle stability of TiNiCuHfNb SMA shows the thermal stability increases until the Nb content raises up to 1 at.% and the 2 at.% Nb alloy has the best thermal cycle stability. 218

Figure 7.11. Influence of Nb content on transformation heat during the third and the eleventh thermal cycle. The transformation heat increases as Nb content increasing. 219

Figure 7.12. Transformation heat difference between austenite and martensite transformation 219

Figure 7.13. DSC curve of $\text{Ti}_{43}\text{Ni}_{33}\text{Hf}_{10.5}\text{Cu}_{11}\text{Nb}_{2.5}$ sample showed low Ms (251 K), board transformation peak (50 K) and good thermal cycle stability (three cycles overlapped). 221

Figure 7.14. DSC curve of $\text{Ti}_{44}\text{Ni}_{34}\text{Hf}_{10}\text{Cu}_{10}\text{Nb}_2$ sample showed high Ms (305K), narrow transformation peak (30K) and poor thermal cycle stability. 221

Figure 7.15. Backscatter image of low Ms $\text{Ti}_{43}\text{Ni}_{33}\text{Hf}_{10.5}\text{Cu}_{11}\text{Nb}_{2.5}$ sample shows fine dendrite and Ti(Hf)-rich precipitates around dendrite boundary. The EDS area analysis result show the composition of sample is $\text{Ti}_{44.8}\text{Ni}_{34}\text{Hf}_{10}\text{Cu}_{8.5}\text{Nb}_{2.7}$. 223

Figure 7.16. Backscatter image of high Ms $\text{Ti}_{44}\text{Ni}_{34}\text{Hf}_{10}\text{Cu}_{10}\text{Nb}_2$ sample shows larger dendrite size and 4 different type of precipitates, which are dark contrast, medium contrast, light contrast and flower shape. The EDS area analysis result shows the sample composition is $\text{Ti}_{42}\text{Ni}_{33}\text{Hf}_{10.5}\text{Cu}_{12}\text{Nb}_{2.5}$ 224

Figure 7.17. EDS mapping around the precipitates in $\text{Ti}_{43}\text{Ni}_{33}\text{Hf}_{10.5}\text{Cu}_{11}\text{Nb}_{2.5}$ low Ms sample shows three different types of precipitates. 226

Figure 7.18. EDS mapping around the precipitates in $\text{Ti}_{43}\text{Ni}_{33}\text{Hf}_{10.5}\text{Cu}_{11}\text{Nb}_{2.5}$ low Ms as-built sample shows high Nb content in the precipitates with the darkest contrast. The precipitates generally have higher Ti and Nb content. 228

Figure 7.19. EDS line analysis cross precipitates in $\text{Ti}_{43}\text{Ni}_{33}\text{Hf}_{10.5}\text{Cu}_{11}\text{Nb}_{2.5}$ low Ms sample shows high Ti content in precipitate but the Ti content start decreasing at the darkest contrast area while the Nb content increases. The Ni content is slightly higher near the precipitates. 229

Figure 7.20. EDS mapping around the precipitates in $\text{Ti}_{44}\text{Ni}_{34}\text{Hf}_{10}\text{Cu}_{10}\text{Nb}_2$ high Ms sample shows three different types of precipitates. 230

Figure 7.21. EDS line analysis cross precipitates in $\text{Ti}_{44}\text{Ni}_{34}\text{Hf}_{10}\text{Cu}_{10}\text{Nb}_2$ high Ms sample shows high Ti content in precipitate but the Ti content decreases in the flower shape precipitates while the Nb content increases. 231

Figure 7.22. XRD result of high Ms (marked as TiNiHfCuNb₂) alloy at room temperature shows martensite due to the Ms is higher than room temperature, while the low Ms (TiNiHfCuNb_{2.5}) shows austenite with some small martensite peak at room temperature. 232

Figure 7.23. High temperature DSC testing result of as-built Ti₄₄Ni₃₃Hf₁₀Cu₁₀Nb₂ high Ms sample indicates multi-phases and changed of local composition in some phases. 234

Figure 7.24. Magnified peak areas of high Ms Ti₄₄Ni₃₃Hf₁₀Cu₁₀Nb₂ DSC curves (a) the endothermic/melting peak of the lowest melting phase during heating, (b) the exothermic/solidification peak of the lowest melting phase during cooling, (c) the endothermic/melting peak with the highest transformation energy phase during heating, (d) the exothermic/solidification peak with the highest transformation energy phase during cooling, (e) the endothermic/melting peak of the highest melting point phase during heating, (f) the exothermic/solidification peak with the highest melting point phase during cooling. 236

Figure 7.25. Backscatter image of heat treated TiNiHfCuNb low Ms sample shows the change of precipitates. 238

Figure 7.26. High magnification backscatter image and EDS mapping of precipitates in heat treated TiNiHfCuNb low Ms sample 239

Figure 7.27. DSC testing result of heat treated Ti₄₃Ni₃₃Hf_{10.5}Cu₁₁Nb_{2.5} low Ms alloys show narrow transformation peaks and stable transformation behavior with similar transformation temperature to as-built sample. 240

1 Chapter 1. Introduction, aims and objectives

1.1 Ti-Ni-based Shape memory alloys

Since they were first reported by the U.S. Naval Ordnance Lab in 1962 [1-3], Shape Memory Alloys (SMAs), have attracted much attention for their unique shape memory effect (SME) and superelasticity (SE) or pseudoelastic performance. The characteristic of SME is observed because of a diffusionless reversible martensitic transformation (MT) between two phases; martensite and austenite [2]. The phase transformation is accompanied by a shape change, which occurs due to the volumetric changes associated with the change in the crystal structure. SME is a phenomenon where the apparent plastic strain caused by deforming below the austenite start temperature (A_s) can be recovered by heating the material above the austenite finish temperature (A_f) because of the crystallographically reversible martensite transformation. If the material does not change its shape upon cooling, it is called a one-way SME. Alternatively, a two-way shape memory effect (TWSME) means the material will shift to its low temperature shape between the martensite start temperature (M_s) and martensite finish temperature (M_f) upon cooling. Austenite experiences detwinning during loading, which is retained on unloading. Heating transforms the detwinned martensite into austenite, which forms twinned martensite on cooling. The recoverable strain in one-way SME can be as large as

20%, while the strain in TWSME is lower, below 5% in most SMAs [2, 4]. Generally, the hysteresis in SMA is defined as the temperature difference between A_f and M_s ($\Delta T = A_f - M_s$) as shown in Figure 1.1. A typical strain-temperature curve of two-way SMA is shown in Figure 1.2.

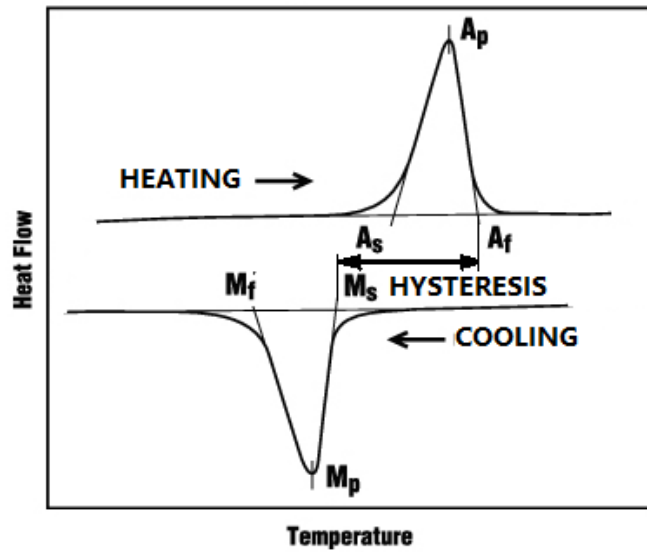


Figure 1.1. Typical Differential Scanning Calorimetry curve of shape memory alloys showing thermal parameters of transformation including A_s , A_p , A_f , M_s , M_p , M_f and hysteresis.

The other phenomenon observed in some SMAs, SE, is a pseudoelastic effect that occurs in austenite because of a stress-induced martensitic transformation upon loading. The strain induced during loading can be fully recovered in a reverse martensite to austenite transformation on unloading [2, 5].

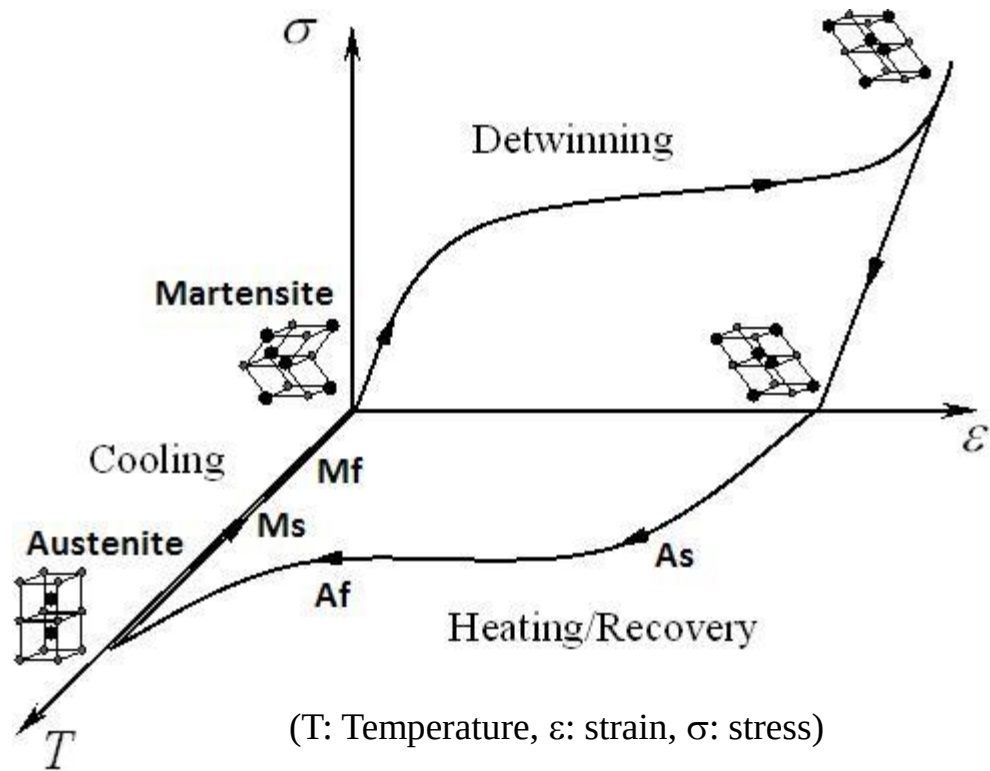


Figure 1.2. A stress-strain-temperature curve for the two-way SME observed in Ti-Ni-based SMAs [6].

SMA (either employing SME or SE) can be used for many applications including couplings, actuators, sensors, stents, implants, structural materials and surgical tools due to their unique properties. However, some characteristics of SMA (e.g. poor thermal and thermo mechanical stability, relatively low transformation temperature, low transformation stress and high hysteresis) have limited their application. Hence, developing SMA with good thermal and thermal-mechanical stability as well as high M_s temperature (above 373K) are necessary for many applications, such as actuators and implants. However, the number of alloying elements that could be

added into Ti-Ni-based SMAs to optimise the desired properties makes it prohibitive to use standard alloy development routes. Most researches on SMAs nowadays use arc-melting, followed by homogenisation, hot rolling and heat treatment to produce bulk materials for testing, which is a time-consuming approach for alloy development. Thus, a new high throughput alloy development route is required, which is capable of producing samples with different compositions faster and to assess the properties, is necessary for developing SMAs. In addition, complicated shapes of accurate dimensions are commonly required for SMAs components. However, SMAs manufacturing still relies on casting, hot rolling, and/or machining SMAs. The machinability of SMAs is known to be poor, combined with their sensitivity to oxygen pickup which could happen during casting or hot rolling [7]. Hence, a new netshape manufacturing process needs to be investigated for complex structural SMAs components.

1.2 Aims and objectives

The thesis focuses on the development and additive manufacturing processing of Ti-Ni-based SMAs, through investigating the application of a novel laser-based combinatorial alloy development route, Suspended Droplet Alloying (SDA) method, in the development of Ti-Ni-based SMAs for high temperature applications (373K) with high thermal-mechanical stability. Additionally, the utility of a netshape additive

manufacturing (AM) process, selective laser melting (SLM), for producing complex structural SMAs components is assessed.

The specific objectives of this work are:

1. To assess the SDA method, focusing on its ability to produce microstructurally and chemically homogeneous samples.
2. To compare the SDA method to other combinatorial alloy development techniques, through comparing the influence of the alloying additions on the SME for samples synthesised using SDA and other techniques.
3. To apply SDA for alloy development of a high temperature Ti-Ni-based SMA.
4. To investigate the utility of SLM in producing complex Ti-Ni-based auxetic structures.

SDA is a multi-wire laser combinatorial metallurgy system that was developed in the EU-funded project Accelerated Metallurgy (AccMet). As a part of the project, the SDA method was used to build Ti-Ni-based SMAs of varying compositions in order to develop new high temperature SMAs. The project aims to accelerate the discovery and optimisation of high-performance alloys by rapidly synthesising large numbers of composition-varying samples, followed by investigating the microstructure and properties. As the samples are produced and tested in a much shorter time than the

traditional alloy development routes, it is hoped that the process will lead to the discovery of promising alloy compositions. The prototype SDA system at the University of Birmingham uses a 1900W CO₂ laser with 6 wire feeders.

The thesis also investigates the use of laser-based powder bed netshape processing techniques, namely SLM, in the manufacture of negative Poisson's ratio (NPR) auxetic structures. The complexity of the auxetic structures limits the potential manufacturing approaches into laser micro-machining or electron beam melting (EBM). The thesis details the influence of SLM processing parameters on structural integrity, shape memory properties of Ti-enriched TiNi binary SMAs, in addition to impact of the process on the microstructure, chemical inhomogeneity, and phase transformation behaviour. Using the optimum SLM parameters, an auxetic structure was produced and its mechanical properties were assessed.

The thesis is divided into 8 chapters. The basic principles of Ti-Ni-based SMAs, the combinatorial synthesis process, SLM and Negative Poisson's Ratio (NPR) materials are introduced in Chapter 2. Chapter 3 covers the materials and experimental methods used in this study including: Optical Microscopy (OM), Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), Electron Backscattered Diffraction (EBSD), X-ray Diffraction (XRD), Differential Scanning Calorimetry (DSC), and mechanical testing of the SME using a test method referred

to as Thermo-Mechanical Fatigue (TMF) testing. Chapter 4 reports the microstructural and chemical homogeneity of SDA samples based on Ti-Ni-based binary and ternary SMAs. In addition, the influence of post-SDA heat treatment on the homogeneity of SDA samples and their performance is studied. Chapter 5 compares the TMF testing results among literature results, reference sample, SDA built Ti-Ni and TiNiCu sample. Chapter 6 discusses the development of NPR Ti-Ni structures using SLM, highlighting the influence of the process parameters on microstructural, structural integrity, mechanical properties, and SME development. Using the alloying-property correlations obtained in Chapter 4, new TiNiCuNb and TiNiCuHfNb SMA alloy are developed by SDA and are investigated in Chapter 7. Chapter 8 summarises the work carried out in this thesis and suggests areas for further work.

2 Chapter 2. Literature Review

2.1 Metallurgy of Ti-Ni-based shape memory alloys

2.1.1 Phases and crystal structure of Ti-Ni-based shape memory alloys

Martensitic transformation is a diffusionless transformation, which allows the SME to occur at low temperatures and reasonably rapidly. The crystal structure of the high temperature phase (the austenite phase) is B2 (see Figure 2.1 (a)). Figure 2.1 (b) and (c) are the crystal structures of the low temperature martensite phases, which are the orthorhombic B19 phase, which shears on (110)[1-10] from the B2 phase, and the monoclinic B19' phase, shears on (001)[1-10] from B2 phase [2, 8]. Another phase could occur in heat treated Ni-rich Ti-Ni SMA during phase transformation or some alloyed Ti-Ni-based SMA, is R phase.

This low temperature twinned martensite phase can be detwinned under load, allowing the material to show high strain on the macro-scale. Due to the low shear resistance of martensite (c' or c_{44}), the shearing stress in martensite is about 300 MPa [3, 9]. At high temperature, however, the materials transform back to the cubic B2 phase, allowing the material to recover to its original shape. The material does not show any strain during cooling until there is enough stress applied on it, for the twinning martensite to accommodate the original shape. This behaviour is the one-way shape memory effect, whereas thermo-mechanical treatment (known as

training) is essential to the two-way shape memory effect (TWSME). After 20 to 50 thermo-mechanical cycles, dislocations accumulate. The martensite accommodates these defects at low temperatures, showing strain on the macro-scale. Obviously, this strain is much lower than the one in one-way SME, and as such becomes unstable as the temperature increases [4, 10].

Many researchers have also reported an alternative pathway for the phase transformation, which involves the rhombohedral R-phase, Figure 2.1 (d). The rhombohedral R-phase forms as an intermediate phase between the B2 phase and B19' phase after a suitable heat treatment in Ni-rich Ti-Ni SMAs, after adding certain alloying elements (e.g. Fe and Al) or under a certain stress field [2]. Recent research has shown that the R-phase transformation is combined with B19' transformation, while it occurs due to the B19' transformation temperature decreases faster than R-phase transformation temperature under these conditions [2]. The crystal structure of the R-phase is $P\bar{3}1m$ space group structure, which is obtained by elongating the B2-phase along the $\langle 111 \rangle$ direction. The lattice parameter of R phase in Ti-NiFe is $a_r=0.602\text{nm}$, corner angle $\alpha=90.7^\circ$. Although the R-phase has a much smaller temperature hysteresis (about 2 K) than the B2 to B19' transformation (about 30 K), it is not stable in Ti-Ni SMAs. Furthermore, the recoverable strain due to the R phase transformation is lower than B2 to B19' transformation [11].

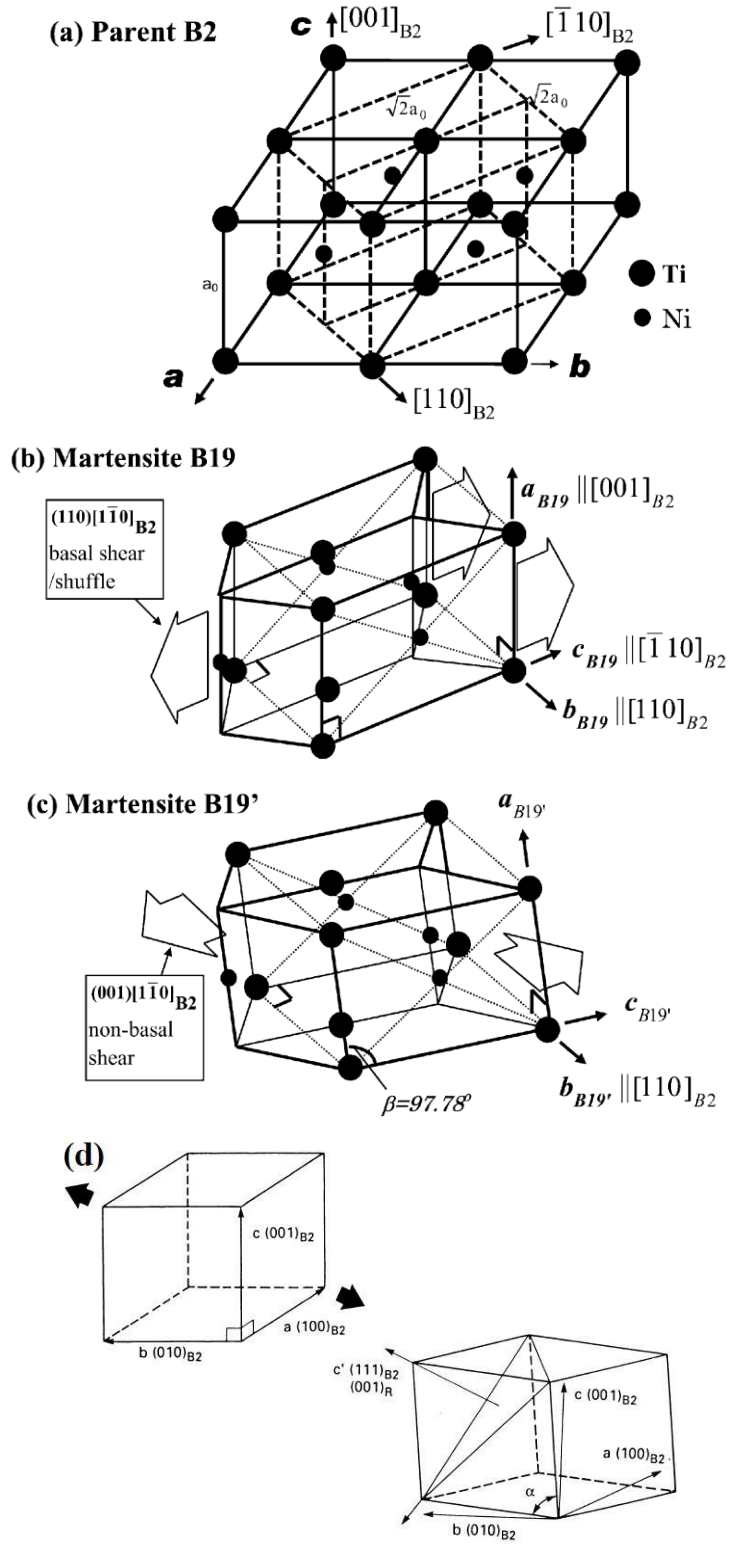


Figure 2.1. The crystal structures of the phases observed in Ti-Ni-based SMAs (a) B2 austenite phase with cubic structure, (b) martensite orthorhombic B19 phase, (c) martensite monoclinic B19' phase, and (d) rhombohedral R phase[2].

Table 2.1 Lattice parameters and crystal structure of Ti-Ni-based alloys with different composition [12-15].

Alloys	phase	a (nm)	b (nm)	c (nm)	α	β
Ti-Ni	B2	0.3015	-	-	-	-
	B19'	0.2889	0.4120	0.4622	-	96.8°
TiNiFe	R	0.6020	-	-	90.7°	-
TiNiCu	B2	0.3030	-	-	-	-
	B19	0.2881	0.4279	0.4514	-	-
TiNiHf	B2	0.309	-	-	-	-
	B19'	0.293	0.411	0.473	-	100.4°
TiNiZr	B2	0.309	-	-	-	-
	B19'	0.297	0.412	0.472	-	98.6 °

The crystal structure of the B2 austenite phase is transformed from body-centered cubic (BCC) to B2 (CsCl) at 1363K [13]. The lattice parameter of this phase is $a=0.3015\text{nm}$. This parameter will slightly vary when the other elements are added in the alloys, with 10 at. % copper for example the $a_c = 0.3030 \text{ nm}$ [14]. B19' martensite is a monoclinic phase belonging to $P2_1/m$ space group. The lattice parameter of B19' has been determined by using single crystal X-ray diffraction as $a_m=0.2889\text{nm}$, $b_m=0.4120\text{nm}$, $c_m=0.4622$, $\beta_m=96.8^\circ$ [15]. When the other elements are included (for example Cu higher than 10 at.%), the martensite can be altered to B19 orthorhombic martensite with the lattice parameters as $a_o=0.2881 \text{ nm}$ $b_o=0.4279$

nm, $c_0=0.4514$ nm in $\text{Ti}_{49.5}\text{Ni}_{40.5}\text{Cu}_{10}$ alloy [14].

The habit plane is an important characteristic for the martensitic transformation. As described above, the martensite phase is transformed from austenite parent phase by shearing. The habit plane is the invariant plane in the lattice before and after transformation, Figure 2.2 (b). There are two types of twinning modes in the martensitic transformation (i.e. Type I and Type II), which have two different types of habit plane. In Type I twinning, the habit plane originates from a mirror plane of the parent phase, while the Type II twinning originates from a twofold axis of the parent lattice. As illustrated in the circle in Figure 2.2 (a), there are five twinning elements, K_1 , η_1 , K_2 , η_2 and s , for twinning description. The half circle in Figure 2.2 (a) presents the twinning before deformation and the half ellipsoid, which is deformed from the half sphere, presents the lattice after deformation. K_1 is the shearing plane or the first undistorted plane (i.e. the habit plane, normal to the paper), while η_1 is the shearing direction. The plane of shear, which is the plane of the paper in this case, is normal to K_1 plane and contains the η_1 direction. K_2 represent the second undistorted plane, the intersection of the plane of shear and K_2 is the second shearing direction η_2 . s is the twinning shear which creates the twinned lattice. Any three of the elements above can be calculated from the other two elements by using Bilby–Crocker theory [16]. If the twinning with rational indices K_1 and η_2 , the K_2 and

η_1 are irrational and the crystals between each other are mirror symmetry to the K_1 plane, then it is Type I twinning. The Type II twinning, however, has rational indices of K_2 and η_1 , irrational indices of K_1 and η_2 , and the crystals are related by rotating the next crystals 180° around the η_1 . The Type I and Type II twinning are conjugate to each other. If all the elements K_1 , η_1 , K_2 , η_2 and s are rational indices, the twinning is called compound twinning, which means the twinned crystals have the symmetry properties of both Type I and Type II. All the twinning for B19' are listed in Table 2.2

Twinning modes of B19' martensite. There are four twinning modes, which are Type I, Type II, compound and a special twinning mode for B19' martensite [2].

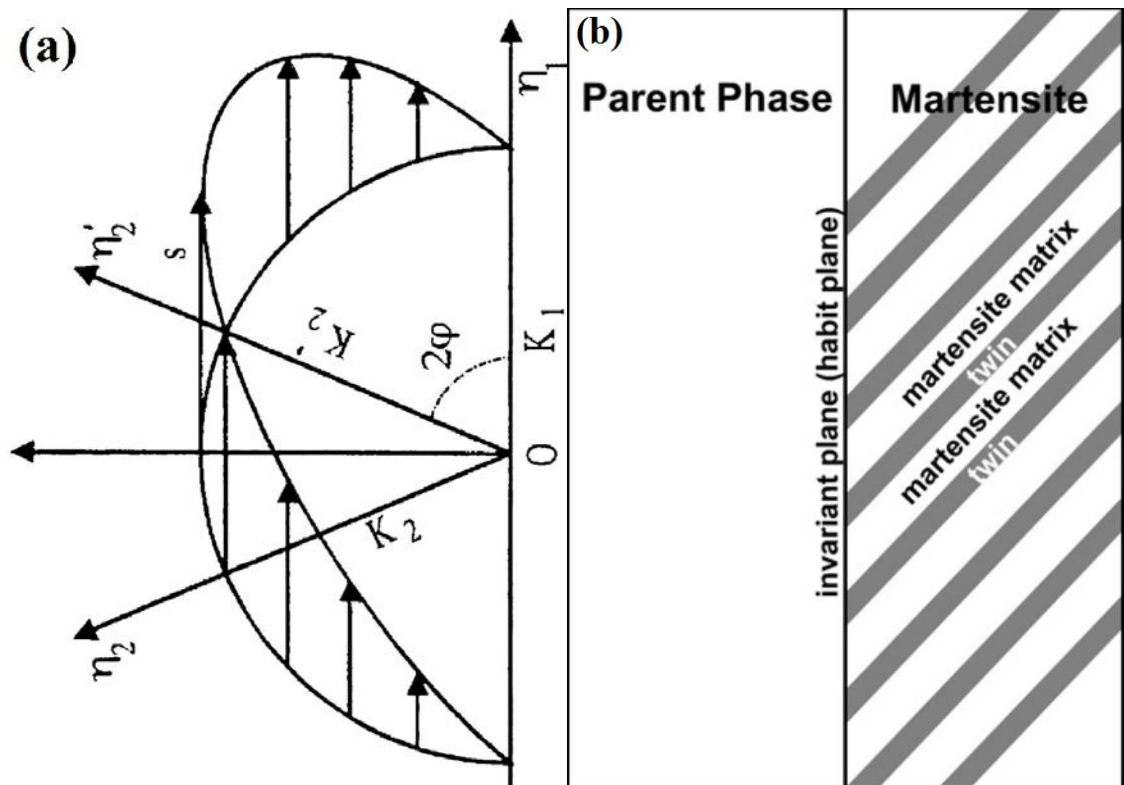


Figure 2.2. Shearing elements in martensite twinning (a) and sketch of martensite twinning deformed from parent phase (b).

Table 2.2 Twinning modes of B19' martensite. There are four twinning modes, which are Type I, Type II, compound and a special twinning mode for B19' martensite [2].

Twinning modes of B19' martensite

Twinning mode	K_1		η_1		K_2	η_2	s
$\{\bar{1}\bar{1}1\}$	$(\bar{1}\bar{1}1)$	$(\bar{1}\bar{1}0)_p$	$[0.540430.459571]$		$(0.246950.506111)$	$[\bar{2}\bar{1}1]$	0.30961
Type I	$(\bar{1}11)$	$(\bar{1}01)_p$	$[0.540430.459571]$		$(0.246950.506111)$	$[\bar{2}11]$	0.30961
$\{111\}$	(111)	$(101)_p$	$[\bar{1}.511720.511721]$		$(\bar{0}.668750.337501)$	$[211]$	0.14222
Type I	$(1\bar{1}1)$	$(1\bar{1}0)_p$	$[\bar{1}.511720.511721]$		$(\bar{0}.668750.337501)$	$[2\bar{1}1]$	0.14222
$\{011\}$	(011)	$(001)_p$	$[1.572711\bar{1}]$		$(0.720531\bar{1})$	$[011]$	0.28040
Type I	$(01\bar{1})$	$(010)_p$	$[1.5727111]$		$(\bar{0}.7205311)$	$[01\bar{1}]$	0.28040
$\langle 011 \rangle$	$(0.720531\bar{1})$		$[011]$	$[001]_p$	(011)	$[1.572711\bar{1}]$	0.28040
Type II	$(\bar{0}.7205311)$		$[01\bar{1}]$	$[010]_p$	$(01\bar{1})$	$[\bar{1}.5727111]$	0.28040
Compound	(001)	$(0\bar{1}1)_p$	$[100]$	$[100]_p$	(100)	$[001]$	0.23848
	(100)	$(100)_p$	$[001]$	$[0\bar{1}1]_p$	(001)	$[100]$	0.23848
$\{20\bar{1}\}$	$(20\bar{1})$	$(41\bar{1})_p$	$[\bar{1}0\bar{2}]$	$[\bar{1}2\bar{2}]_p$	$(00\bar{1})$	$[100]$	0.4250

As shown in Figure 2.1 (a), the axis of the martensite phase is different from the B2 phase. The $[100]_M$ direction is the $[1-10]_P$ direction of the B2 phase while $[010]_M$ is $[-1-10]_P$ in parent phase. Also the β , which is the angle between $[010]_M$ and $[001]_M$ is 96.8° [2]. If the B2 phase matrix is $\mathbf{B}$, the $\bar{\mathbf{B}}$ is the lattice deformation matrix. The B2-B19' transformation can be described in a matrix form as

$$\mathbf{B} = \bar{\mathbf{R}}\bar{\mathbf{B}}\mathbf{R}^T \quad \text{Equation 2.1}$$

where $\bar{\mathbf{B}} = \begin{pmatrix} 1 & 0 & \cot \beta \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} a/a_0 & 0 & 0 \\ 0 & b/\sqrt{2}a_0 & 0 \\ 0 & 0 & c/\sin \beta \sqrt{2}a_0 \end{pmatrix}$, a_0 is the lattice

parameter of parent phase. $\mathbf{R} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1/\sqrt{2} & -1/\sqrt{2} \\ 0 & -1/\sqrt{2} & -1/\sqrt{2} \end{pmatrix}$ is coordinate transfer

matrix.

For the arbitrary vector transferring from the parent B2 phase $[\mu \nu \omega]$ to the B19'

martensite phase [U V W], the transformation can be expressed as

$$\begin{pmatrix} u \\ v \\ w \end{pmatrix} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & -1 \\ 0 & -1 & 1 \end{pmatrix} \begin{pmatrix} U \\ V \\ W \end{pmatrix} \quad \text{Equation 2.2}$$

For the B2 to B19 martensitic transformation, however, there is no lattice invariant shear since the $b/\sqrt{2}a_0$ component in the transformation matrix is 0.999 (close to the lattice without invariant shear) [17, 18]. There are only two types of twinning of the B19 martensite, which are type I twinning with {111} habit plane and compound twinning with {011} habit plane. The morphology of B19 martensite is a self-accommodating triangular morphology [2, 18]. As discussed above, the twinning of Ti-Ni is mainly along {111} plane, which indicates anisotropy transformation and deformation.

2.1.2 Influence of the alloying elements on the transformation temperatures of Ti-Ni-based SMAs

Although the SME has been known for more than 60 years, the applications of SMAs are limited due to the limited transformation temperatures (TTs) range available for application, the limited transformation stress, recoverable strain, and stability due to thermo-mechanical fatigue. Adding other elements to Ti-Ni-based alloys can modify the aforementioned properties in different ways. Initially, it was found that the TTs of Ti-Ni SMAs are very sensitive to the composition on the Ni-rich side, but relatively

stable on the Ti-rich side, Figure 2.4 [19]. As shown in the phase diagram of Ti-Ni alloys (Figure 2.5), the TiNi phase region is almost vertical on the Ti-rich side, while the solubility of Ni reaches as high as 55 at. % at 1391 K. This means the Ti-content in TiNi matrix cannot exceed 50 at. %, and the excess titanium will form Ti₂Ni precipitates in Ti-rich SMAs. On the Ni-rich side, however, the Ni-content in the matrix is affected by the cooling rate or heat treatment due to the solution difference according to temperature [20]. Although the stable Ni-rich precipitate is TiNi₃, there are two more precipitates (Ti₂Ni₃ and Ti₃Ni₄), which form between the TiNi matrix and TiNi₃. Ti₃Ni₄ is stable below 873 K, while Ti₂Ni₃ is metastable in that temperature range (Figure 2.3) [2, 21]. Thus, ageing at such a temperature range can alter the Ni-content in the TiNi matrix, also altering the TTs in Ni-rich Ti-Ni SMAs. It has also been reported that the ageing time below 873 K can affect the M_s at the first six hours, which means that the density and size of Ti₃Ni₄ precipitates can alter the M_s in Ni-rich Ti-Ni alloys [22]. This was attributed to the lattice distortion of the TiNi matrix around the Ti₃Ni₄ precipitates, providing a strong resistance to the B19' transformation. As such, the composition of TiNi in the Ni-rich side must be controlled precisely, as well as optimising the heat treatment, in order to achieve the required TTs.

Although the precipitation kinetics are relatively simple in the Ti-rich side, the Ti₂Ni

is still able to alter the TTs in some non-equilibrium situations by withdrawing Ti from the matrix. This could also produce local chemical inhomogeneity, affecting the TTs of TiNi matrix.

Besides Ni, the TTs in Ti-Ni-based alloys are also affected by impurity content (oxygen, carbon, nitrogen and hydrogen). $(\text{Ti}_2\text{Ni})_2\text{O}$ phase forms due to O-pickup in the Ti-rich side, as well as at some near equiatomic Ti-Ni SMAs [23]. As reported by Frenzel *et al.* [19], Ti_2NiO_x is an intermetallic oxide phase, which has a very similar crystal structure to Ti_2Ni , might also affect the Ti_2Ni precipitates and TTs, alongside any dissolved oxygen in the TiNi matrix. A relationship between oxygen content and M_S can be represented using Equation 1.1, which was obtained experimentally by Honma [24], whereby:

$$M_S[^\circ\text{C}] = 78 - 92.63 \times X_O[\%] \quad \text{Equation 2.3}$$

where M_S is the martensitic transformation start temperature, X_O is oxygen content in wt. %. For bulk Ti-Ni below the melting temperature, Xu *et al.* [25] investigated the oxidation behaviour of Ti-Ni from 450 to 700 °C, and found a multi-layer structure forming at the surface, which are (from surface to substrate) TiO_2 , $\text{Ni}(\text{Ti})\text{-TiO}_2$, Ni_3Ti , and the TiNi substrate.

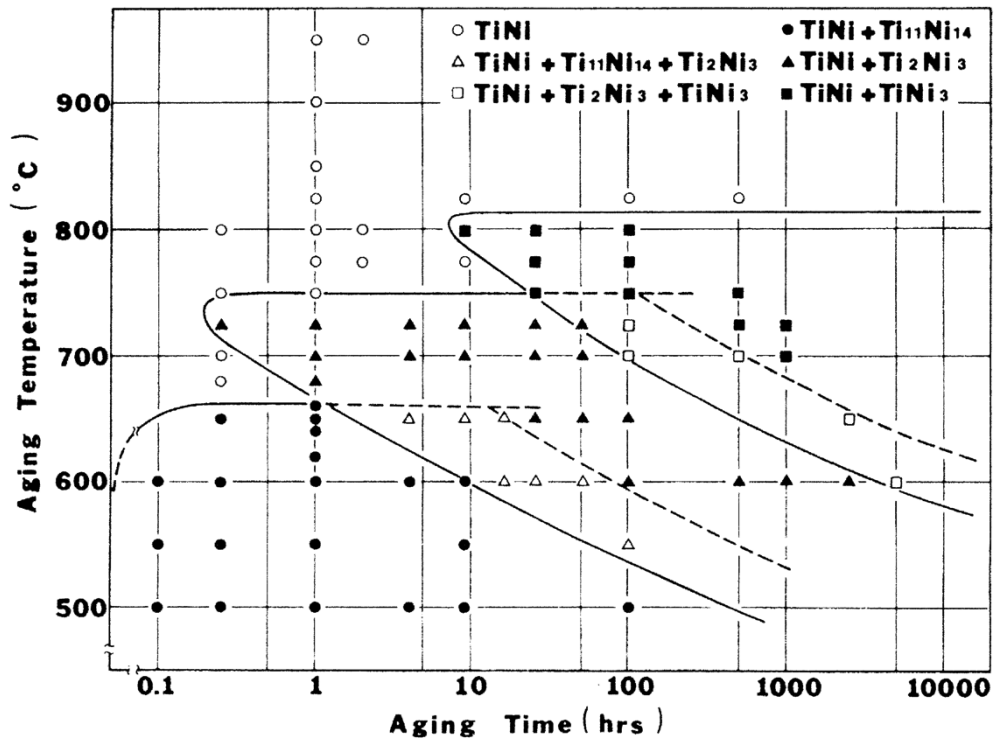


Figure 2.3. A Time Temperature Transformation (TTT) diagram of $\text{Ti}_{48}\text{Ni}_{52}$ alloys, showing the evolution of Ni-rich precipitations in Ni-rich SMAs [2].

Carbon decreases the TTs in Ti-Ni by Ti-depletion by forming TiC . Frenzel *et al.* [26] used Differential scanning calorimetry (DSC) to investigate the TTs of $\text{Ti}_{50.7}\text{Ni}_{49.3}$ containing 0.08-0.31% C picked up from a graphite crucible during melting. It was found that the phase transformation (PT) peak widths increased with the increase in carbon content. This is because of the carbon-containing inhomogenieties within the sample, which lead to local variations in chemistry, and hence affecting the TTs. Although some researchers have reported the relationships between the TTs and carbon or oxygen content, the complex relationships between these elements are difficult to define. Otubo *et al.* [27] also investigated the influence of carbon and

oxygen on the TTs and the PT enthalpies in Ti-Ni SMAs, but found no clear relationship between the TTs and carbon or oxygen content, although the enthalpies including enthalpy changes (difference between low contamination reference and contaminated samples) increase linearly as the TTs decrease.

A few researchers also studied the effect of nitrogen on the TTs. Olier *et al.* [28] found Ti(C, N) carbo-nitrides have a similar effect, decreasing the TTs. Furthermore, $\text{Ti}_2\text{NiH}_{0.5}$ phase have been reported in Ti-Ni/ Ti_2Ni alloys by Zhao *et al.* [29], which indicates that hydrogen also affects the TTs in a similar way to oxygen.

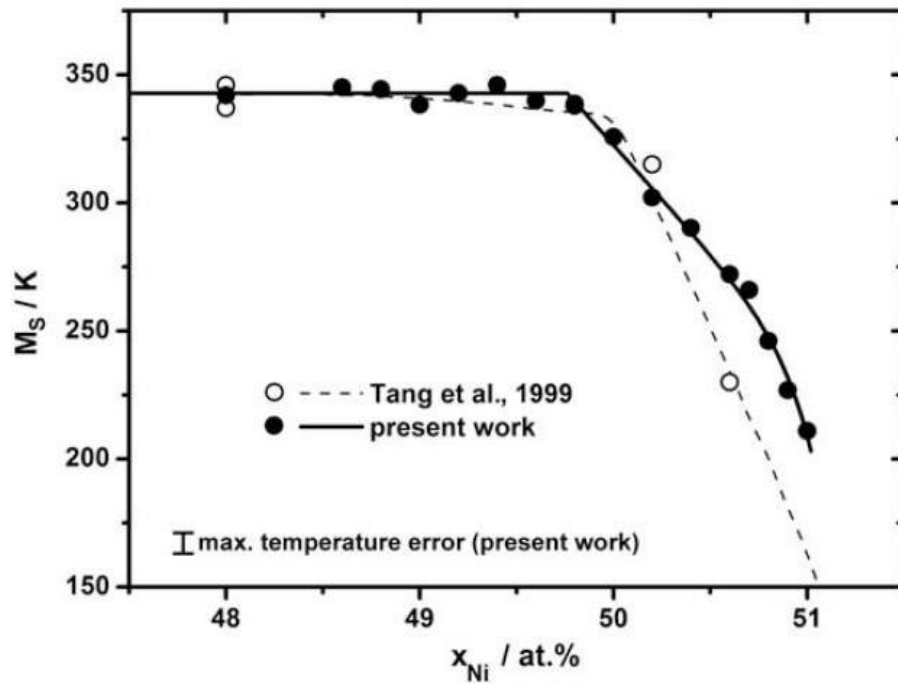


Figure 2.4. Influence of Ni-concentration on the M_s temperature in Ti-Ni-based SMAs, with the M_s dropping significantly on the Ni-rich side [19].

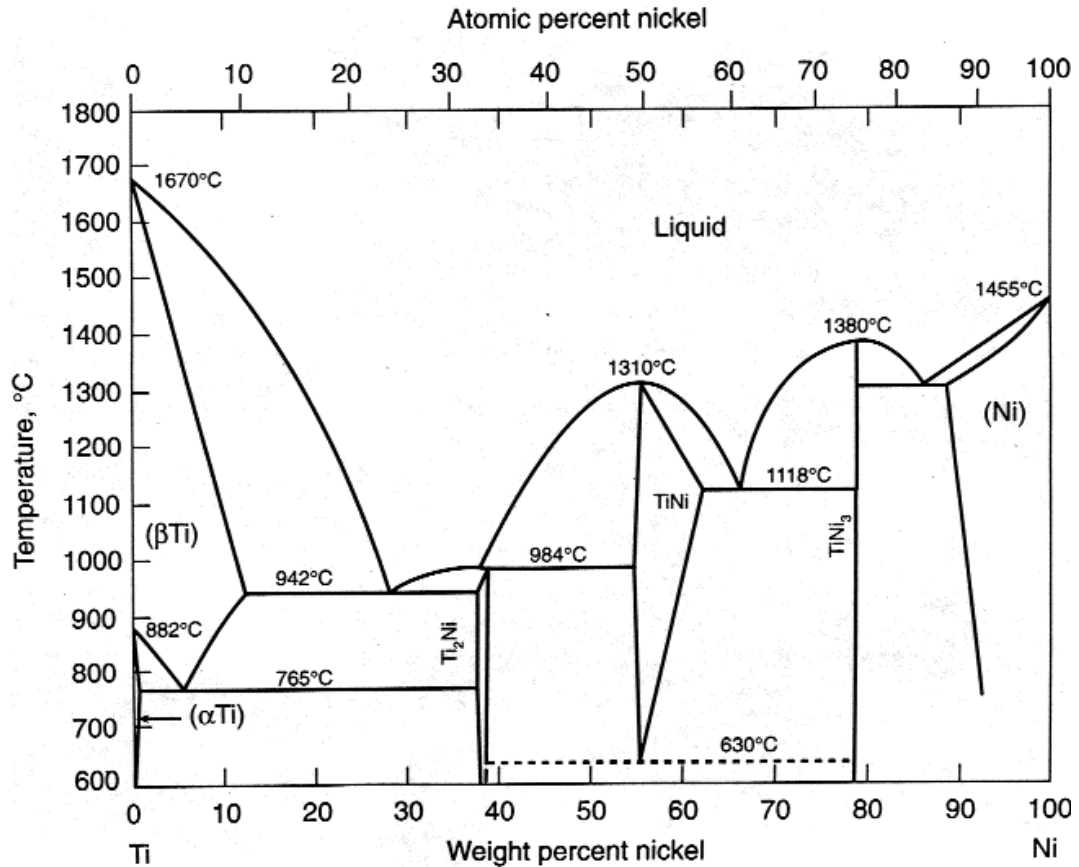


Figure 2.5. Phase diagram of Ti-Ni alloys [2].

2.1.3 Ternary Ti-Ni-based shape memory alloys

Adding different alloying elements into Ti-Ni-based SMAs can modify their performance, notably the TTs, temperature hysteresis, thermo-mechanical stability, and recovered stress and strain.

Some elements are known to improve the performance of Ti-Ni-based SMAs. New alloys have been developed into a series of commercial SMAs. For instance, TiNiNb and TiNiCu alloys.

Replacing Ni by Cu can reduce the temperature hysteresis (4K when Cu-content is 20

at.%) and improve stability during thermal cycling of Ti-Ni-based SMAs. However, the TiNiCu alloys have different transformation types according to the copper content and the total recoverable strain decreases to 5.4% or even lower [30]. The reason for the small temperature hysteresis of TiNiCu alloys could be the volume change as the copper content as well as the copper reduces the shear stress between twin boundary, which can avoid the introduction of dislocations during thermal cycling [2]. The influence of Cu-content on transformation behaviour of TiNiCu SMAs is shown in Figure 2.6. The transformation stays in B2-B19' one-step transformation when the copper content is lower than 7.5 at.%, which indicates the change in volume and shear stress is not strong enough. B2-B19-B19' two-step transformation occurs when the Cu-content is higher than 7.5 at.%. A slightly increasing B2-B19 transformation temperature can be seen while the transformation temperature of B19' phase decreases significantly as Cu-content increases. Although the recoverable strain in B2-B19 transformation is less than the one in B2-B19', B19 martensite is known as a phase insensitive to defects, which means low flow stress in B19 phase, low temperature hysteresis and stable thermal cycle response [31]. As the characteristics described above, TiNiCu SMAs are very suitable for actuators which work below 373K.

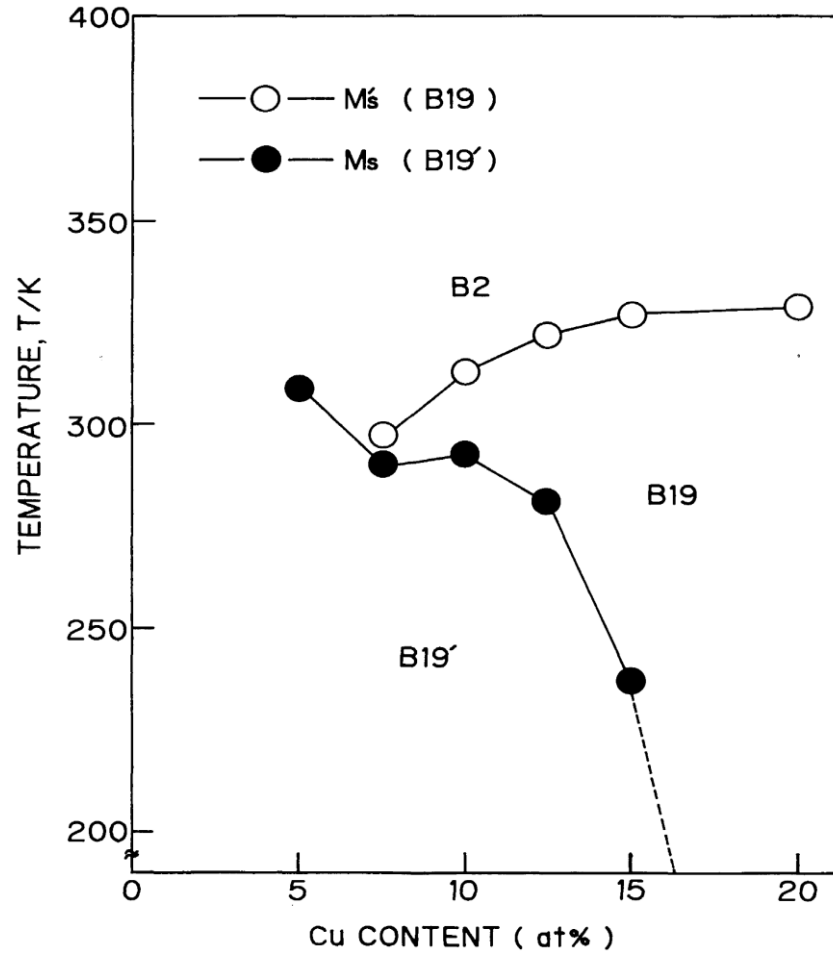


Figure 2.6. Effect of Cu-content on the transformation behaviour of TiNiCu SMAs. One-step B2-B19' transformation occurs at Cu-content lower than 7.5 at. %, while a two-step B2-B19-B19' transformation happens at higher copper content [30].

The addition of Nb has the opposite effect to Cu, increasing the width of the temperature hysteresis dramatically (~ 180 K) [32]. As shown in Figure 1.1, the wide temperature hysteresis means the material remains as austenite phase at temperatures lower than A_s temperature. The phases in TiNiNb SMAs are the TiNi matrix and β -Nb particles. The β -Nb particles play an important role in the transformation behaviour, as they hinder the transformation from austenite to martensite and the

recovery of twinning Figure 2.7, which means more under cool or over heat are needed for martensitic transformation and hence the hysteresis is larger. The plastic deformation of β -Nb particles under stress also relaxes the elastic strain in martensite and increases the A_s as shown by Rong *et al.* [32]. Jiang *et al.* also reported that the shape recovery ratio and cycling stability remarkably improved in $\text{Ti}_{44}\text{Ni}_{47}\text{Nb}_9$ SMAs [33]. Thus, TiNiNb alloys are suitable for applications like couplings.

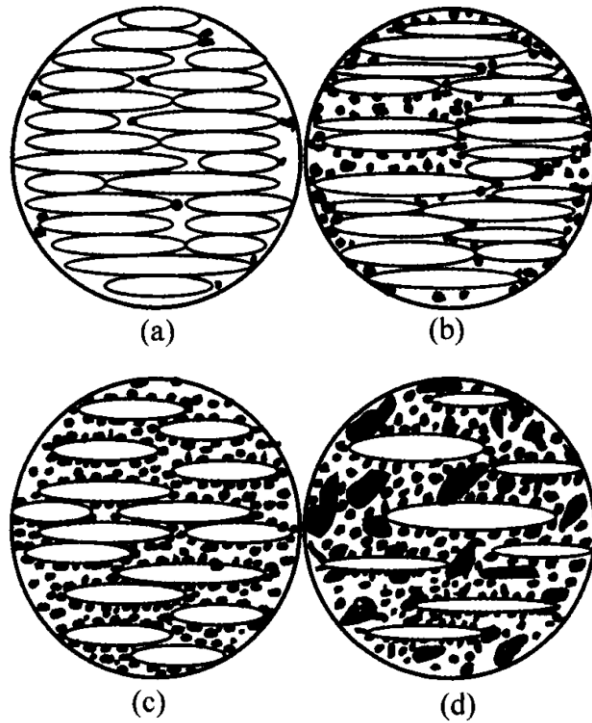


Figure 2.7. Schematic diagram illustrating the influence of Nb particles on the transformation hysteresis in TiNiNb alloys: (a) Nb-content < 3 at. %; (b) Nb-content from 3 at.% to 20 at. %; (c) Nb-content 20 at.%; (d) Nb content >20 at. % [32].

Since the operating temperature requirement for SMAs has been getting higher and

higher (e.g. considering applications in the aero-engine field), the TTs of Ti-Ni-based SMAs (currently no more than 373K) need to be increased for high temperature use. A lot of research has focused on the development of high temperature SMAs (HTSMAs), which are achieved by adding alloying elements that increase the TTs. As shown in Figure 2.9, Pd, Pt, Au replacing Ni, or Hf or Zr substituting Ti can increase the TTs in Ti-Ni-based ternary alloys. These elements are similar to Ni or Ti in terms of chemical properties and electronic structure. Pd and Pt are in the same column as Ni, while Hf and Zr falls below Ti in the periodic table of the elements. The binary phase diagrams between these elements and Ti or Ni are also very similar. The increase in the TTs due to these alloying elements in Ti-Ni-based alloys is attributed to the fact that these elements have larger atom radii and higher electron concentrations than Ni and Ti, so the resistance to volume change and to crystalline shear increases, which leads to an increase in the TTs. Unfortunately, most of these elements (e.g. Pd, Pt, Ag and Au) are expensive and are of high density, which makes them not ideal for various applications. Although Hf has a higher density to Zr, Hf has a stronger impact on increasing the TTs than Zr for the same amount of alloying additions. Additionally, the TiNiHf alloys are known to have higher recoverable strain than TiNiZr alloys with the same M_s [34]. As such, Hf attracted more interest for altering the TTs of Ti-Ni-based alloys. As reported by Potapov *et al.*, the lattice parameter of the B19' in TiNiHf alloys gradually increase from 0.305 nm to 0.310

nm as the Hf-content increases from 9.5 at. % to 20 at. % [35]. Also, the volume variation before and after transformation reduces from 0.42% to 0.10% as the Hf-content increases from 9.5 at. % to 20 at. %, which means that the higher the Hf-content is in TiNiHf alloys, the less recoverable strain the alloys have. Most studies of TiNiHf/Zr alloys focus on the Ni-rich side, where it was found that the $\text{Ni}_4(\text{Ti} + \text{Hf/Zr})_3$ precipitate size will be significantly affected by the cooling rate. Furthermore, the interface between the precipitates and the matrix includes misfit dislocations and crystalline distortion [12]. Santamarta *et al.* measured the lattice parameters of these alloys, which are $a_{B19'} = 0.293$ nm, $b_{B19'} = 0.411$ nm, $c_{B19'} = 0.473$ nm, $\beta_{B19'} = 100.4^\circ$ and $a_{B2} = 0.309$ nm for TiNiHf and $a_{B19'} = 0.297$ nm, $b_{B19'} = 0.412$ nm, $c_{B19'} = 0.472$ nm, $\beta_{B19'} = 98.6^\circ$ and $a_{B2} = 0.309$ nm for TiNiZr alloys [12].

Some quaternary SMAs have also been investigated by other researchers. Vermaut *et al.* investigated $\text{Ti}_{25}\text{Ni}_{50-X}\text{Zr}_{25}\text{Cu}_X$ SMAs with high Cu content (15 and 20 at.%), which were produced by melt spinning. These alloys showed SME after a recrystallisation treatment [36]. But the material was not fully crystalized and the mechanical properties were not studied. Lin *et al.* reported a linear relationship between M_s , ΔH_c (transformation enthalpy during cooling) and Cu content in $\text{Ti}_{50}\text{Ni}_{25-X}\text{Pd}_{25-Y}\text{Cu}_{X+Y}$ alloys [37], whereby:

$$M_s (^{\circ}\text{C}) = 424.2 + 2.7X - 9.7Y \quad \text{Equation 2.4}$$

$$\Delta H_c (\text{J/g}) = 17.1 + 0.2X - 0.6Y \quad \text{Equation 2.5}$$

Although the $\text{Ti}_{50}\text{Ni}_{15}\text{Pd}_{25}\text{Cu}_{10}$ alloy shows excellent thermal stability within 100 cycles, Pd is too expensive for commercial application, and so far the thermal mechanical stability of this alloy has not been assessed. Meng *et al.* studied the thermal stability, TTs, and microstructure of $\text{Ti}_{36}\text{Ni}_{49-x}\text{Hf}_{15}\text{Cu}_x$ alloys [38-40], but the use of Cu did not show significant improvement in the thermal stability, suggesting that the thermal mechanical properties are unlikely to be stable, although they were not reported. It was also reported that the M_s does not show a linear relationship with the Cu-content (Figure 2.8). The Cu-content does not appear to affect the M_s within the range 1 at. % to 8 at. %, except for the 3 at. % sample.

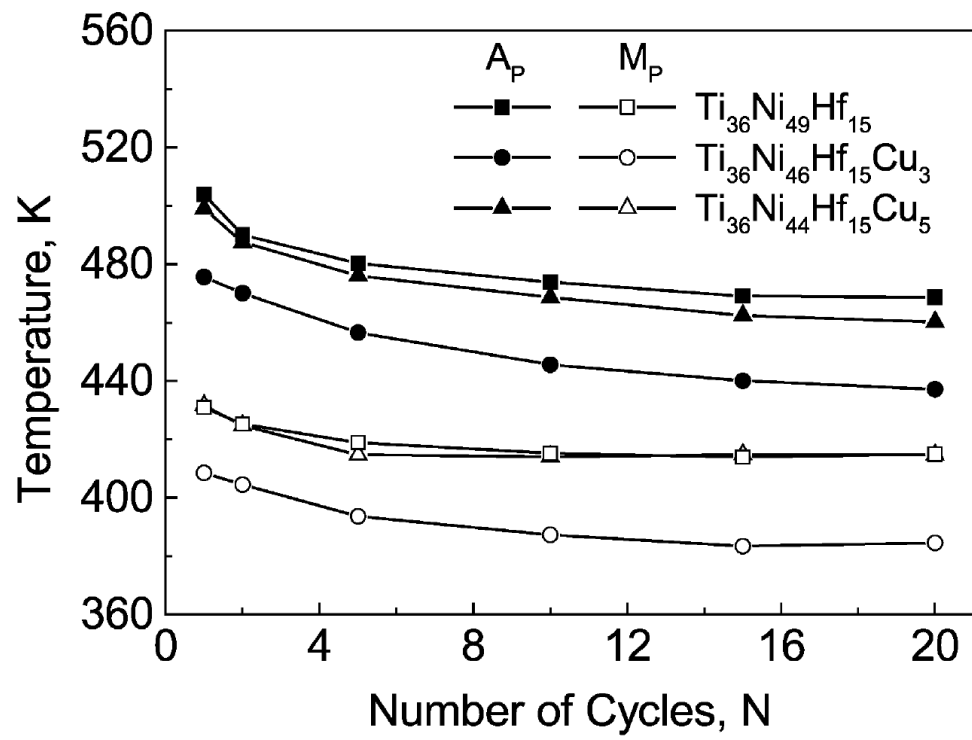


Figure 2.8. The thermal stability of TiNiHfCu alloys, showing that Cu does not significantly improve the thermal stability of TiNiHf alloys [41].

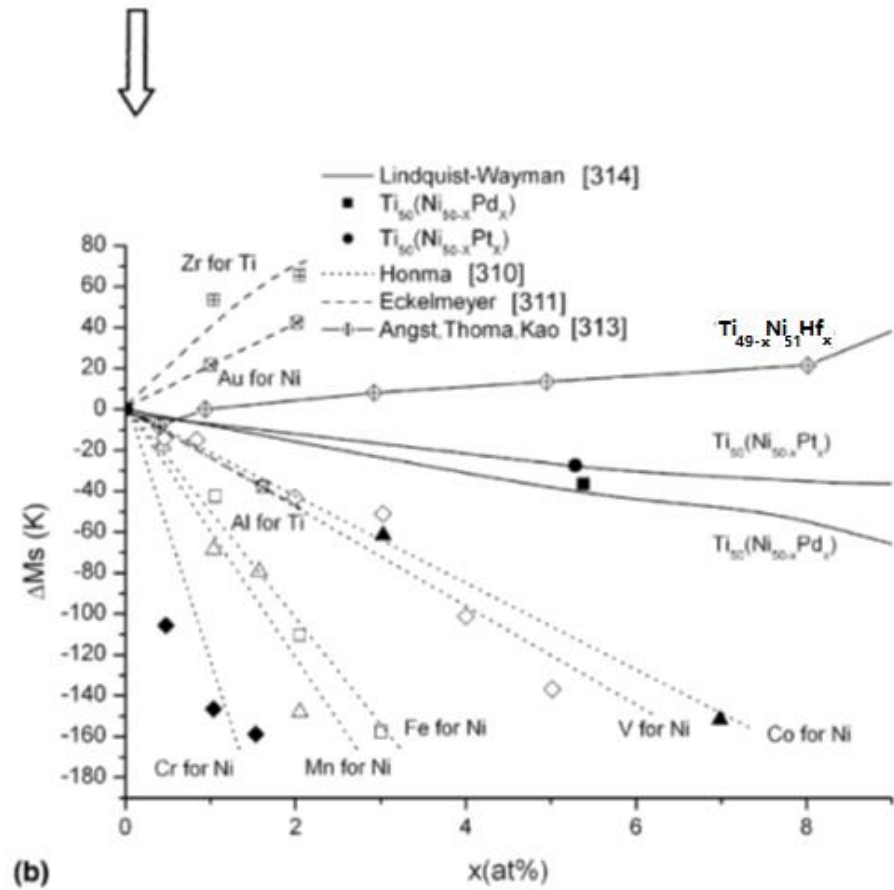
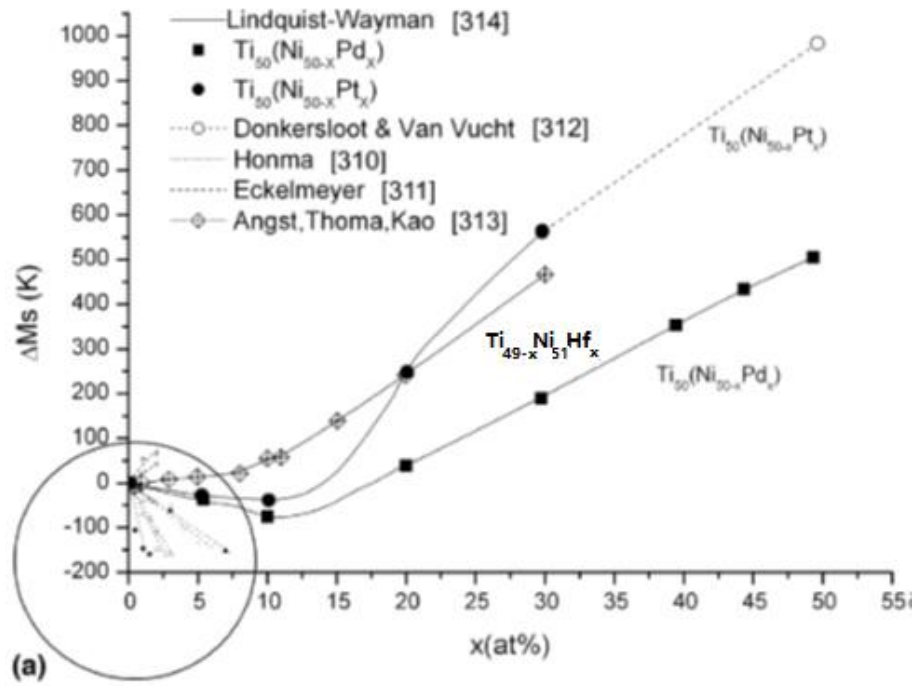


Figure 2.9. Influence of different alloying elements the M_s of Ti-Ni-based SMAs [2].

The influence of a number of alloying elements on the SME has been assessed for Ti-Ni-based SMAs, including Al, V, Cr, Co, Mn, Fe, and Mo. All of these elements decrease the TTs, but to different extents. They also increase the recoverable stress, elongation and Young's modulus to a certain extent. V was reported to decrease the M_s by 100 K for every 1 at. %, when the V content is less than 2 at. %, while the recoverable strain and SE property are improved [42]. Nonetheless, the composition $Ti_{47.2}Ni_{48.8}V_3$ was found to show a martensitic transformation at room temperature, and a smaller recoverable strain than Ti-Ni due to the secondary phases produced due to the presence of V [43]. Moreover, the R-phase was observed in low V-content samples [42]. Al was also reported as an R-phase inducing element, with the M_s temperature decreasing rapidly when Al replaces Ni, with the M_s of $Ti_{50-x}Ni_{50}Al_x$ being around 273 K [44]. Sn also induces R-phase, with stable transformation temperature around 280 K, but the recoverable strain reduces because of the formation of the Ti_3Sn phase [45, 46]. Cr, Co, and Fe were found to decrease the TTs by 40 K/at. %, 10 K/at.%, and 60 K /at.%, respectively. They also increased the yield stress to 800 MPa or 1100 MPa, and raised the elongation to 12% [47]. Mn was also found to decrease the TTs linearly at 60 K/at. %, and also increase the yield stress [48, 49]. Ta has been reported as an element for reducing sensitivity of Ni-content in Ni-rich Ti-Ni when the Ta-content is lower than 4 at. %. Nonetheless, the solubility of Ta in Ti-Ni is limited, so a large amount of β -Ta phase forms in high Ta-content

SMAs, which reduces the ductility and the recoverable strain [50]. A small amount of Mo (0.29 at. %) has also been added into Ti-Ni powder, inducing R-phase transformation and martensite transformation at ~280 K [51]. Nonetheless, the SME and mechanical properties of TiNiMo SMAs with larger Mo-content have not been reported yet. Finally, W was found not to affect the TTs significantly when replacing Ni, but the TTs decrease rapidly as W replaces Ti. W also is able to strengthen the TiNi matrix and improve the recoverable strain [52]. The influence of different elements in Ti-Ni-X SMA is listed in Table 2.3.

Table 2.3 Influence of different alloying elements on the SME in ternary Ti-Ni-based SMAs [42, 44-52].

Ti-Ni-X	ΔM_s B2-B19' (K / at.%)	ΔM_s B19 (K/at.%)	R (K)	Hysteresis (K)	Yield stress (MPa)	Recover able strain (%)	Fatigue life (cycles)
None	$M_s = 345 \text{ K}$		315	30	$\sigma_{B19'}=250$ $\sigma_{B2}=300$ $\sigma_R=120$	$\epsilon_{tw} = 4$ $\epsilon_r = 10$ $\epsilon_R = 1$	
Ni	-220						
Cu	$M_s = 333 \text{ K}$ ($\Delta M_s \approx 0$)			17 to 4 (-1K/at.%)	$\sigma_{B19'}=100$ $\sigma_{B2}=200$	$\epsilon_{tw} = 2$ $\epsilon_r = 4$	10^7
Fe	-10			30	360-580	$\epsilon_r = 4$	10^4-10^5
Zr	+8.5			60			
Hf	+9			60 (15 at.%)	560	$\epsilon_r = 4$	
Co	-55	3	240	80/30	700-900	$\epsilon_r = 5$	
Cr	-250				1000	$\epsilon_r = 2.5$	
Mn	-60		300	30			
Al	-30(-90) replacing Ti(Ni)	1.85	253	50			
W	-20 (up to 2 at.%)		320	30			
Dy	+100 K at 10 at.% Ni			35			
Sn	-70 $M_s=200 \text{ K}$ (8 at.%)	0.5-2	300	100 (2at.%)	$\sigma_{B2}=100$ 450	$\epsilon_r=2$ $\epsilon_b=6$	
Si	-10						
V	-60				$\sigma_{B2}=450$	$\epsilon_r=5$	
Ta	-100K at 1 at. % Ta >1 at.%. $M_s=60 \text{ K}$			30			
Mo	-600		290				

2.1.4 Other factors affecting the TTs in Ti-Ni-based SMA

Beside the chemical composition and the precipitates that form in the microstructure,

the stress (stress field of precipitates and dislocations), thermo-mechanical history and testing method will also affect the TTs on SMAs. Jones *et al.* reported that the TTs of Ti-Ni SMAs increase with increasing load during transformation cycles [53]. The aging time [54], aging temperature [55] and cooling rate [56-58] also affect the TTs as well as transformation behaviour (e.g. single stage to multi-stage) by changing the Ni-rich precipitation in Ni-rich Ti-Ni SMAs. Moreover, both the reduction in thickness and rolling temperature during hot rolling of Ti-Ni SMAs were reported to affect the TTs and transformation peak width in DSC due to recrystallisation and residual stress during hot rolling [59]. Furthermore, the transformation behaviours of SMAs are also affected by the testing methods. For example, Yin *et al.* reported that the thermo-mechanical stability of Ni-rich Ti-Ni SMAs is affected by the deformation frequency (in the range 4×10^{-4} Hz to 1 Hz) in carefully designed room temperature thermo-mechanical fatigue (TMF) tests [60]. The deformation stress for a certain strain increases (maximum level varied from 400MPa to 611MPa) as the deformation frequency is increased before reaching a steady stage. The mean temperature during TMF test also increased from 298K to 333K. This suggests that the temperature of specimen could vary by up to 50 K during testing, so the testing temperature should be at least 50 K higher than the A_f temperature. This phenomenon occurs because of the generation and saturation of dislocation in the materials during deformation, as well as thermal cycling, the

generation and transferring of heat during deformation, and the phase transformation.

As a result, the experiment result can be affected by various conditions, including the specimen size, grain size, deformation rate, stress, cycling frequency, testing temperature, heat capacity, and resolution of machines. The increasing rate of stress and mean temperature starts to increase from 0.07 Hz, thus the deformation frequency has a smaller effect at low frequency (< 0.07 Hz). The deformation process varies before reaching a steady-state. The hysteresis loop area D_n , which is the mechanical energy dissipation per unit volume of the n^{th} cycle (i.e. the integration of the stress over the strain for the n^{th} cycle) has also been predicted from experiment. It was found that the D_n and the isothermal hysteresis loop area at the testing start temperature D_0 are related to the test start temperature T_0 (i.e. the setting temperature for the experiment), nominal strain ε , the angular frequency ($\omega=2\pi f$, rad/s related to deformation frequency), temperature coefficient for isothermal forward transformation $k_f=6.56\text{MPa/K}$, temperature coefficient for isothermal reverse transformation $k_r=7.09\text{MPa/K}$, and the latent heat per unit volume $l_0=7.74\times 10^7\text{J/m}^3$. These coefficients can be used to calculate the hysteresis loop, the details of this equation can be found in reference [60].

The texture of SMAs also affects the TTs as reported by Shu *et al.* [61]. The recoverable strain of Ti-Ni-Cu was found to be reduced with increase in the loading angle from $[111]<110>$ or $[110]<110>$ orientation. The recoverable strain in Ti-Ni

was found to slightly increase as the angle between loading axis and [111]<110> crystallographic direction is increased and then starts decreasing from 30°. This possibly explains why different studies reported varying levels of the recoverable strain (from 4% to 6%) in Ti-Ni-based SMAs.

2.2 Theoretical analysis of the martensitic transformation

Since the transformation behaviour of SMAs are complicated, many theories have been proposed to predict the TTs of SMAs. The basic mechanism of martensitic transformation is the fact that the Gibbs free energy of the austenite phase becomes higher than the martensite phase as the temperature is decreased. However, the Landau theory claimed that there is a pre-martensitic transformation (precursor phenomenon) that occurs before the martensitic transformation. Figure 2.10 shows the function of free energy of the lattice (Landau free energy) for the parent phase and martensite phase as a function of lattice distortion at different temperatures [2, 62]. The order parameter is shown as below:

$$F=a(T-T^*)\eta^3-b\eta^4+c\eta^6 \quad \text{Equation 2.6}$$

where F is the free energy for transformation, a, b, c are coefficients factors a, b and c are all >0 and T is temperature. T* is the temperature where the parent phase phonon reaches zero and η is the order parameter. The lattice can be symmetrically distorted in two directions where the order parameter η is positive or negative,

respectively. The parent phase is undistorted as the order parameter η is zero. T_0 in Figure 2.710 is the temperature where the free energies of parent phase and martensite phase are the same. At the temperature increases above T_0 , the parent phase has less free energy than the martensite phase, so the parent phase is stable. The energy required for transformation includes shearing energy of twinning, friction of shearing, variation of volume etc. From the Landau free energy point of view, the order parameter can also be affected by the disorder at atomic level, stress field, and compositional variations. Thus, from calculating the Gibbs free energy and shear stress of SMA with different composition, it is possible to predict the TTs of SMAs with different additional elements.

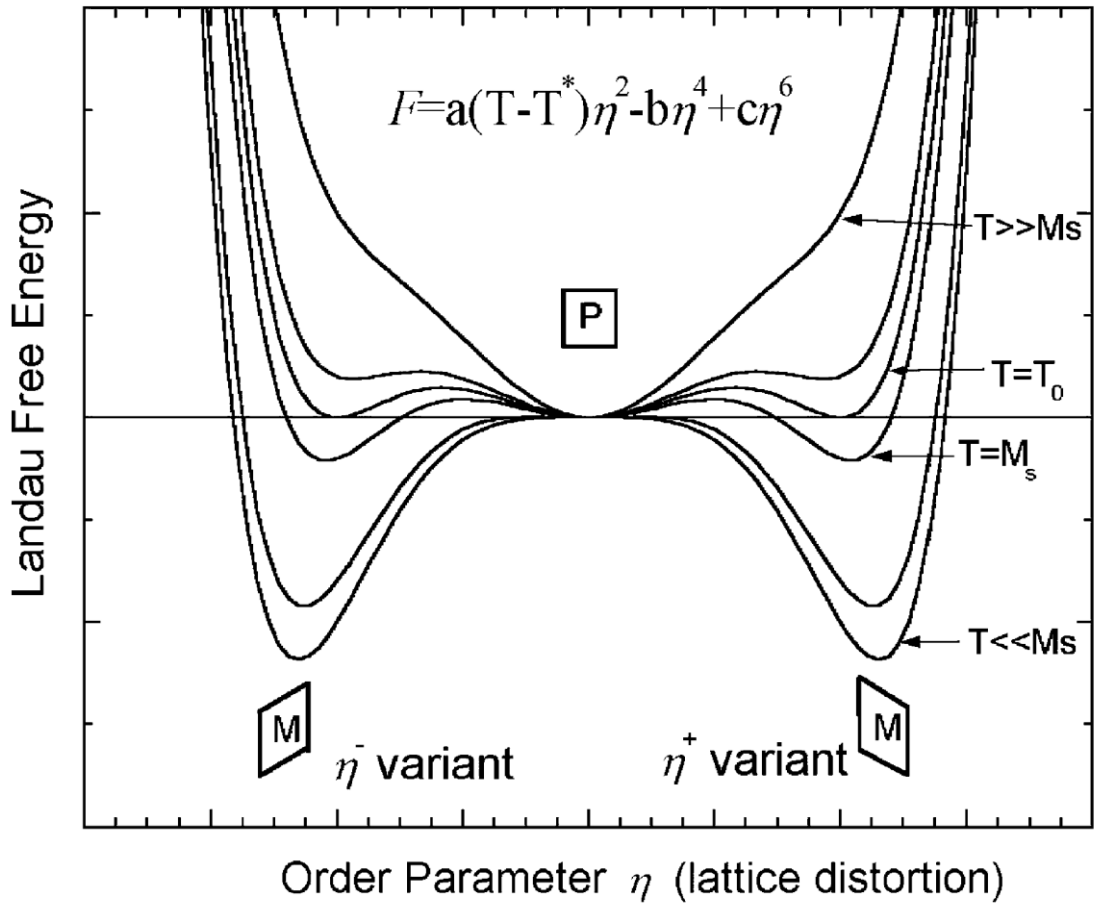


Figure 2.10. The Free Energy as a function of lattice distortion at different temperatures for a first order martensitic transformation. Martensite is marked as “M” and “P” for parent phase. Shear strain is presented as order parameter η which indicates the shear distortion of the lattice [2].

First-principles and density functional theory (DFT) calculations use some basic properties of atoms (approximate relative atomic positions, cell size, space-group symmetry), and energy derivatives, with some assumptions, to calculate the structure and properties of the crystals from their chemical composition [63, 64]. Povoden-Karadeniz *et al.* used Computer Coupling of Phase Diagrams and Thermochemistry (CALPHAD) method and metastable solvi to calculate the

thermodynamics of equilibrium phases, precipitation and transformation temperature of Ti-Ni SMAs with different levels of approximation [65]. Gou *et al.* used DFT successfully to calculate the crystal structure of TiNiCu-ternary SMAs with different Cu content, but no TTs were calculated [66]. Guillermo *et al.* used DFT to calculate the influence of additional elements including Fe, Pd, Pt, Au, Al, Cu, Zr, and Hf on the energy and lattice parameters of Ti-Ni SMAs [67]. Since the martensitic transformation involves shearing from the cubic phase, the shear elastic constants values (c' and c_{44}) are very important for the transformation [68]. Wang *et al.* calculated the twinning stress in NiMnGa and Ti-Ni SMAs using DFT and compared his data with experiments [69]. Besides the first-principles and DFT, the electron concentration e/a , which is the number of $4s+3d$ electrons per atom, was believed as a simple calculation method for TTs. The e/a value of Ti-Ni SMAs shows different results when being calculated in different ways. If the Hume-Rothery rule is used, and the s and d electrons were not counted, the e/a value is zero [70], otherwise the electron concentration is 7 in Ti-Ni SMAs, which is different from the value for β -alloys (1.5) [15]. Huisman-Kleinherenbrink *et al.* used electron concentration to calculate the variation in TTs for different Mn-content in $\text{Ti}_{50-x}\text{Ni}_{50-x}\text{Mn}_{2x}$ SMAs, which showed good agreement with the experimental results [71]. However, it was found that the electron concentration calculations fail to predict the influence of some elements like Al and Sn [72].

2.3 Applications of Ti-Ni-based Shape memory alloys

Due to the unique characteristic of SMAs, they can be applied as couplings, actuators, sensors, implants, structure materials and surgical tools. Their application in couplings has been the most successful applications. Raychem Corp. applied SMAs for hydraulic system couplings and electric connectors on the F-14 Tomcat navy jet fighters, reporting that they work reliably during the whole service period [1]. The SMAs couplings need to be deformed in the martensite phase, then heated up to the austenite phase to hold and connect the components. As such, a large temperature hysteresis is needed for this application, so that the couplings can retain their shape after deformation during storage and after connecting.

Almost half of Ti-Ni-based SMAs have been used for medical applications [1]. The SE of Ti-Ni-based SMAs has been used by Terumo Corp for guide wire for catheters in surgery and in diagnosis [3]. The Ti-Ni wires can provide ~10% recoverable strain, with the bending stress being much lower than stainless steel. Orthopedics is another important field for the application of SMAs. The deformed martensite phase materials can be inserted into the human body easily, then expanded to the required shape when heated up by the body temperature. By adding elements like Fe and Co, the recoverable stress can be adjusted. The TTs can also be adjusted by changing the composition of the wire so that the total force can be easily increased by heating up

the implant a few degrees, instead of having surgery every time. The Ti-Ni (nitinol) wires for oral orthopaedic procedures have been widely used as well. The SMAs can be applied as blood vessel support structures, which are designed so that they can be deformed at low temperature, injected into the blood vessels, expanding at the body temperature.

SMAs are also a good candidate for actuators for energy absorption in various systems, including mixing water valves, automotive engines, aerospace and jet engines. For example, the angle of attack of stators in jet engines needs to be adjusted for different working conditions, the stators nowadays need a complicated hydraulic-mechanical system for angle adjustment. This system can be replaced by SMA stators with electrical heating system, so the angle of stators can be changed according the temperature controlled by coil heater. A similar concept can be applied on any temperature-dependent valves in the other machines. For instance, a temperature-dependent spring made of SMAs, which can be extend at high temperature and be compressed under low temperature, has been designed for mixing water valves. The Ti-Ni spring has been trained with TWSME, so that it can expand or contract according to the temperature variation and adjust the amount of hot water accordingly [1]. This automatic mixing valve can control the water temperature precisely, without any electric device.

One significant advantage of SMAs for actuator application is that only a SMAs spring and a heating coil are needed to create a whole actuator system, instead of a complicated electric-magnetic device, which reduced the weight and simplified the systems. For instance, the SMAs actuators can be used for radiator/louver vanes, fuel cap, side mirror and spoiler on motor vehicles [73]. In these parts, the working temperature is under 323 K, and the requirement of positioning accuracy is not very high. Thus, the common Ti-Ni or TiNiCu SMAs are good enough for these applications. Another application field for SMAs is by utilising the SE effects, which can be applied in bumpers, panels and structural parts on motor vehicles. The high strain and higher Young's module in the austenite phase allows these parts to absorb higher amount of impact energy, recovering effectively after deformation. Since there are two phases with different Young's modulus in Ti-Ni-based SMAs at different temperatures, they can also be used for suspension springs which are able to change the height or stiffness in cars.

In the aerospace sector, SMAs have attracted a lot of interest for similar functions to those in automotive sector. Ideally, wing sections in aircraft should be twisted continuously and smoothly at different airspeeds for aerodynamic reasons [74]. A full scale wing section with SMAs-powered torque was demonstrated as part of a Defence Advanced Research Projects Agency (DARPA) contract to Northrop

Grumman, supported by the Air Force Research Lab (AFRL), Figure 2.11 [75]. A continuously variable wing structure made of SMAs has also been designed for testing. National Aeronautics and Space Administration (NASA) also tested a full scale F-15 inlet with SMAs rotating inlet cowl, which can change the cross section area of the inlet continuously during wind tunnel tests. The 34 wires SMAs bundles embedded in the cowl are able to provide 26.7 kN force and turn the cowl up to 9° [76]. The most successful demonstration of SMAs in aircraft was carried out by NASA and Boeing, who applied Ti-Ni SMAs fibres on a chevron nozzle cowl of a high-bypass jet engine (Figure 2.12), which had a series of flight tests [77]. Theoretically, the exhaust temperature of the fan increases during take-off and landing for the slow flying speed, as well as low altitude, which causes the SMAs to transform to the high temperature phase and open the nozzle to maximum cross section area. While the low temperature during cruise allows the nozzle to minimise the area, optimising high altitude performance. A series of heating coils have been added on the SMAs bundles to vary the nozzle as required. This experiment proves that the variable nozzle based on SMAs reduced fuel consumption, as well as noise during take-off and landing. SMAs can also be applied on the Inlet Guide Vanes (IGV) and Variable Stator Vanes (VSV) systems, which currently uses complex and heavy hydraulic systems to change the angle of these vanes [78]. By replacing these vanes with SMAs, they cannot only change their profile continuously under the

control of heating coil, but also reduce the weight of these systems. Moreover, the high strain rate of SMAs allows these vanes to absorb more energy and protect the engine from foreign object damage (FOD). For spacecraft applications, SMAs actuators are much better than the other systems in micro-gravity, zero-atmosphere, and vibration environment for their simple, reliable, and low-shock actuation. For example, the antenna and solar cell panels need to be folded during launch then expanded in space. The sunlight in space is able to heat up these components to temperatures higher than 373 K easily, so SMAs with one-way SME represent the ideal material choice for these components. Using SMAs for solar array actuators has already been tested by Lockheed Martin and NASA-Goddard, which allow the solar battery array to expand and become flexible [79].

Another application for SMAs is micro-robot or micro-machines, which need actuators with extremely small size[73]. It is very hard to make traditional electronic actuators, with micrometer size, but the SMAs can be made into this size easily with the required functions. The battery or power unit is even not necessary in some temperature-dependent micro-machines, for the SMAs can react to the temperature by themselves, which is a huge advance over the other actuators. Furthermore, the movement induced by the SME is very similar to muscle movement, which can be applied for bio-robotic applications.

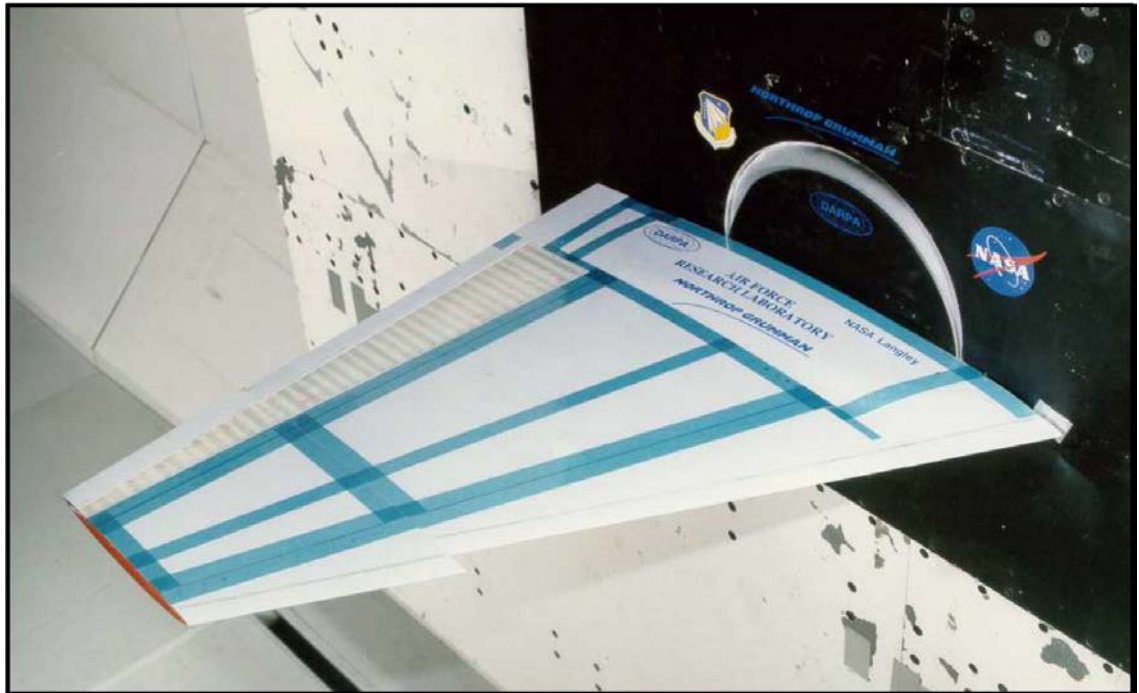


Figure 2.11. Model wing with SMA torque tube in in a wind tunnel (developed by Northrop Grumman) [76].



Figure 2.12. Variable geometry chevron nozzle of a high-bypass jet engine during a flight test by Boeing [76].

2.4 Combinatorial metallurgy

Although SMAs demonstrate unique properties, there are some properties that need to be improved if they are to find more areas of application. For instance, the TTs need to be increased for high temperature applications. The thermo-mechanical stability during repeated cycling needs to be improved as it is a critical factor to enable further utilisation of SMAs in actuators. The stress required to induced the martensitic transformation needs to be improved for some SE applications. Thus, ternary, quaternary, or even more complicated Ti-Ni-based alloy systems need to be studied. However, there is a massive amount of work that needs to be done for mapping the influence of the the alloy combinations for all potentially beneficial alloying elements. Thus, a high-throughput method for building materials libraries is necessary for Ti-Ni-based SMAs development. This approach is known as combinatorial synthesis.

Combinatorial synthesis for materials discovery was first published in a study by Xiang *et al.* in 1995, in which binary masks of thin film materials were used to develop compositional libraries [80]. After that, a lot of different types of combinatorial synthesis methods based on sputter deposition [81], laser ablation [82], ion beam deposition [83] and other chemical/physical vapour depositions have been developed. In thin film methods, a binary or ternary material library, with under a

few hundred microns thickness thin films can be deposited rapidly on a silicon wafer substrate (a typical sputter deposition system for ternary SMAs is shown in Figure 2.13). Some characterisation systems (e.g. parallel nanoscanning calorimeter (PnSC), Figure 2.14), can be attached together with the substrate, which reduces the process time dramatically [84].

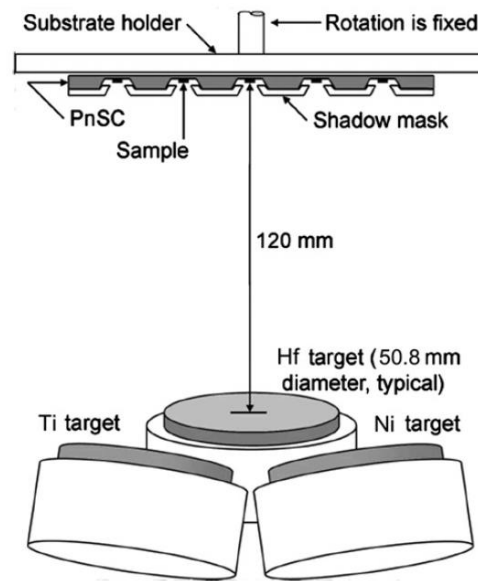


Figure 2.13. Schematic illustration of a sputter deposition system to create Ti-Ni-Hf thin film libraries [84].

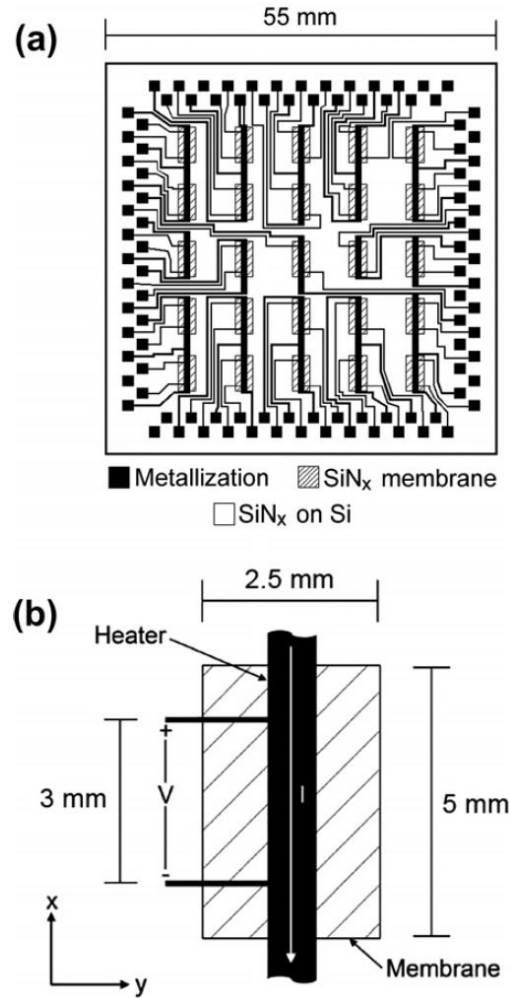


Figure 2.14. (a) Schematic illustration of parallel nanoscanning calorimeter, and (b) layout of the calorimeter cell [84].

However, these methods can only produce thin film materials, which usually have different performance compared to bulk produced SMEs [11]. Furthermore, understanding the thermo-mechanical performance is very important for SMAs development, but it is hard to have mechanical or thermo-mechanical tests on thin films. Nanoindentation can be applied to measure some mechanical properties of thin films but some mechanical testing including thermos-mechanical testing is not

available for thin films[85]. Thus, most SMAs development still relies on bulk materials produced by vacuum arc-melting or induction melting. Although some improvements have been applied on these processes, re-melting during for arc-melting for at least 6 times is necessary to limit segregation, while the induction-melted samples have limited size and gravity segregation [86]. Also, these methods are not suitable for building materials libraries rapidly. Other processes, like self-propagating high-temperature synthesis (SHS), a technique using exothermic reaction to synthesis mixed fine powder reactant and metal, have also been applied for production of SMAs samples, but they are still not high-throughput methods [87].

Recently, the development of laser-based additive manufacturing technology (shown in Figure 2.15) provides a new solution for alloy development. Polanski *et al.* developed a combinatorial synthesis process based on laser engineered net-shaping (LENS) for hydrogen storage alloys, which can produce graded composition samples and bulk materials libraries (Figure 2.16) [88]. However, the process is based on a powder system, which uses coaxial powder feeders for deposition. The feeding rates of the different materials powders are different, as well as the amount of powder being deposited into the melt pool is different for different powders. Hence, the accuracy of this system is limited by the ability to control the powder ratios. In addition, most powders are hard to manufacture and the price is higher than the other

forms of materials. The powder-based laser system also requires fine powder, typically finer than $150\text{ }\mu\text{m}$, for deposition. The other problems of powder-based systems are pores, balling effect and stress, which affect the integrity of the samples and sometimes they cause the failure of the samples during deposition or testing [89].

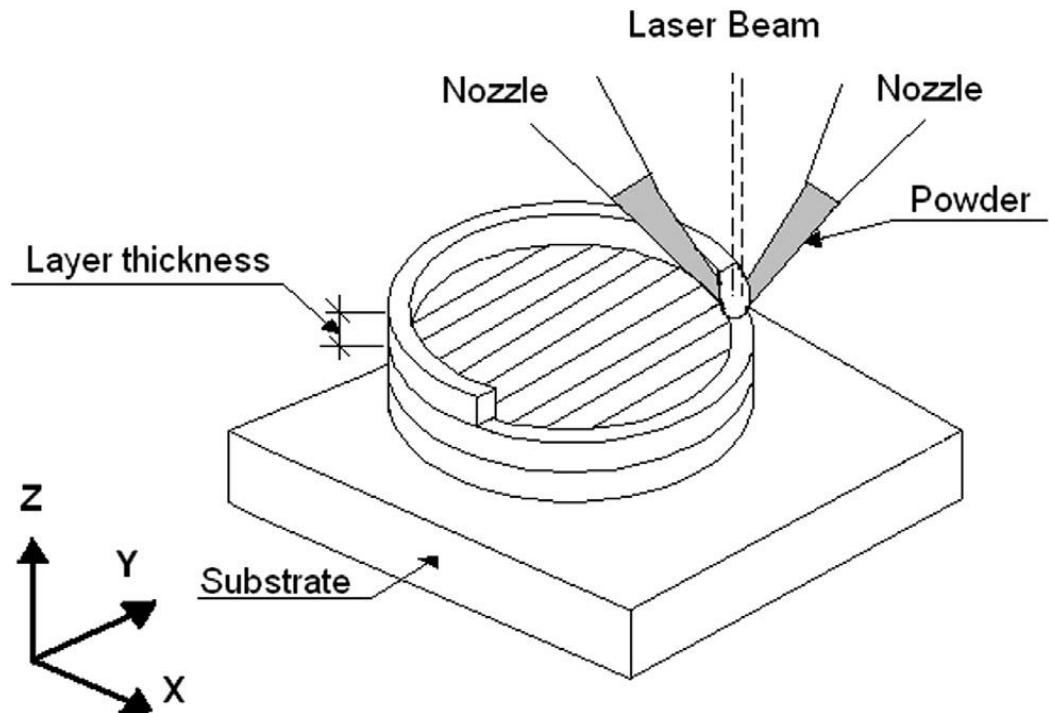


Figure 2.15. Schematic drawing of the LENS process with coaxial nozzle feeders [88].



Figure 2.16. Ti-Ni-Fe ternary materials library deposited by powder-based LENS combinatorial synthesis [88].

The natural characteristics of powder system and laser scanning systems limit powder-based laser combinatorial synthesis system for manufacturing crack-sensitive materials. In the present study, a wire-based laser combinatorial synthesis system, named as Suspended Droplet Alloying (SDA), is applied to develop the materials libraries for Ti-Ni-based alloys [90]. In this system, the powder feeder and nozzles around the laser beam in a Direct Laser Deposition (DLD) system have been replaced by wire feeders. Six wire feeders feed the wires into a wire delivery system and each wire is set up to go through the focal point of the laser beam. The laser

beam melts the wires so that they can join each other as a droplet and mix, before dropping down to the substrate under the nozzle. The laser beam heats up the sample during the building process, creating a cooling rate which is much slower than the DLD and laser powder bed systems (about 100K/min), which avoid cracking and generating residual stresses in the material. The droplet has enough time (about 30 min) for mixing and letting the gas escape from it before drops down, so the pores are eliminated in the most part of samples.

Nevertheless, feeding materials as wires makes the laser reflectivity and absorption of materials critical to the melting process, as the size of wire is much larger than the size of the laser spot. The relationship between the absorption coefficient and reflectivity coefficient value for metals is as below [91].

$$R = 1 - A \quad \text{Equation 2.7}$$

where R is reflectivity, A is absorptivity.

The free electrons in metals predominantly absorb the radiation and oscillate or re-radiate the energy without disturbing the solid atomic structure of metals, which makes the metal have a high reflectivity. This phenomenon means that the radiation does not penetrate the metals further than one to two atomic diameters. The reflection coefficient for normal angles of incidence from a metal surface in air ($n = 1$) can be calculated from the refractive index (n) and the extinction coefficient or absorption

coefficient (k) as the equation below:

$$R = [(1 - n)^2 + k^2] / [(1 + n)^2 + k^2] \quad \text{Equation 2.8}$$

Thus

$$A = 4n / [(n + 1)^2 + k^2] \quad \text{Equation 2.9}$$

where k, n and R are constants for some metals, and are given in Tables 1.2 and 1.3.

The value of the reflectivity R, shown in Table 1.2 is 1 for a perfectly flat clean surface.

Table 2.4. Complex refractive index and coefficient of reflection for some materials to 1.06- μm radiation [91].

Materials	k	n	R
Al	8.50	1.75	0.91
Cu	6.93	0.15	0.99
Fe	4.44	3.81	0.64
Mo	3.55	3.83	0.57
Ni	5.26	2.62	0.74
Sn	1.60	4.70	0.46
Ti	4.0	3.80	0.63
W	3.52	3.04	0.58
Zn	3.48	2.88	0.58

Table 2.5. Refractive index and Brewster angles for various materials [91].

Materials	λ (μm)	Refractive index k	Refractive index n	Brewster angle
Al	1.06	8.5	1.75	60.2
	10.6	34.2	0.108	88.3
Fe	1.06	4.49	3.81	75.2
	10.6	32.2	5.97	88.2
Ti		3.48	2.88	70.8

Furthermore, the metal absorption of light also varies with the wave length. The absorption coefficient of most metals decreases as the wavelength increases, as shown in Figure 2.17 [92]. As indicated in Figure 2.17, the absorption of most metals is less than 10%, with CO₂ laser (wavelength of 10.6 μm) and the Cu, Au, Ag and Al are less than 3%.

Additionally, the elements within the droplets will be affected by gravity, laser absorption and different melting point of the wires, which induce gravity segregation and inhomogeneity. According to the different process parameters, in terms of laser power, wire diameter and feeding speed, the suspending time of each droplet varies from 3 seconds to 40 seconds before dropping down, which may introduce gravity segregation within the droplets. On the other hand, the differences in melting point and the laser energy absorption in different materials may make some wires start melting first, while the others cannot be melted until they penetrate the hot droplets. In the case of Ti and Ni, for instance, the melting point of Ni is 213 K lower than

titanium, so the Ni will be melted by the laser beam first and form a droplet, the titanium wire joins the droplet from the top and melted as the Ni droplet is being heated up by laser beam. Thus, the high Ti concentration stays at the top of the Ti-Ni droplet, where the Ti wires joins it leading to segregation in the droplets. Cu, which has low CO₂ laser absorption [92], does not melt until it touches the droplet or until the atmosphere around is hot enough, so it causes similar segregation to Ti-Ni. The homogeneity of the samples will be the most important issues for laser-based combinatorial synthesis method. But these segregations are all within one droplet, which is about 3 mm to 10 mm thickness in the sample, so they could be eliminated easily by heat treatment.

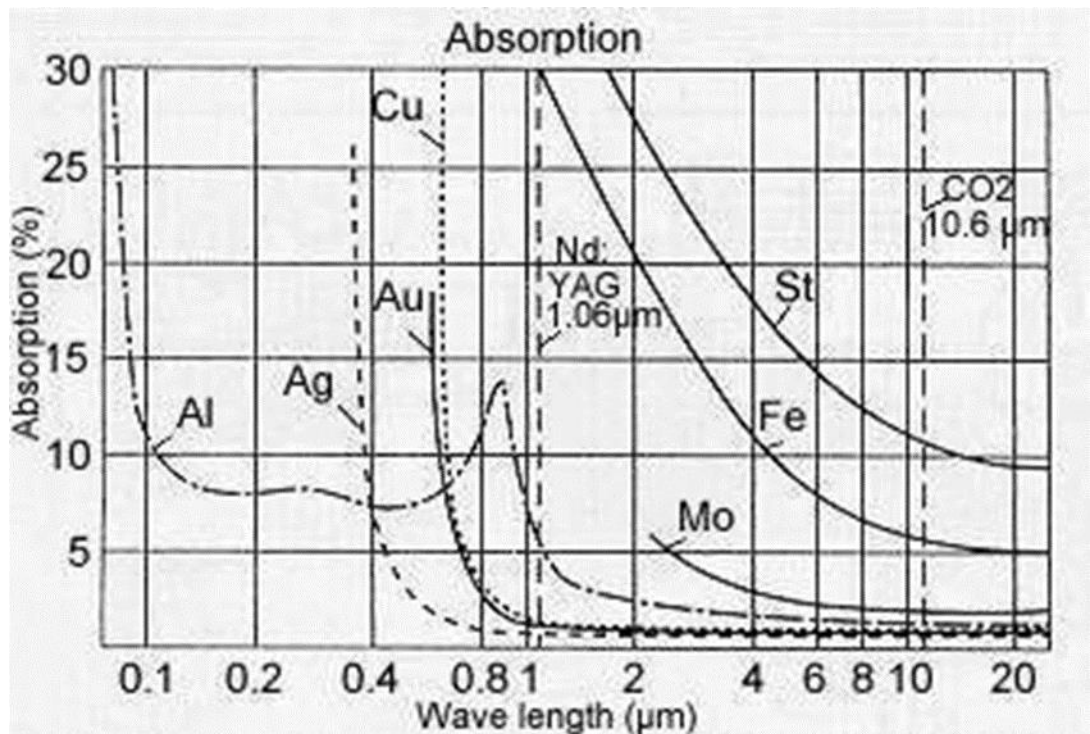


Figure 2.17. Laser absorption of different metals under different wavelengths. Most metals show decreasing absorption as the wave length increases [92].

2.5 Selective laser melting

Selective laser melting (SLM), known as a laser powder bed (fusion) additive manufacturing (AM) technology, was developed initially for rapid prototyping for the production of engineering components [89, 93]. As illustrated in Figure 2.18. A schematic diagram for SLM process with building chamber, powder chamber, laser system, scanning system and wiper [98]., a 3D computer-aided design (CAD) file of the component is loaded into a special software to slice the component into many layers, typical thickness for each layer is 20 to a few hundred microns. Fine powder (normally below 60 μm) is spread uniformly by a wiper blade across the substrate in the building chamber from the powder chamber to form successive layers. A 2D slice of the component has been defined by the computer from CAD file, and a laser beam scans the 2D path to melt the powder in the building chamber. The whole powder bed is lowered by the layer thickness and the next layer of powder is spread over the previous layer. The laser then scans the defined path of the next two dimensional slice. Finally, a three dimensional component, which is surrounded by unmelted powder is produced layer-by-layer, and can be removed from the bed as a net-shape sample. The advantage of this technology includes not only producing complex structure components with different materials varying from pure metals, alloys and ceramics, but also having better surface finish than DLD technology, due to the finer

powder and smaller layer thickness, laser power, and spot size.

Nonetheless, studies on AM suffered from a number of shortcomings. First, although the surface finish of SLM built components on the top surface is acceptable, whereas the other sides, which are surrounded by the powder tend to have poorer surface finishing due to some unmelted powder being partially melted onto the surface [94]. Second, the rapid heating and cooling brings high cooling rates and finer grains in SLM built components, which affect the SME and mechanical properties of SLM-built SMAs [2, 15, 95]. Second, the repeated rapid heating and cooling also increases the stress level in the components, which affects the structural integrity of SLM-built components. Third, since there are gaps between the powder particles and the evaporation of powders, plasma pressure and turbulence during laser moving create a lot of gas during melting, which could be captured and remain in the components as pores. So far, research on SLM has been mainly focused on solving the problems above by adjusting the parameters and scan strategies.

Although a wide range of materials have been investigated for SLM processing, Ti-Ni-based SMAs on SLM is relatively under researched. The poor machinability of Ti-Ni makes SMA difficult to produce, especially for complex structure components [7, 96]. In addition the response of Ti-Ni-based alloys is very sensitive to composition and the thermo-mechanical history and the route processing used, which

leads to difficulties in manufacturing components with reproducible behaviour [19, 97]. The extent of segregation is limited in powders, because they are usually produced by rapidly cooling molten alloys, and the powders from ingot are sieved and mixed before processing. On this basis, the processing of Ti-Ni alloys using a powder route offers some potential advantages.

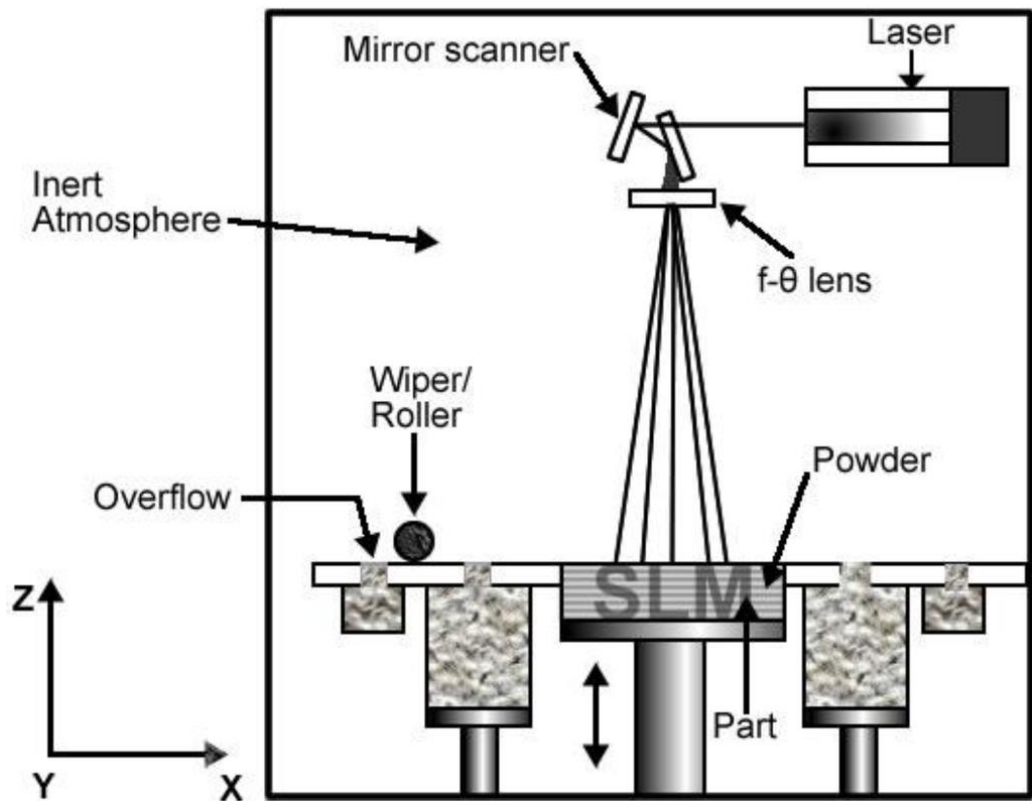


Figure 2.18. A schematic diagram for SLM process with building chamber, powder chamber, laser system, scanning system and wiper [98].

There are a number of shortcomings reported in the available literature on SLM of Ti-Ni SMAs. First, the Ni-rich and equi-atomic Ti-Ni were the topics of the majority of SLM Ti-Ni studies [99, 100], where SE is the dominant regime, understandably

since the most of SMA applied in the medical field (e.g. stents) rely on the SE effect rather than the SME. The equi-atomic or Ni-rich SMA has the advantage of adjusting TT by changing composition or heat treatment parameter (Figure 2.4) [22]. In contrast, Ti-rich Ti-Ni has stable TTs, and they demonstrate a higher strength than equi-atomic Ti-Ni due to Ti_2Ni precipitation strengthening. Nonetheless, cracking during SLM processing is more challenging, because both precipitates (Ti_2Ni and Ti_2Ni_3) are very brittle [2, 101]. Second, the previous studies overlooked the need for post-processing homogenisation heat treatments to reduce segregation. It is known that homogenisation of Ti-Ni results in a reproducible behaviour, with less TTs variation [2]. Finally, Ti-Ni component with fully dense state is hard to achieve in SLM processes. Some researchers studied elemental powder, while others investigated the possibility of building porous parts with controlled porosity for bone implants application, which has better biomechanical compatibility (i.e. closer to the bone's specific strength and modulus) [102, 103]. Unlike porous components in medical implants, fully dense material is necessary for structural components. Bormann *et al.* investigated the microstructure of SLMed near fully dense Ni-rich Ti-Ni but the porosity obtained was higher than 1% [100, 104]. A comprehensive review on AM of Ti-Ni can be found from the review by Elahinia *et al.* [105].

2.6 Negative Poisson's ratio materials

Negative Poisson's ratio (NPR) materials, namely auxetic materials, are specially designed interconnected structures which get thicker under stretching as shown in Figure 2.19 [106, 107]. Compared to conventional materials, this unique property offers the material significant advantages, such as an increased plane strain, tunable density, fracture resistance, shear modulus, indentation resistance and acoustic response [108]. NPR materials have been considered for a wide range of structural materials and functional devices. Possible applications for which NPR materials are energy absorption, smart antennas, armor and stretchable sensors [109, 110]. It can also be used for protective structure as well as sandwich lightweight structure in aircraft or many other applications (e.g. from biomedicine to defence and aerospace) [106, 111].

Despite the aforementioned advantages of NPR materials, the applications of NPR are limited by manufacturing for their complex structure. Most of the previous research on NPR materials were focusing on theoretical analysis and the response of material. Different types of NPR materials, including cellular solids, porous polymers, composites, and textiles, have been developed [112-121].

Up to now, only a few trials to produce cellular solids NPR materials have been reported. Cellular NPR structures as well as thin film NPR structures were

constructed by conventional sheet forming processes. However, the main barrier to produce NPR material with complex shape is the size and design limitations. A few reports have been published using foam materials for NPR structure, however the homogeneity of pores and uncontrollable foam structure limited their application [122]. Co-Fe Spinel thin film spring also has been produced with NPR structure, but the size limits the application [108].

As discussed in the last section, AM is very suitable to produce complicated structures like auxetic structure comparing to conventional process. Electron Beam Melting (EBM), is one of the additive manufacturing processes that has been applied to fabricate 3D re-entrant structure made from Ti-6Al-4V and pure copper and that has a negative Poisson's ratio [108, 123]. Selective Laser Melting (SLM), or laser powder bed fusion, however, can create complex 3D structures with better geometrical and surface accuracy than those in the EBM due to smaller penetration distance and therefore it is more suitable to produce fine structures [124].

The combination of NPR materials, SMA and AM hold the potential to develop smart structures further, such as armour, energy absorption and metal wheels etc. The general purpose of the processing study in this thesis was to introduce a novel type of smart metal structure combining the properties of both NPR structure and SMA in one component via the use of SLM.

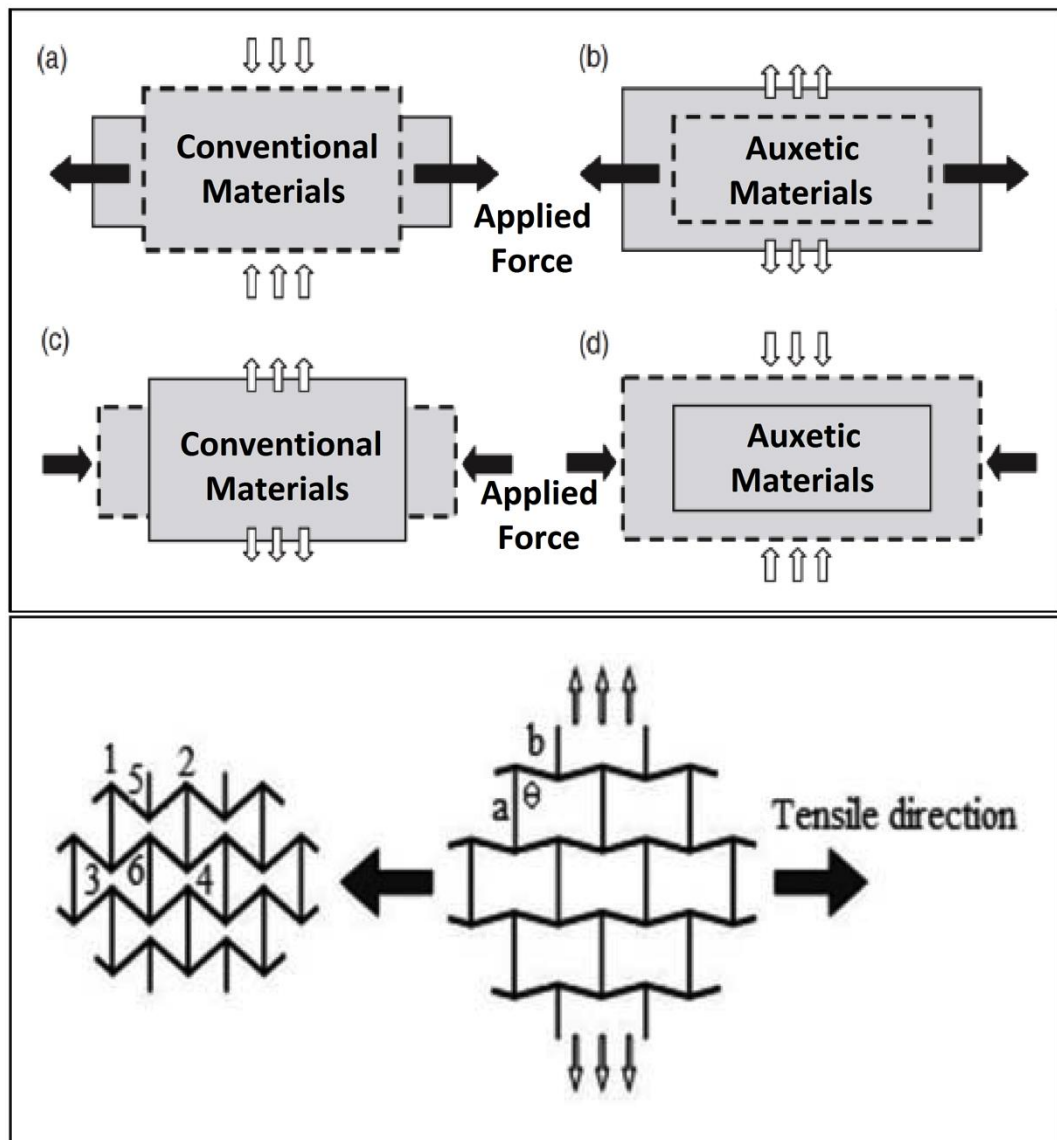


Figure 2.19. Negative Poisson's ratio or auxetic materials, which shrinkage during compress, act contrarily to convention materials can be applied for many structural and functional applications [120].

There are several different types of geometries and structures with NPR response have been researched and tested. The mechanical behaviour of NPR structures including re-entrant, chiral, and rotating have been reported [125].

One of the most popular examples of NPR structures are re-entrant structures, which

has the highest negative Poisson's ratio among the other types. This is due to the cell links in this structure deformed by the unit cell exhibit a negative Poisson's ratio deformation on the level of each unit [126, 127]. It is important to note that despite the chiral and rotating structures have isotropic properties, the NPR range of these structure is -1 to 0 , which are limited by their deformation mechanism [125, 128]. The NPR structures mentioned above are very useful, as geometrical information they provided helps researchers to establish a manufacturing route to process the proposed materials according to the design.

The re-entrant angle (θ) and width x are the key factors for re-entrant structure. For the whole NPR structure, the theoretical Poisson's Ratio (ν) values were calculated by dividing strain in the transverse direction ($\epsilon_{\text{transverse}}$) by the strain in the vertical dimensions ($\epsilon_{\text{vertical}}$), as shown below.

$$\nu = -\frac{\epsilon_{\text{transverse}}}{\epsilon_{\text{vertical}}} \quad \text{Equation 2.10}$$

The conventional unit cell has simple overhanging links but the stress concentration is higher around the joint, which are not desired in SLM processes. Theoretically, SLM has the capabilities to build almost any complex structure. However, in reality, this is not true. Overhanging links are generally described as critical structures to build by SLM. SLM of overhanging structures links onto loose powder resulting in poor underside surfaces and resolution. Accordingly, the conventional design has

been modified to overcome this problem by replacing all the overhanging structures with inclined ones.

2.7 Summary

In this chapter, the basic metallurgy properties of Ti-Ni-based SMAs, the development of these alloys and the potential applications of Ti-Ni-based SMAs have been introduced. Additionally, the studies and application prospect of new manufacture process for SMAs, which is SLM, has been introduced.

1. Binary and ternary Ti-Ni-based shape have been well researched during the last few decades and have been used for many applications due to their unique properties.
2. It is clear that there are some defects of the properties of SMAs itself as well as the manufacturing method obstructed the further application of this material. The low thermal-mechanical fatigue life of these alloys become the greatest obstacle for the application of actuator and the working temperature of these alloys also need to be improved to broaden the applications.
3. It has been proved that shape memory properties of Ti-Ni-based SMA can be altered by alloying, but the quaternary and quinary Ti-Ni-based alloy are under researched. The relationship between the combination of different alloying elements and shape memory properties are not clear.

4. Furthermore, the poor machining properties of these alloys limited the application for complicated structure components and increases the cost of manufacturing. Therefore, a novel process, AM, is necessary for further application of SMA.
5. Combination of smart materials and smart structure (e. g. SMA and NPR structure) has good properties and wide range of potential application, which can be produced by AM.

In this thesis, the author tried to solve these problems by using SDA method to develop SMAs with new composition and investigate the heat treatment and thermal-mechanical properties of these alloys. On the other hand, an AM process, SLM, has been applied to overcome the manufacturing shortage of SMAs with complicate structure.

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3 Chapter 3. Materials and experimental method

3.1 Metals and alloyed wires

A series of metal wires were used to produce alloys in AccMet project (see Table 3.1).

The AccMet (FP7) project, known as accelerate metallurgy project, was found by European Space Agency and aimed to improve the development speed of alloy development and metallurgy. In order to optimise the deposition parameters, commercial metal wires of various diameters were used. Since some pure elemental wires from Advent company are hard to produce, alloyed wires were used in order to add these elements into the alloys. For example, Ni-Cr wires were used to add Cr into the alloys.

Table 3.1 Table of element wires used in SDA process.

Elements	Diameters (mm)	Weight (g/m)	Melting point (K)	Purity (wt.%)
Ti	1	3.48	1941	99.6
Ni	1	6.86	1728	99.6
Cu	1	6.81	1358	99.9
Zr	0.5	1.34	2128	Zr+Hf: 99.2
	1	5.10		(Hf $\leq$ 4.5 wt.%)
Hf	0.5	2.74	2506	Zr+Hf: 97.0
	0.7	6.74		(Zr $\leq$ 3 wt.%)
Nb	0.5	1.66	2741	99.5
Fe	1	1.69	1811	99.9
Co	1.2	7.41	1768	99.9
Al	1	1.03	993	99.9
NiCr	0.5	1.54		70/30

3.2 Ti-Ni pre-alloyed powder

A Ti₅₆Ni₄₄ (55.7 at.% Ti content) cast, homogenised, and hot forged ingot was argon atomised by TLS Technik GmbH&Co (Germany). The powder was later sieved to separate the <65 µm particles, which were used for SLM processing. The oxygen content of the as-received powder was measured using a Leco TC436AR ANALYSER, and was found to be 1000 ppm. The particle size distribution of the powder was measured using a CoulterLS230 laser diffraction particle size analyser.

3.3 List of samples

As shown in table 3.2 a range of SMAs were produced for testing. The typical size of the SDA built samples was 10 mm to 20 mm in diameter and the height 20 to 40 mm, Figure 3.1. The sample sizes for microstructure, chemical composition and thermal cycling behaviour investigation were varied according to the composition and the process parameters, which will be discussed in the Chapter 4. The raw sample size for thermal mechanical testing was 10 to 20 mm in diameter, and 60 to 100 mm in height, so that they could be cut into a dogbone-shaped tensile test piece. All SDA built samples were deposited on a steel substrate with dimensions 20 mm diameter and 2 mm thick.

The coordinate system of SDA samples was defined as follows: the horizontal plane or substrate surface plane is XY-plane and the Z direction is the building direction, as shown in Figure 3.1. All samples were cut along the ZX plane to investigate the

microstructure and chemical inhomogeneity in the vertical section and then cut along the XY-plane for further microstructural and phase transformations investigations.

Table 3.2 Table of samples produced in this research.

Sample name	Target composition (at.%)	Manufactured process
Ti ₅₀ Ni ₅₀	Ti50-Ni50	SDA
Ti ₅₂ Ni ₄₈	Ti52-Ni48	SDA
Ti ₄₈ Ni ₅₂	Ti48-Ni52	SDA
Ti _{50.5} Ni _{49.5}	Ti50.5-Ni49.5	SDA Mechanical testing
Ti _{50.4} Ni _{49.6}	Ti50.4-Ni49.6	Hot-rolled reference
Ti _{49.6} Ni _{41.4} Cu ₉	Ti49.6-Ni41.4-Cu9	Hot-rolled reference
Ti ₅₄ Ni ₃₄ Cu ₁₂	Ti54-Ni34-Cu12	SDA
Ti ₅₀ Ni ₂₅ Cu ₂₅	Ti50-Ni25-Cu25	SDA
Ti ₅₂ Ni _{48-x} Cu _x	Gradient Cu: 0 to 20	SDA
Ti _{52-x} Ni ₄₈ Hf _x	Gradient Hf: 0 to 25	SDA
Ti ₃₆ Ni _{49-x} Hf ₁₅ Cu _x	X = 0, 1, 3, 5, 8, 10	SDA
Ti ₄₉ Ni _{49-x} Hf ₁₀ Cu _x	X = 0, 1, 5, 8, 10	SDA
Ti _{51-x} Ni _{39-x} Cu ₁₀ Nb _{2x}	X=0, 0.5, 1, 1.25, 1.5	SDA
Ti _{51-x} Ni _{39-x} Hf ₁₀ Cu ₁₀ Nb _{2x}	X = 0, 0.25, 0.5, 1	SDA
High Ms	Ti42-Ni36-Hf10-Cu10-Nb2	SDA
Low Ms	Ti43-Ni33.5-Hf10-Cu11-Nb2.5	SDA

A few commercial SMAs materials also have been used as a reference as a comparison with SDA built samples. The Ti_{49.6}Ni_{50.4} and Ti_{49.6}Ni_{41.4}Cu₉ SMAs, which were hot rolled into 3.5 mm thick sheet and aged at 873K for 30 min, were supplied from Institute of Metals Research (IMR), China. The ingots of 10 kg weight for both

compositions were vacuum-induction melted (VIM), cast using calcia crucible and homogenised in vacuum at 1133 K for 2 h. Then the ingots were forged several times to approximately 310 mm × 20 mm × 60 mm size followed by hot rolling at a 1093 K. The thickness was reduced by 0.5 to 1 mm per pass until the thickness reaches approximately 3.5 mm. The material was held at 1093 K for 2 h between the passes.



Figure 3.1. TiNi sample built by suspend droplet alloying process. The diameter of steel disk substrate is 20mm. The different color on sample surface is due to different Ti oxide thicknesses.

3.4 Selective Laser Melting

SLM samples of dimensions (x,y,z) of $5 \times 5 \times 10 \text{ mm}^3$ were built using a Concept Laser M2 Cusing®SLM (laser powder bed system) in Ar atmosphere, with an oxygen-content <0.1%. The system uses a continuous wave fibre laser with variable power output up to 400W, and a laser track width of 150 μm . In order to achieve defect-free builds, a total of 30 build conditions were applied to optimise the process parameters. The process parameters (laser power, scan speed, and scan spacing) were varied in the range of 50-120 W, 100-300 mm/s, and 45-150 μm , with a layer thickness of 20 μm and the M2 system island scanning strategy [129], with an island size of 5 mm with 30 build conditions in total. Following the optimisation of the process parameters, auxetic structures were built using the optimum parameters.

3.5 Sample preparation

Samples were cut using AgieCharmilles CUT 20 P Electrical Discharge Machining (EDM) which is a process using electrical discharges (i.e. sparks) to remove materials from the specimens by rapidly recurring current discharges between two separated electrodes. The workpiece and electrodes are immersed in dielectric liquid for cooling. The electric voltage between the two electrodes, which are tool and workpiece, cause a breakdown of a capacitor or condenser occurs as the distance between two electrodes is

reduced and the material of the electrodes is removed [130]. The tool electrode used in this machine is 0.25mm brass wire. Although there is an oxide and brass layer on the surface after cutting by EDM, the characteristic of low stress, high cutting speed and low temperature variation during cutting make EDM very suitable for machining SMAs. After cutting, the oxide and brass layer can be removed by grinding.

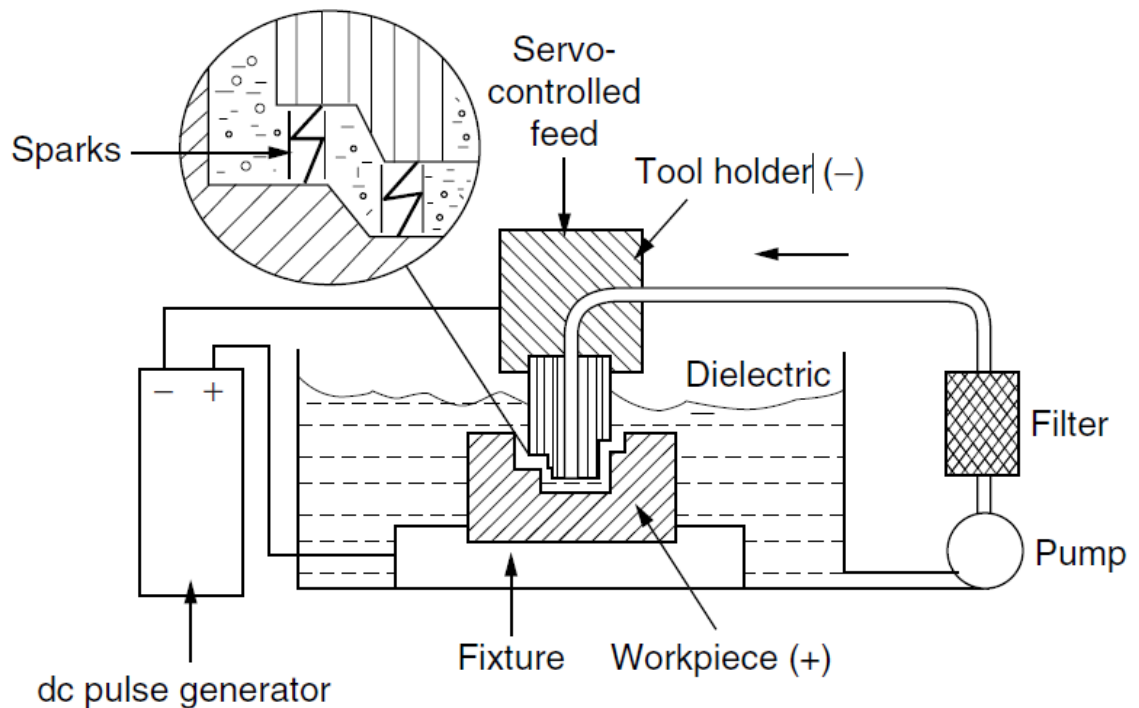


Figure 3.2. Schematic drawing of electrical discharge machining used for sample cutting [130].

The samples were ground by Silicon Carbide grinding paper and polished down to 0.04 μ m colloidal silica OP-S solution. The as-polished samples were used for XRD, SEM, EDS and EBSD investigation. The samples for Optical Microscopy (OM) were etched by using Kroll's reagent (2% HF+10% HNO₃+88% H₂O) after polishing to

reveal the microstructure. The microstructure was characterised using a ZEISS Axioskop 2 optical microscope and Leica DMRX Polarized Optical Microscope.

3.6 Microstructural and phases characterisation

X-ray Diffraction (XRD) was performed using a Philips X'Pert system, equipped with a Cu K α anode, at room temperature to identify the phases. The operating voltage is 35kV and scanning angle is from 20° to 120°. The peaks for different phase and orientation were determined according to the published literature [15, 29, 131].

A JOEL 6060 Tungsten filament Scanning Electron Microscopy (SEM) and a JOEL 7000 field emission SEM, equipped with Oxford Inca Energy-Dispersive X-ray Spectroscopy (EDS) system were applied to investigate the microstructure and chemical composition. A Philips XL30 field emission SEM equipped HKL Channel 5 Electron Backscattered Diffraction (EBSD) systems was also used to investigate the microstructure and texture of the coupons.

Further microstructure and orientation analysis were carried out on a JOEL 2100F Transmission Electron Microscopy (TEM). The samples were cut to 0.3 mm to 0.5 mm by EDM and ground down to lower than 200 μ m using grinding paper. The samples were then mechanically punched to a 3 mm diameter disk and ground to about 120 μ m. 10% Perchloric acid (HClO₄) solution in methanol was used for twin-jet polishing at 233K and the voltage is 20V from 60 s to 90 s.

SEM and EDS were applied to analyse the microstructure, chemical homogeneity, fracture surface and any cracks. Since some higher atomic number elements like Nb are in the materials, the accelerating voltage of 20kV was used for all samples. EBSD was applied to investigate the texture of sample and compare with the SMAs made by arc-melting. The texture and orientation of the sample not only affect the transformation behaviours but also indicate the heat transfer during sample building. The phases occur in the sample during alloying are mainly B2 phase and Ti_2Ni precipitates. The primarily growth direction of B2 phase is [100] direction while the primarily growth direction of Ti_2Ni is [111] direction. Since the B19' martensite plates are very fine (typically 2 to 10nm wide), it is hard to use EBSD to analyse the martensite in Ti-Ni alloys. As such, EBSD mapping was based on the B2 phase, either using Ni-rich sample at room temperature (RT) or analysis at high temperature (higher than A_f).

3.7 Heat treatment

A horizontal tube furnace, operating from room temperature (RT) to 1473K, was applied for heat treatment. The samples were wrapped in tungsten or tantalum wire to prevent oxidation and diffusion and sealed in an evacuated steel tube to prevent oxidation during heat treatment. The samples in contact with the steel tube via metal wires are able to cool down as fast as possible during quenching without being contaminated. The steel tube was cut after heat treatment to remove the sample.

3.8 Shape memory properties characterisation

After chemical composition investigation, samples were cut from selected area by EDM to provide samples for Differential Scanning Calorimetry (DSC). Since the DSC result can be affected by the sample size, the size of samples was limited to 3 mm to 5 mm in diameter and 0.5 mm to 1.5 mm in thickness. In order to make sure that the correlation of the chemical composition of DSC test sample to the predicted behaviour was correct, the test area was identified using EDS in the vertical section before cutting from a horizontal slice. An Al pan with an Al cap was used as the sample holder in the DSC test. Mettler Toledo DSC1 DSC system with testing temperature range from 203 K to 773 K was used for SME investigation. The heating and cooling rate in DSC test are 10 K/min. The first thermal cycle of all samples was not counted as it is affected by the sample preparation process.

Thermal stabilities and transformation temperature of samples were characterised by using Differential Scanning Calorimetry (DSC). A Mettler-Toledo DSC1 system was used to determine the TTs, by cycling the samples at a rate of 10°C/min during heating and cooling, between -70 and 450°C. A few DSC tests were undertaken with different size samples of the reference hot-rolled $\text{Ti}_{50.4}\text{Ni}_{49.6}$ sample. The first test was performed using 2 mm thick 4×4 mm square sample (Thick 2×4 mm in Figure 3.3), the second test is the same sample as the first one but after it had been polished down to 1mm thickness

with the same area size (labelled as Thin 1×4 mm in Figure 3.3), the third testing was using the same sample as the previous one but it has been polished to 1mm thickness 2×2 mm square sample (labelled as thin half 1×4 mm in Figure 3.3). The DSC testing result of these samples shows the size of the sample affects the transformation performance especially the transformation heat. This may be due to the influence of work hardening of the surface during sample preparation, heat transfer in the sample, the bulk stored energy in thicker samples, and the accuracy of sample weight measurement. In order to keep the accuracy of DSC measurement, the size of sample was kept as 1mm ± 0.5mm thick 4mm±1mm diameter in this study.

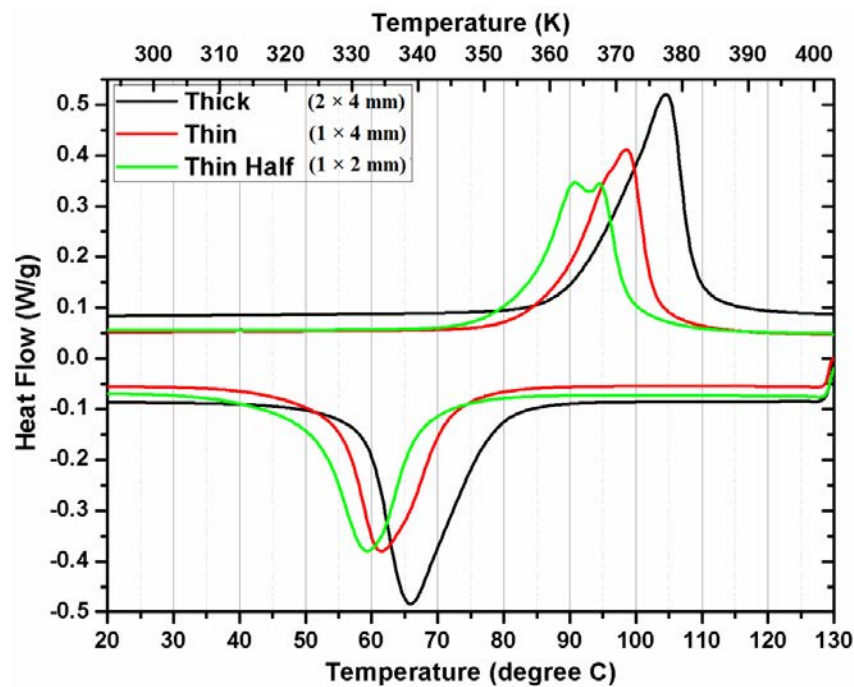


Figure 3.3. DSC testing result of hot-rolled Ti-Ni reference sample with different sample dimension. The result shows that the larger size sample has a higher transformation temperature as well as higher amount of heat in transformation.

3.9 Thermo-mechanical testing on shape memory alloys

The thermo-mechanical fatigue (TMF) testing was applied to investigate the SME of the samples. The geometry of the sample is shown as Figure 3.4. Schematic diagram of dog bone shape shape memory alloys sample used for thermal mechanical testing. The sample surface with gauge area was ground by P1200 SiC paper., sample surface was ground to Ra 25 nm (P1200) by SiC grinding paper after EDM cutting. The grip areas were ground to Ra 1050 nm (P120) in order to avoid slipping during testing. There are mainly two ways to test the TMF properties of SMAs [53, 132, 133]. One method is to keep the load applied on the specimen constant, while cycling the temperature of the sample, while using load control so that the displacement of machine can move according to the strain occurring during the transformation. However, the cycling frequency is limited by the temperature variation speed of this testing method, as changing the temperature is related to the thermal conductivity of the sample. Considering the sample geometry, the heating and cooling rate is far below the typical testing frequency (i.e. 0.1 Hz to 1 Hz) of SMAs TMF test [60]. Some studies have applied an air blast gun to alter the sample temperature via hot air and cold air in high frequency testing [134]. However, the sample temperature is indicated by thermocouples that were attached on the surface of the sample, and therefore the temperature inside the sample cannot be known accurately, making it difficult to assess

the influence the temperature on the bulk transformation. The other method is to hold the testing temperature above the austenite finish temperature (A_s) so that the sample is kept in the austenite phase, then cycling the load. In this method, the material has two deformation stages, which are the elastic deformation stage in austenite phase and superelastic (SE) deformation stage or stress induced martensite transformation stage, respectively. During elastic deformation, the material is still in the austenite phase; similar to the elastic deformation of the other materials in tensile test. In SE stage, the stress-strain curve shows a plateau line and the materials starts transform to martensite. It was known that the testing temperature and internal stress in the specimens affects the testing results significantly [135, 136]. Even though the test method and chemical composition are the same, the stress-strain curve of SMAs could be varied due to different heat treatments. As such, the samples investigated in this thesis are kept within the same condition as solution treated/homogenised samples. The schematic diagram of thermo-mechanical testing sample is shown in Figure 3.4. It is known that the flat dog-bone shape testing sample could introduce stress concentration at the corner and causes cracks during fatigue testing, but the rod tensile testing sample was not used in this study due to the difficulty of machining Ti-Ni.

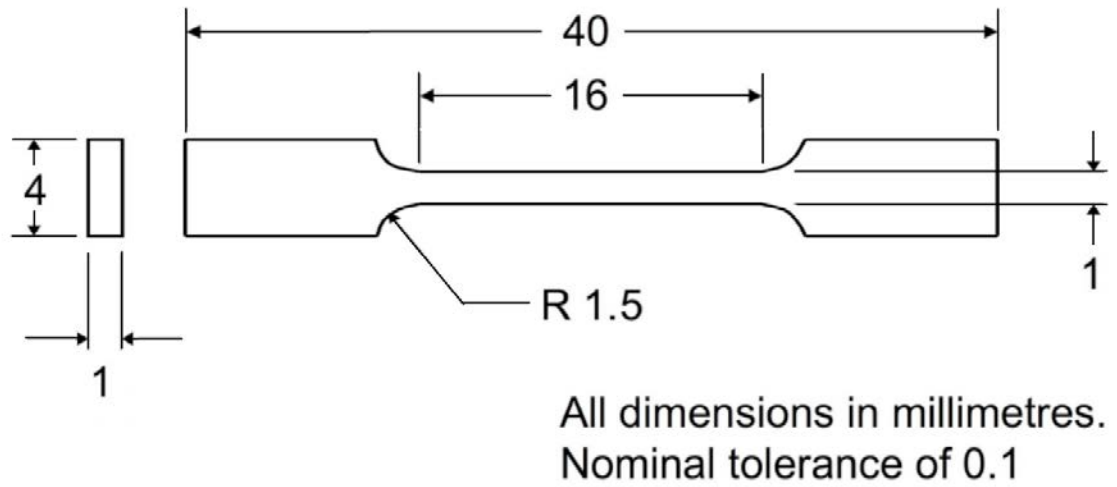


Figure 3.4. Schematic diagram of dog bone shape memory alloys sample used for thermal mechanical testing. The sample surface with gauge area was ground by P1200 SiC paper.

The TMF test machine used in this thesis is an ESH hydraulic driven mechanical testing machine with 1 kN load cell (see Figure 3.5). The machine has been calibrated to ± 2 N within the 200 N to 1 kN range and the maximum head speed of the machine is 5 mm/s. Most SMA TMF tests in the literature are performed using compression test. However, the compression testing stage of this machine is too large to be fixed in the furnace and therefore, compression testing in the austenite phase was not possible. It should be noted that the stress-strain behaviours of SMA under compression testing and tensile testing are different so the results measured cannot be directly compared with the literature. The maximum load for each sample is determined by using a tensile test from

20 N until the second stage deformation, i.e. the stress induced martensite transformation stage occurs and the strain for second stage reaches 1 to 3 %. Since the SMAs in some conditions need complete unloading to reveal the recovery strain, the loading method for TMF test was selected as 0.1 Hz sine wave loading and the minimum load was set as about 0 ± 1 N. A vertical tube furnace was applied to control the temperature for TMF testing, a K-type 1mm diameter thermocouple was attached on the sample surface to measure sample temperature during testing. Once the sample was attached on the machine, a 20 N tensile force was applied and the machine was switched to load control mode. Then, the furnace was switched on to heat up the sample, in order to eliminate the thermal expansion of the system, the tests were carried out after the sample had reached the test temperature for at least 1 hour. Due to the limits of the sample size and the furnace, no extensometer was applied to record the strain, the strain for TMF test was calculated from the displacement of the machine. Since the TMF test focus on the variation of strain against cycling number and the strain of machine is stable in each loading process, using displacement for TMF test is acceptable.

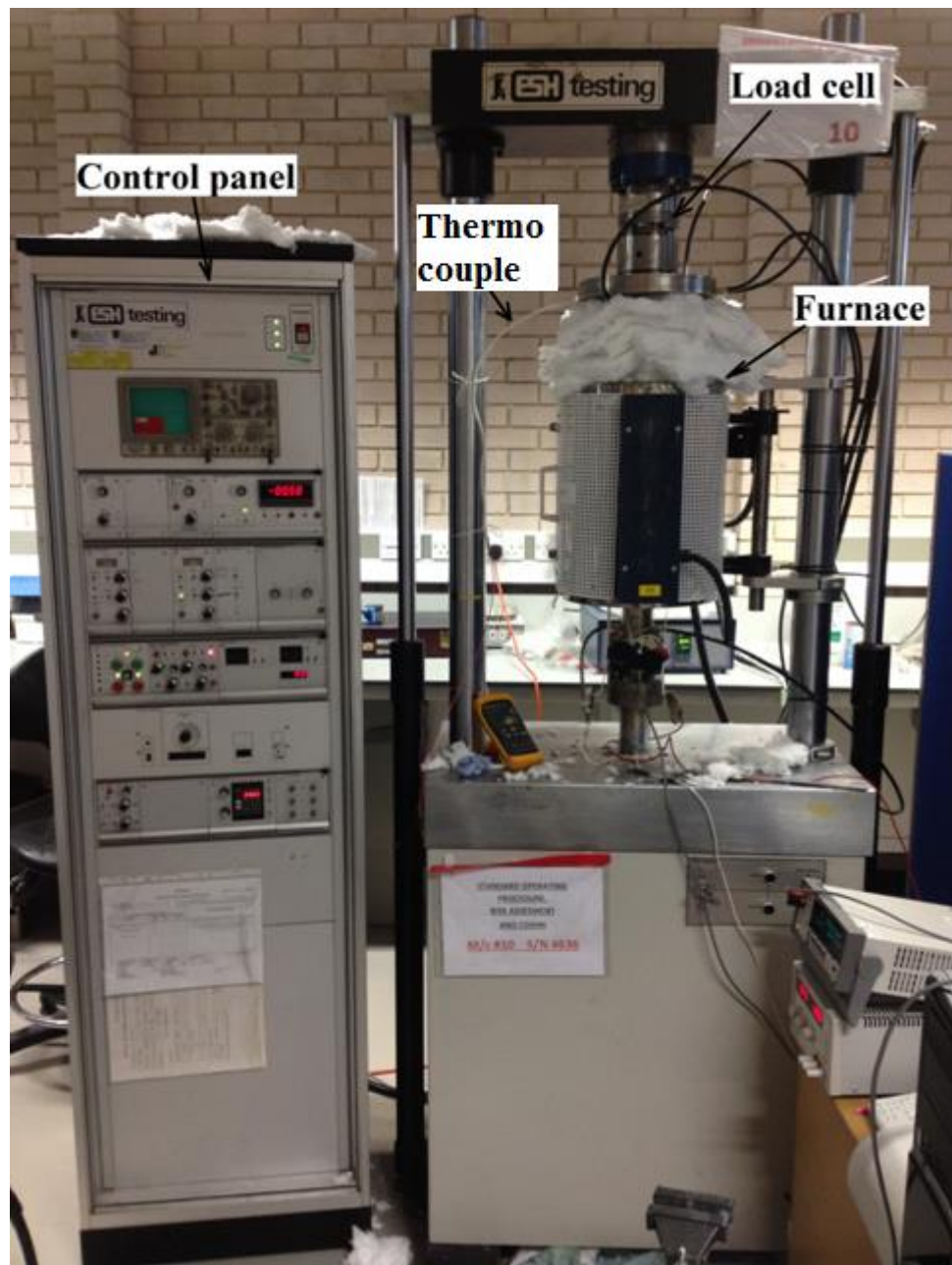


Figure 3.5. ESH hydraulic mechanical testing machine with vertical tube furnace was applied for thermal mechanical testing

3.10 Reference

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4 Chapter 4. Suspended Droplet Alloying process and shape memory alloys

4.1 Introduction

As Suspended Droplet Alloying (SDA) is a new alloying method, the characteristics of the process are not yet fully studied. Attributes of samples produced by SDA, including microstructure, chemical composition and thermal history, are investigated in this chapter using Ti-Ni-based binary and ternary shape memory alloys (SMA) samples as examples. Wires of pure Ni, Ti and Cu have been melted using simultaneous laser melting of wires, to create small coupons of Ti-Ni-based SMA. The microstructures and transformation temperature of the coupons have been compared with those of commercial hot-rolled samples. It has been found, using SEM and XRD that the microstructural and chemical homogeneity, in terms of the phase fraction distribution and chemistry, is comparable in the SDA laser melted coupons to cast samples in most SMA combinations investigated. Post-processing heat treatment can be used to improve the microstructural homogeneity.

4.2 Microstructural investigation and phase determine

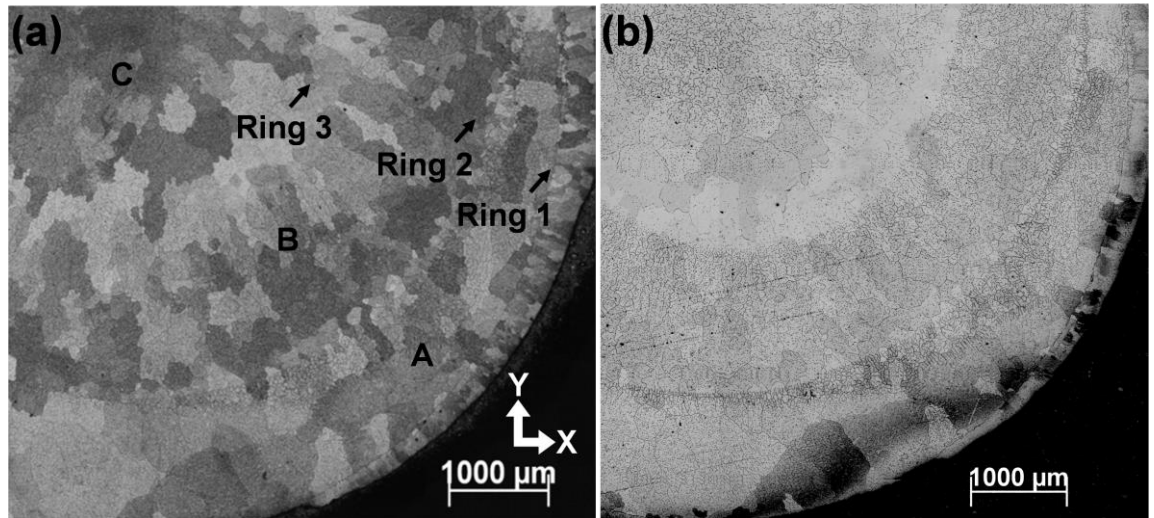
Since the Suspended Droplet Alloying (SDA) process is recently developed, an investigation of the microstructure and composition of SDA samples is necessary.

The samples were deposited using 800W to 1000W laser power, 305 to 475 mm/min

feed rate for Ti, 174 to 189 mm/min for Ni. Since the laser power need to be adjusted during the deposition, the specified parameters are not listed here.

Optical images of a quarter of the XY section of a SDA built $\text{Ti}_{50}\text{Ni}_{50}$ sample are shown in Figure 4.1 (a) and (b), where three ringed microstructural zones can be seen. The XRD data in Figure 4.1 (c) shows the B19' martensite phase matrix, in addition to Ti_2Ni [131]. Neither TiNi_3 nor Ti_3Ni_4 precipitates were found, which is as expected for an alloy of composition corresponding to TiNi , from the phase diagram shown in Figure 4.5. To quantify the Ti_2Ni fraction, an optical image (Figure 4.1 (b)) and several backscattered images were taken from the various regions in the coupon. It was found that the microstructure showed considerable amounts of Ti_2Ni , which suggests that the composition may be Ti-rich. The backscatter images was taken every 1.5 mm under 500 magnification and the area percent of precipitates was calculated from the backscatter images above by using ImageJ software. The sample was divided into a few areas according different precipitates concentration. The average Ti_2Ni percentage in each area was calculated from more than 5 images. The area percent of the Ti_2Ni particles was found to locally vary between 3 % to 21 %, with a total average area percentage of 10 %, as summarised in table 4.1. From the edge to the centre, the rings and areas are marked in Figure 4.1 (a). Ring 1 shows a limited fraction of Ti_2Ni precipitates and some

small columnar grains between ring 1 and the edge of the sample. Ring 2 has the highest Ti_2Ni area percentage, and the central zone (ring 3) again has a smaller Ti_2Ni percentage. Ring 1 contains 100~200 μm columnar grains towards the periphery of the coupon, while zone A within ring 1, shows coarse (around 1 mm) equiaxed grains. Ring 2, however, contained fine equiaxed grains up to 100 μm , while ring 3 consisted of a low Ti_2Ni percentage and a uniform grain size. Beyond ring 1, the grain size is uniform, although their morphology changes from columnar grain in zone B to equiaxed in zone C. It is worth mentioning that due to the resolution limit of ImageJ, the Ti_2Ni percentage measurements in this study are all within $\pm 3\%$ error.



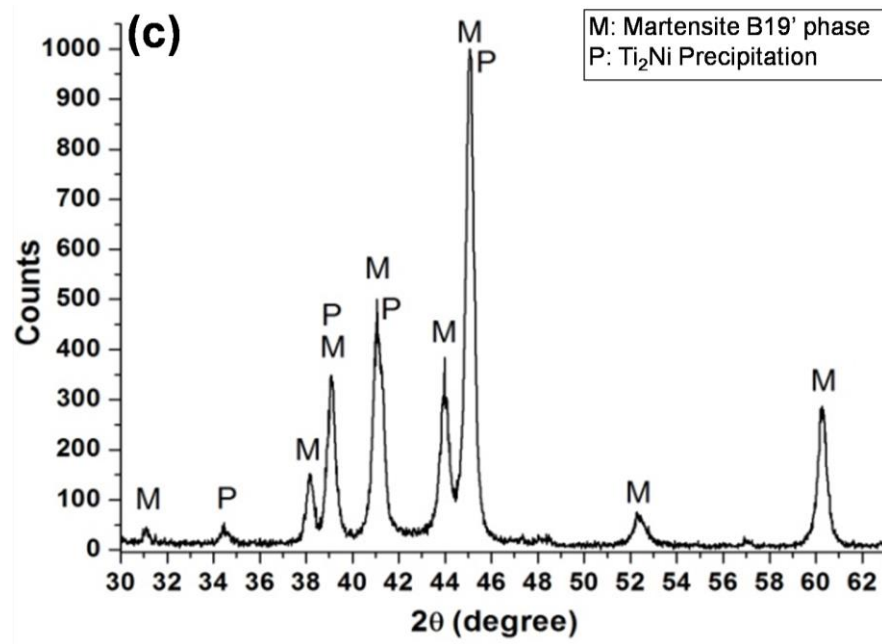


Figure 4.1. (a) Optical micrograph for the cross-section of etched Ti₅₀Ni₅₀ sample, showing the three microstructural zones, and (b) showing the distribution of Ti₂Ni (dark spots). (c) XRD pattern for the same sample showing the phases (B19' and Ti₂Ni).

Table 4.1 Area percentage distributions for the precipitates in Ti₅₀Ni₅₀ sample.

Regions	Ring 1	A	Ring 2	B	Ring 3	C	Total/Average
Area percent of regions (%)	1.7	13.3	4.9	39.7	16.2	24.5	100.00
Precipitate area percentage (%)	6	11	21	11	3	9	10

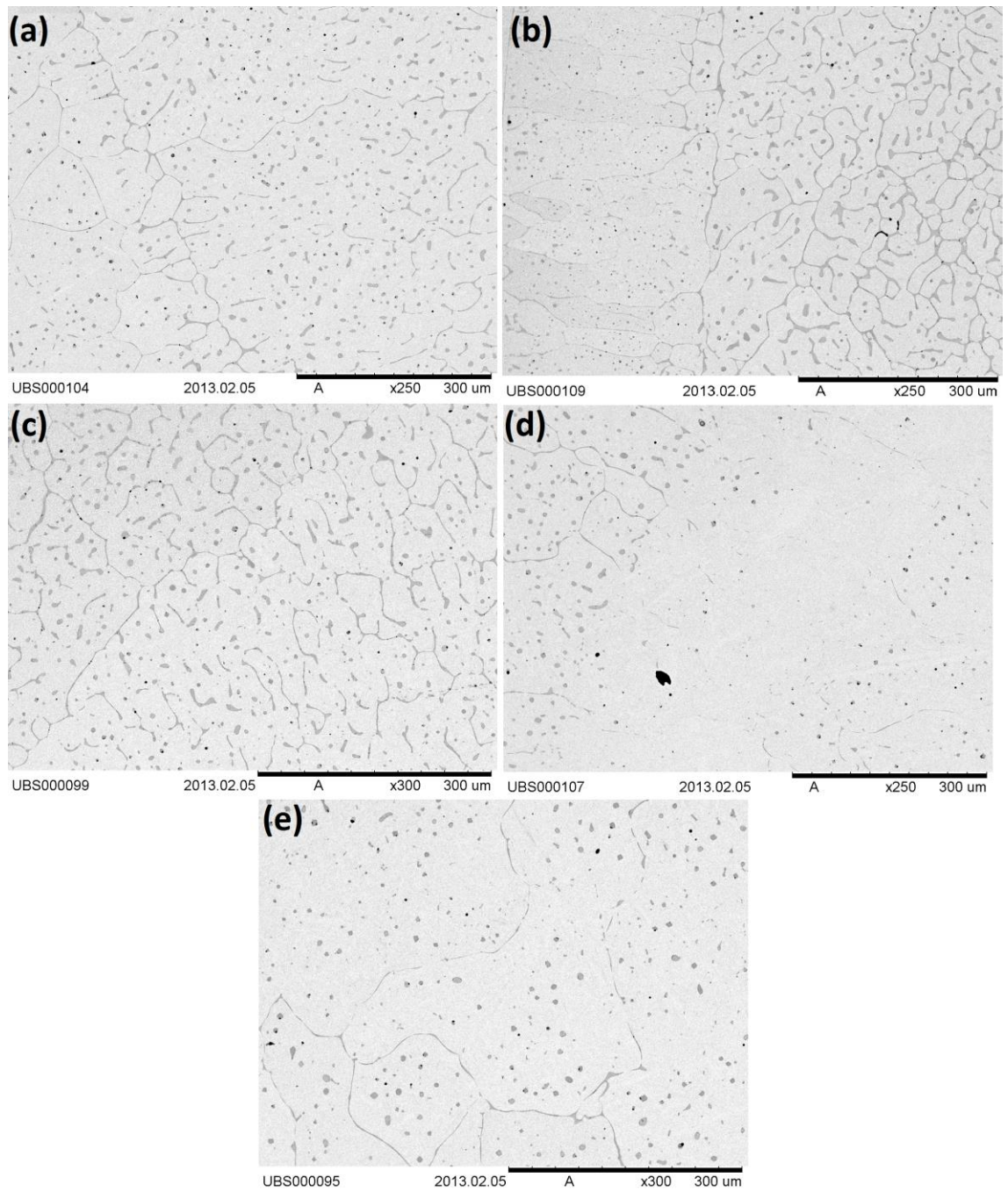


Figure 4.2 Backscatter images of $\text{Ti}_{50}\text{Ni}_{50}$ coupon, (a) shows Ring 1 area, (b) shows area A on left with low precipitation percentage and Ring 2 on the right, (c) shows area B, (d) shows Ring 3 area and (e) shows area C in the center.

The microstructure of XZ section of the $\text{Ti}_{52}\text{Ni}_{48}$ sample in Figure 4.3 shows that the columnar grains are tilted towards the centre between the build centre and edge, whereas the columnar grains in the centre are exactly vertical. On the other hand, some remelted regions, shown in Figure 4.3 (b) and (c), is similar to the typically remelted zone in LENS process [137], along the deposition direction were observed.

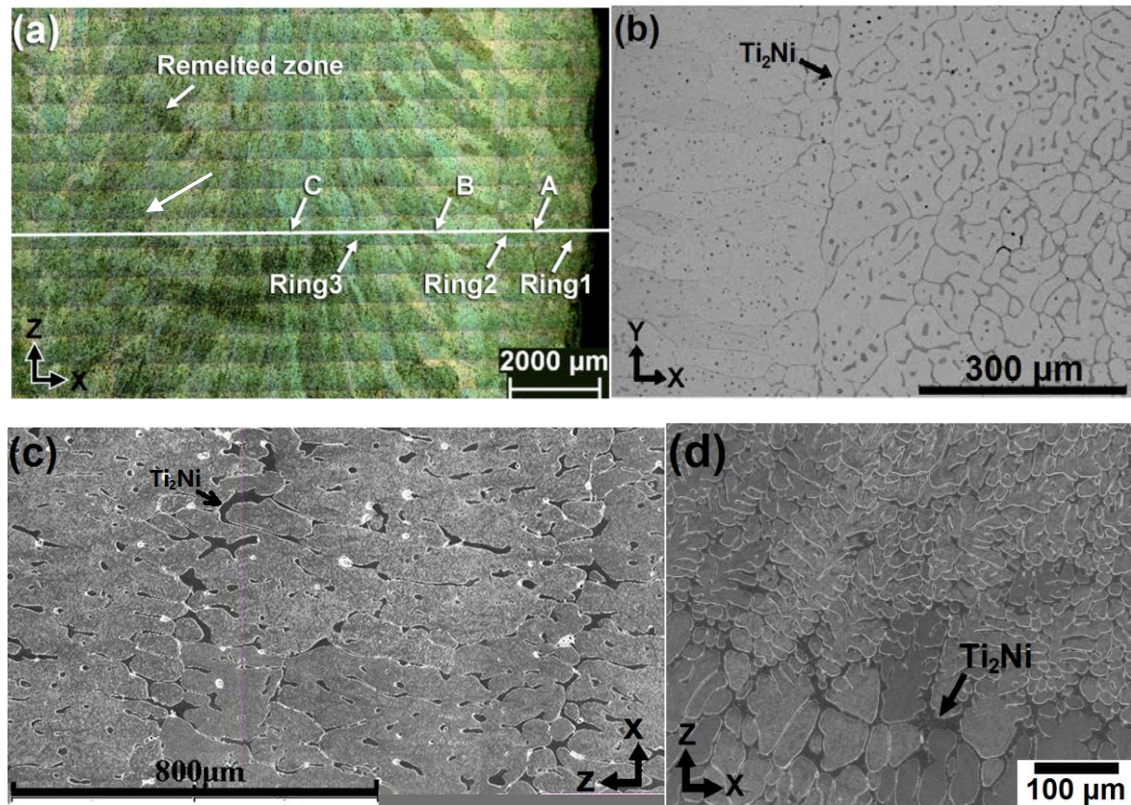


Figure 4.3. The SDA $\text{Ti}_{52}\text{Ni}_{48}$ sample, showing (a) the columnar grain structure oriented towards the central zone, (b) backscattered electron micrograph of the remelted zone in XY plane, (c) secondary image showing the remelted zone in XZ plane and (d) dendrites surrounded by Ti_2Ni in the middle of image.

To explain the microstructure above, the details of deposition process are essential. A schematic illustration of this process is shown as Figure 4.4. The temperature range in the figure was not measured, but rather estimated to introduce the concept (the measured and calculated temperature will be discussed in Section 4.3). The time in the figure was measured during actual building with slow feed rate. The melt pool is heated up by continuous laser beam during the process as shown in Figure 4.4 (time 0 second). On one hand, a cold steel substrate cools down the molten metal droplets quickly and transfers the heat to the platform. This is the first temperature gradient from top to bottom along Z axis in the process. On the other hand, the argon flows in the glove box and the radiation from high temperature sample keep the peripheral surface at lower temperature and solidifies earlier than the central parts, which are exposed under the laser beam. Due to the relatively high cooling rates at the surface, fine columnar grains and Ti_2Ni are found. This is the secondary temperature gradient, which occurs from the surface to the centre in the XY plane, in the process. Also, the solidified surface gives larger cooling rate to the liquid metal when a new droplet flows on it, which brings small columnar grains in ring 2 in XY plane. The internal region, however, is being heated up by the laser beam until the droplet forms and blocks the laser power (shown as the sample at 20 s in Figure 4.4), a part of laser power is heating up the droplet and the deposited sample starts cooling down. Nonetheless, the radiation and convective heat transfer from the droplet limit the cooling rate in this region. These two

temperature gradients and low cooling rate give the 1 to 2 mm columnar grains microstructure in the centre.

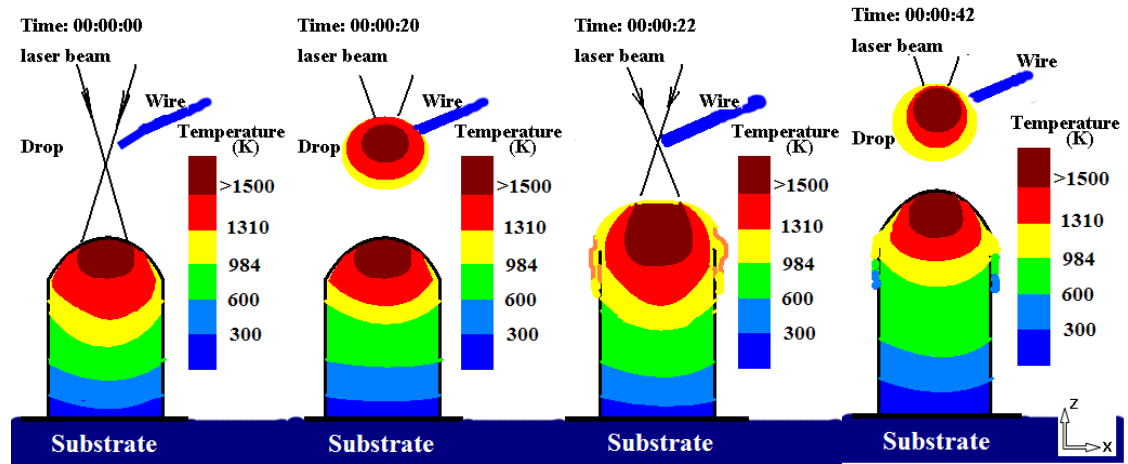


Figure 4.4. A schematic drawing of SDA process. The temperature range in the figure is not measured temperature but estimated to introduce the concept. The time is measured during actual building with slow feed rate.

Ring 3, however, is referred to as the remelted patterns in the XZ plane which may result from the remelting/re-heating effect or segregation. According to the Ti-Ni phase diagram (Figure 4.5), Ti_2Ni precipitates below 1237 K while TiNi solidifies at 1583 K [1], which means without remelting the Ti_2Ni only forms at the edge of dendrites. This was proven by observing the top area of the sample, where the TiNi dendrites are surrounded by precipitates, in Figure 4.3 (d). The new droplet, which is above the melting point, not only remelts but also heats up a part of sample after it drops as shown in Figure 4.4 (sample at 22 s has a larger high temperature area than sample at 20 second, which is before the droplet falls in). Once the temperature is above 1273 K, the

Ti₂Ni melts and changes to round shape because of surface tension. The SEM images of both the XY-plane in Figure 4.3 (b) and the XZ-plane in Figure 4.3 (c) show discontinuous Ti₂Ni in the remelted regions. On the other hand, the remelted pattern may result from segregation in the droplet. Since the boundary of Ti₂Ni and the Ti-rich side of TiNi phase in the phase diagram are quite vertical, the Ti₂Ni fraction should not be sensitive to the cooling rate, the formation of this remelted pattern should be caused by a compositional variation in droplet, which will be discussed later. In other words, the special ringed microstructure results from the unique process, whereby when cutting the sample along XY plane, the rings from outside to inside are ring 1 which forms from rapid cooling at surface, followed by ring 2 which forms because of the droplet flow on the cold surface, and ring 3 which shows the remelted zone in centre (shown in Figure 4.3 (a) with arrows).

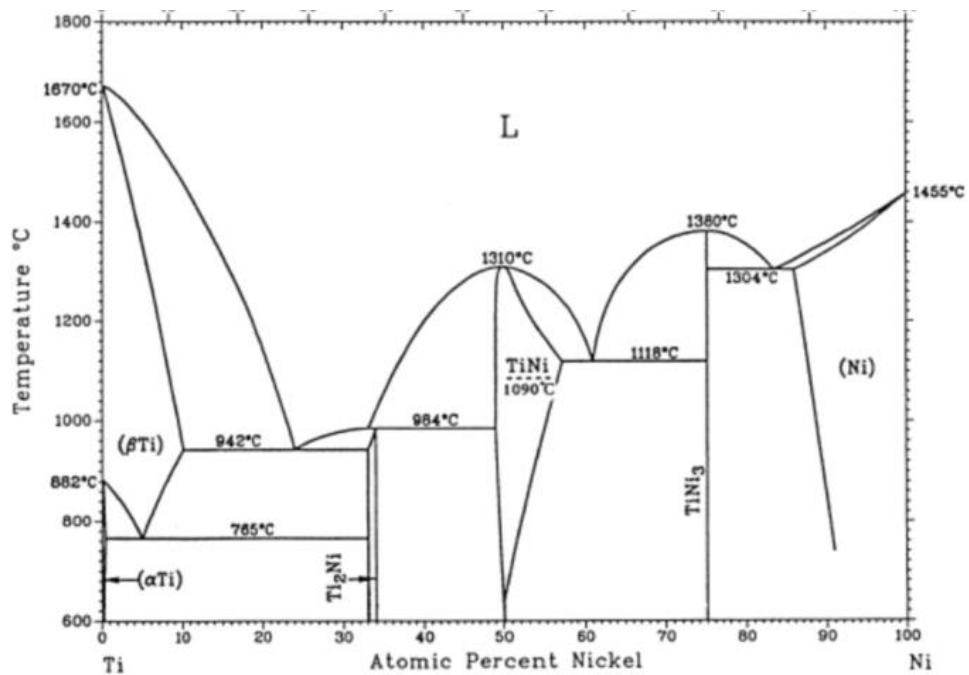


Figure 4.5 Ti-Ni phase diagram [1]

Comparing the microstructure of the $\text{Ti}_{52}\text{Ni}_{48}$ sample in Figure 4.3 with vacuum arc melted and induction melted Ti-Ni sample [86], the microstructure appears to be similar, which suggests that the cooling rates are similar between these two processes. The grain size of the SDA sample is generally finer, but heterogeneous in size distribution compared to the arc melting samples. Since neither eutectic morphology nor Ti_2NiO_x are found in SDA samples, the homogeneity, as well as oxygen pick-up, are better in the SDA process. SDA also builds a sample at a much faster speed than vacuum arc melting and induction melting.

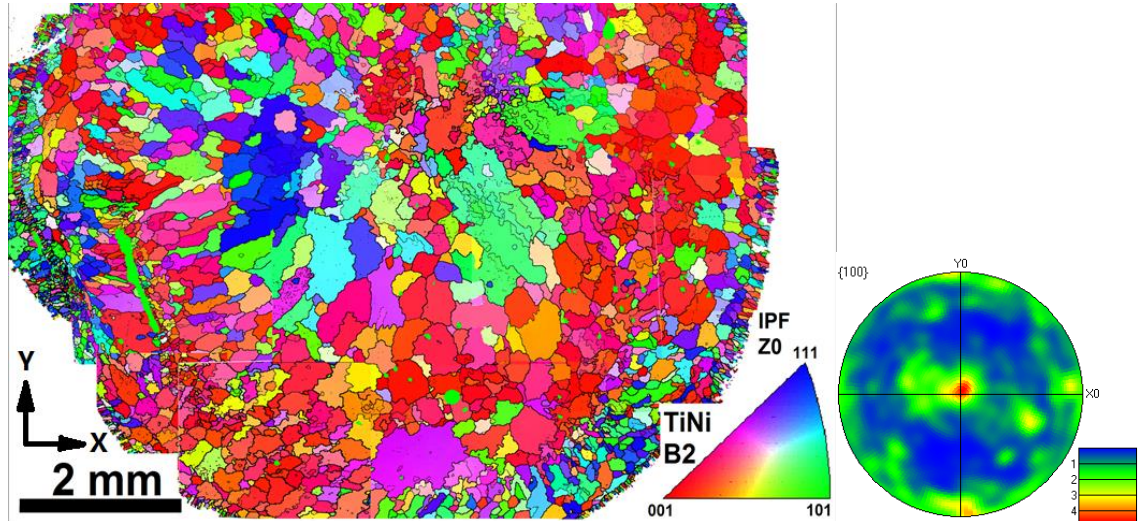


Figure 4.6. The EBSD map of the XY section of Ti₄₈Ni₅₂ sample (a) and {100} pole figure of the whole sample (b) shows strong texture in the {100} direction in XY section.

In order to assess the texture of the builds, a Ti₄₈Ni₅₂ sample (with the B2 (TiNi) phase at room temperature) was used for EBSD mapping at the XY-plane and is shown in Figure 4.6 (a). The presence of fine grains towards the edge of the sample is clear. The grain size increases, towards the centre. Additionally, a pole figure was constructed for the entire sample in Figure 4.6 (b), which showed that the texture of the build is relatively strong {100} direction, which is the growing orientation of B2 phase [2]. The grains with the {100} texture is shown in the microstructure in Figure 4.3 (a) as the vertical columnar grains in the central area. The texture and the microstructure above indicate that the grains in the centre are vertical columnar grains and the small grains are the cross-section of the ends of the inclined large columnar grains.

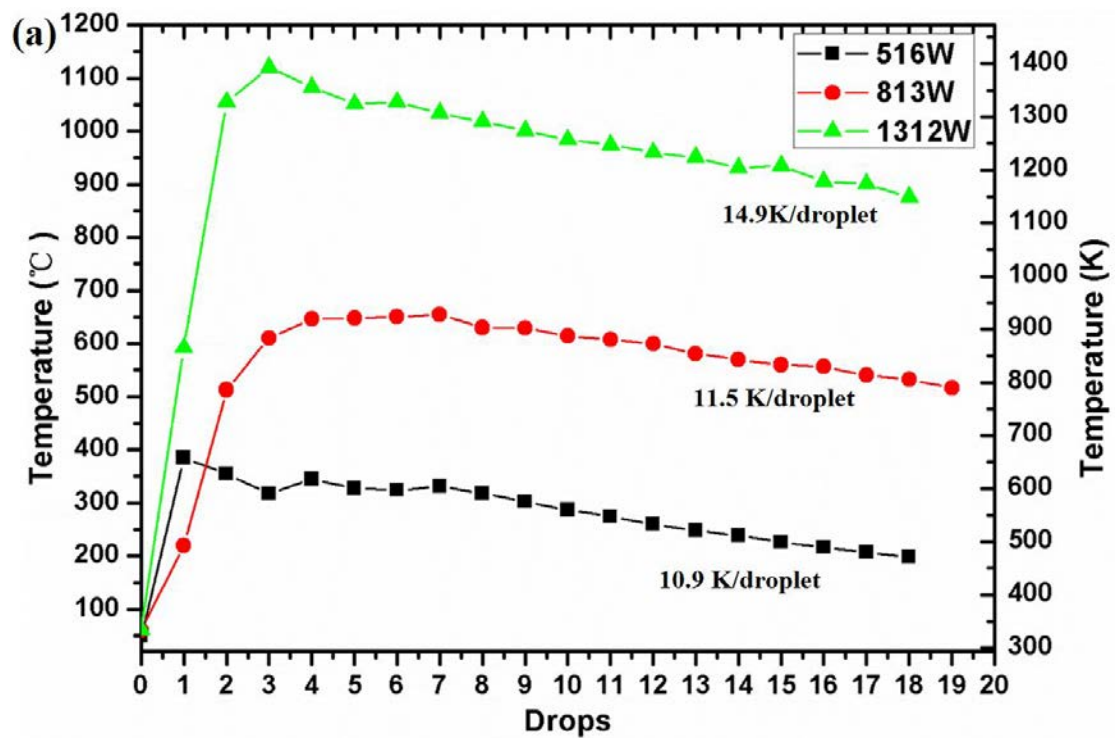
4.3 Temperature measurement and temperature field calculation

In order to investigate the temperature variation of the sample during building, a thermocouple was attached at the bottom of the substrate during deposition. A 0.5 mm width by 0.5 mm depth slot was cut at the bottom of steel substrate and a 0.5 mm diameter thermocouple was attached in the middle of the slot to measure the substrate temperature. As shown in Figure 4.7 (a), different building laser powers, 516 W, 813 and 1312 W were applied. The feeding rate for each experiment were fixed and the time between each droplet falling down took 20 s equally. The temperature was recorded as soon as each droplet landed on the substrate during deposition and the temperature for cooling was recorded every 5 s.

4.3.1 Temperature measurement and temperature calculation during deposition

The 516 W deposition laser power heated up the substrate immediately and the substrate temperature reached peak value (i.e. 658 K) before the first droplets fell in. For the other deposition powers, however, the substrate temperature increased during the beginning of the deposition and reached peak value (i.e. 928 K at the 7th droplet for the 813 W sample and 1393 K at the third droplet for the 1312 W sample). The substrate temperature of the 516 W deposition varied slightly before the 7th droplet, and then gradually decreased with a stable cooling rate to 472 K within 18 droplets deposition (10.9 K/droplet or 0.73 K/s). During the 813 W deposition, the substrate temperature rapidly increased before the third droplet landed and then slowly increased until the 7th

droplet deposited. The cooling rate after the 7th droplet was almost the same as the 516 W deposition (dropped from 928 K to 790 K, 11.5 K/droplet or 0.77 K/s). However, the substrate temperature for 1312 W deposition reached a peak temperature after the third droplet and then dropped from 1393 K to 1324 K within two droplets (34.5 K/droplet or 2.3 K/s) and then slightly increased to 1328 K before slowly cool down to 1149 K at the 18th droplet (cooling rate 14.9 K/droplet or 1 K/s).



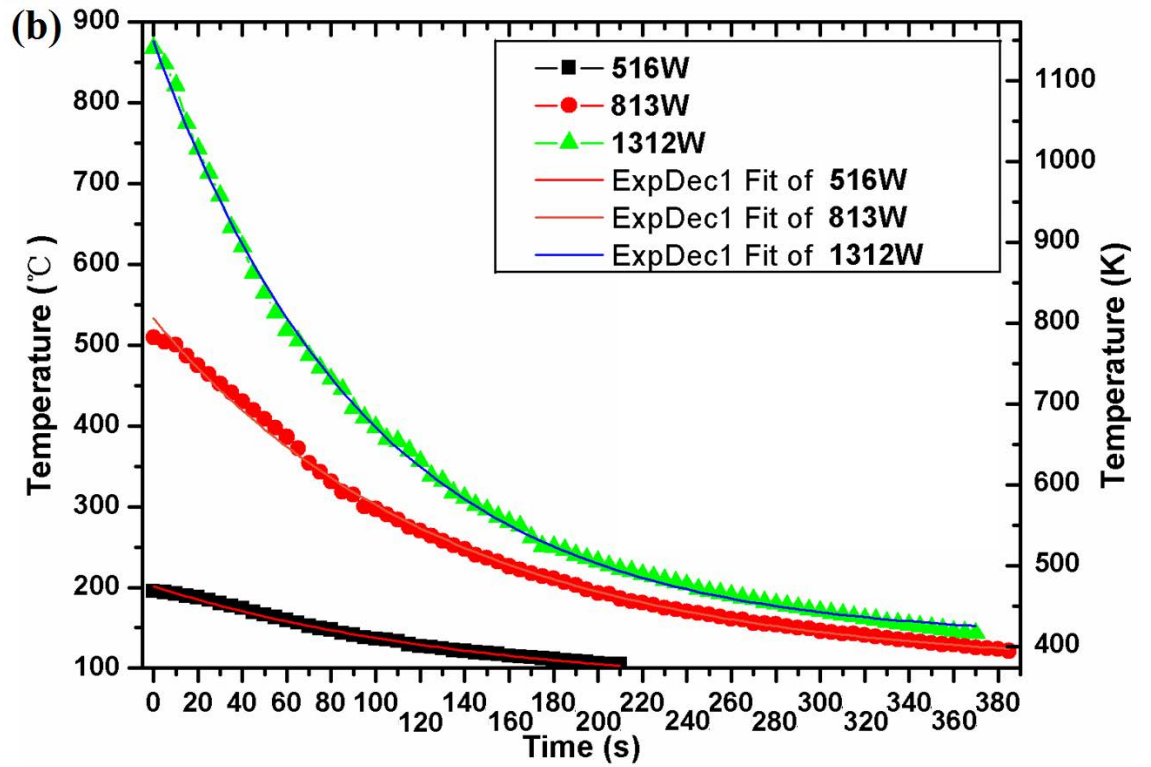


Figure 4.7. Substrate temperature variation in SDA process according drops during heating (a) and time during cooling (b). The black line with square spots is the substrate temperature of 516W deposition, the red line with round spots is for 813W deposition and the green line with triangle spots is for 1312W.

As shown above, the temperature variation during deposition is much smaller than cooling, which means the temperature gradient in the sample is stable during deposition. This is due to the laser beam providing a stable heat input to the top of the sample. Since the temperature of the top part of the sample is stable, the deposition process can be considered as the temperature field from top to bottom. This effectively stays stable while the droplets with temperature equal to substrate temperature are being added to the bottom of the sample. Accordingly, the cooling rate of the material becomes the same as the cooling rate of the substrate during deposition.

In the SDA samples, though the radiation also contributed to the heat transfer, the calculation here just considered the heat transfer in column shape sample via solid metal (substrate at the bottom), so the only transfer direction was from top to bottom in this calculation. Hence, the equation can be simplified to one dimensional heat transferring. From Fourier equation [138], the temperature field $u(x, y, z, t)$ in a solid body without heat source, we have:

$$\frac{\partial u}{\partial t} = \frac{k}{v\rho} \frac{\partial^2 u}{\partial z^2} \quad \text{Equation 4.3.1}$$

where, k is heat transfer coefficient in the materials, v is specific heat capacity of the materials and ρ is the density of materials.

Now we can consider the situation between the droplets falling during deposition, the sample can be considered as a one dimensional heat transfer problem with constant temperature at each end (melting point at the top and substrate temperature at the bottom). Hence, Equation 4.3.1 can be converted as:

$$C = \frac{k}{v\rho} \frac{d^2 u}{dz^2} \quad \text{Equation 4.3.2}$$

By integrating the Equation 4.3.2, the general solution becomes

$$u(z) = \frac{Cv\rho}{2k} z^2 - C'z + C'' \quad \text{Equation 4.3}$$

where C' and C'' are constants. The boundary conditions are as follow: the top position z_m is known as melting temperature U_m , and the substrate temperature is U_0 as measured using thermocouple. By putting the boundary conditions in, the constants can be determined and the temperature field in SDA sample during deposition can be calculated as

$$:u(z) = \frac{Cv\rho}{2k}z^2 - \left(\frac{Cv\rho z_m}{2k} + \frac{U_0 - U_m}{z_m}\right)z + U_0 \quad \text{Equation 4.3.3}$$

where C is the cooling rate of the system, since we consider the temperature of sample does not change until the next droplet drops in, $C = 0$ in this situation. So the temperature field in sample is linear to position z as below:

$$u(z) = U_0 + \frac{U_m - U_0}{z_m}z \quad \text{Equation 4.3.4}$$

As discussed above, the deposition process can be considered as adding droplets to the bottom and the temperature field above stays constant. By putting the temperature and position in Equation 4.3.2, the temperature decrease per each droplet was found to be 10.3 K/droplet in 516 W deposition, 11.4 K/droplet for the 813 W build. and 14.9 K/droplet for the 1312 W, respectively. These are consistent with the experimental results (linear substrate temperature). Although the specific heat and heat transfer coefficient of the materials change according to the temperature, the relationship between these parameters and temperature is unknown in Ti-Ni alloys, and the equation

here is consistent with the experimental result, which means it is good enough for an approximate calculation.

Also, it is worth mentioning that during the temperature measurement of the initial droplets, a variation in temperature was observed especially when high deposition power (813 W and 1312 W) was applied. The substrate temperature decreased and then increased after the droplet fell down, instead of continuously increasing or decreasing. The substrate temperature decreased up by 23 K after the last droplet was deposited and then further increased 6 K higher as the next droplet fell in. This consistent with the analysis in section 4.2 that the laser power was blocked by the droplet when the new droplet formed and was still suspended on the wires. Although this temperature variation cannot be observed directly by measuring the substrate temperature, and the temperature variation between two droplets was not recorded precisely due to lack of automatically recording system, it is reasonable to believe that this phenomenon happens during the whole deposition process based on presented data.

4.3.2 Temperature measurement and temperature calculation during deposition

Figure 4.7 (b) shows the substrate temperature during cooling (immediately after the laser beam was turned off). The sample with 516 W deposition power cooled down from 472 K to 378 K in 210 s, whereas the 813 W deposition cooled down from 790 K to 394 K in 385 s, and the 1312 W deposition dropped from 1149 K to 416 K in 370 s. However, the cooling rate of the substrate fitted well to an exponential function instead

of a linear function after turning the laser beam off, as shown in Figure 4.7 (b). The function for the cooling rate of substrates was generated by exponential fitting according the data, whereby:

$$u_0 = 129.6e^{-\frac{t}{147.6}} + 71.7 \quad (\text{for } 516 \text{ W})$$

$$u_0 = 431.6e^{-\frac{t}{180.6}} + 101.4 \quad (\text{for } 813 \text{ W})$$

$$u_0 = 740e^{-\frac{t}{96.2}} + 136.6 \quad (\text{for } 1312 \text{ W})$$

According Green's formula, the variables in Equation 4.3.1 can be separated by introducing two formula $Z(z)$ and $T(t)$, where $Z(z)T(t)=u(z, t)$. Hence, the equation above can be converted as below:

$$ZT' = \frac{k}{v\rho} TZ'' \quad \text{Equation 4.3.5}$$

By introducing a constant λ ($\lambda \neq 0$), it can be rearranged as below:

$$\frac{T'}{\frac{k}{v\rho}T} = \frac{Z''}{Z} = \lambda^2 \quad \text{Equation 4.3.6}$$

Or

$$\frac{T'}{\frac{k}{v\rho}T} = \frac{Z''}{Z} = -\lambda^2 \quad \text{Equation 4.3.7}$$

The general solution of Equation 4.3.1 (λ^2) is

$$u(z,t) = (C_1 \frac{e^{\lambda z \sqrt{\frac{k}{v\rho}} + \frac{t}{c}} - e^{-\lambda z \sqrt{\frac{k}{v\rho}}}}{2} + C_2 \frac{e^{\lambda z \sqrt{\frac{k}{v\rho}} - \frac{t}{c}} - e^{-\lambda z \sqrt{\frac{k}{v\rho}}}}{2}) e^{-\lambda^2 t} \quad \text{Equation 4.3.8}$$

For $(-\lambda^2)$ is

$$u(z,t) = (C_4 \cos \lambda z \sqrt{\frac{k}{v\rho}} + C_5 \sin \lambda z \sqrt{\frac{k}{v\rho}}) e^{-\lambda^2 t} \quad \text{Equation 4.3.9}$$

where $C_1, C_2, C_3, C_4, C_5, C_6$ and λ are constants which can be determined by boundary condition (measured data). In the SDA process, the substrate (i.e. $z=0$) temperature is $u(0, t)$, which can be measured by a thermocouple. From the experimental result, the substrate temperature is exponential function against time t during cooling. Hence, the substrate temperature of sample is

$$u(0,t) = a e^{-\frac{t}{c}} + b \quad \text{Equation 4.3.10}$$

If the substrate temperature is U_0 at the beginning ($t=t_0=0$), the temperature at the bottom of the melting pool ($z=z_m$) is the melting point of the material:

$$u(z_m, t_0) = U_m = 1310^\circ\text{C} (1683\text{K}) \quad \text{Equation 4.3.11}$$

The Equation 4.3.10 and Equation 4.3.11 are the boundary condition of Equation 4.3.1.

It is worth to mention that the cooling condition of sample change from conduction heat transfer mainly to both conduction and convection heat transfer as the temperature

decreases to about 400 K. Meanwhile, the temperature at the surface of platform, where the substrate placed on, increases to about 370 K during deposition. As shown in Equation 4.3.9, as t increases the temperature $u(z, t)$ tend to decrease to zero, which is not possible in the experiment. Hence constant (C_3 and C_6) have been added behind to set the limit for the equations. By subjecting the boundary condition to the general solution, the constants can be determined. For Equation 4.3.8 (λ^2):

$$ae^{-\frac{t}{c}} + b = C_1 e^{\lambda^2 t} + C_3, \text{ then}$$

$$C_1 = a, C_3 = b \quad \text{Equation 4.3.12}$$

when $t=1$,

$$\lambda = \sqrt{-\frac{1}{c}} \quad \text{Equation 4.3.13}$$

Obviously, during cooling $a>0$, $b>0$ and $c>0$. So $-\frac{1}{c} < 0$, $\sqrt{-\frac{1}{c}}$ can't be the solution.

Thus, it is the second situation ($\frac{\partial u}{\partial t} = \frac{k}{v\rho} \frac{\partial^2 u}{\partial z^2} = -\lambda^2$).

By rearranging the Equation 4.3.9 and adding a constant C_6 , the equation can be simplified as:

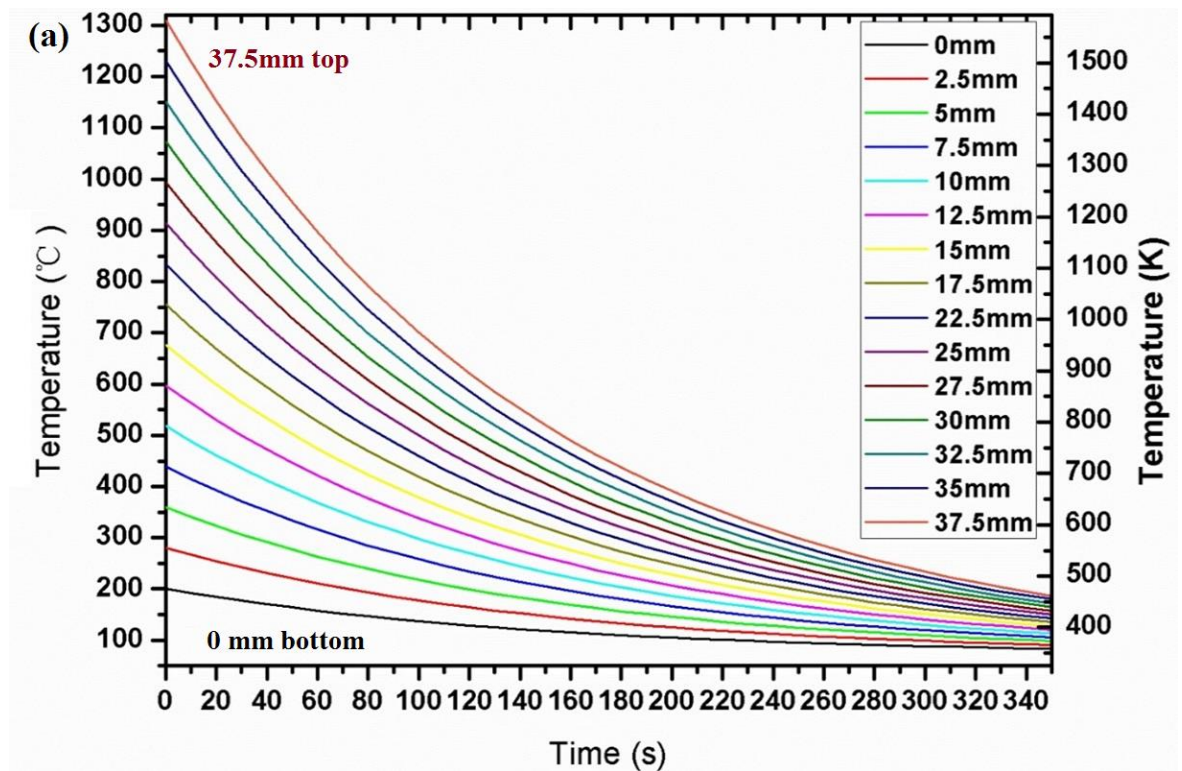
$$u(z,t) = (C_4 \cos \lambda z \sqrt{\frac{k}{v\rho}} + C_5 \sin \lambda z \sqrt{\frac{k}{v\rho}}) e^{-\lambda^2 t} + C_6 \quad \text{Equation 4.3.14}$$

By solving the equations above, the solution of heat transfer in SDA process is

$$u(z,t) = \left(a \cos \lambda z \sqrt{\frac{k}{v\rho}} + \frac{U_m - b - a \cos \lambda z_m \sqrt{\frac{k}{v\rho}}}{\sin \lambda z_m \sqrt{\frac{k}{v\rho}}} \sin \lambda z \sqrt{\frac{k}{v\rho}} \right) e^{-\lambda^2 t} + b \quad \text{Equation 4.3.15}$$

where $\lambda = \sqrt{\frac{1}{c}}$, a , b and c are the constants in the substrate temperature function, z_m is the distance from the substrate to the bottom of the melt pool at the beginning (i.e. the end of deposition) and U_m is the melting point of the materials. The z_m is determined by the microstructure of the op area of the sample (the position of the last re-melted pattern). The thermal properties of the Ti-Ni alloys are material density $\rho = 6.45 \times 10^3$ kg/m³, specific heat $v = 465.2$ J/(kg °C), conduction heat transfer coefficient for austenite $k = 28$ W/m°C [139]. By putting these parameters in the Equation 4.3.15, the calculated temperature against time are shown in Figure 4.8. As shown in Figure 4.8, the height of the sample decreases as the deposition power increases. The temperature gradient ($\Delta T / \Delta z$) in the 516 W sample and 813 W sample is similar, while the temperature gradient in 1312W sample is lower. The highest cooling rate area is the top of the samples and the cooling rate decreases as the laser power increases. The highest cooling rate in these samples is 5 K/s at the beginning of the cooling process, and then the cooling rate gradually decreases. The cooling rate of the sample below the last

droplet (top area) is about 1 K/s during deposition as discussed above and shown in Figure 4.7 (a), and then cools down exponentially as shown in Figure 4.8. Hence the cooling rate of SDA process is slow compared to the other laser fabrication processes, and similar to the cooling rate in casting, which is consistent with the large grain size in the sample. Considering the phase diagram and TTT diagram of Ti-Ni, chemical segregation within the dendrites is expected in SDA samples and $\text{Ti}_{11}\text{Ni}_{14}$ phase is expected to form in Ni-rich TiNi SDA samples. Thus, a post-SDA homogenisation heat treatment is necessary to reduce the chemical inhomogeneity in the builds.



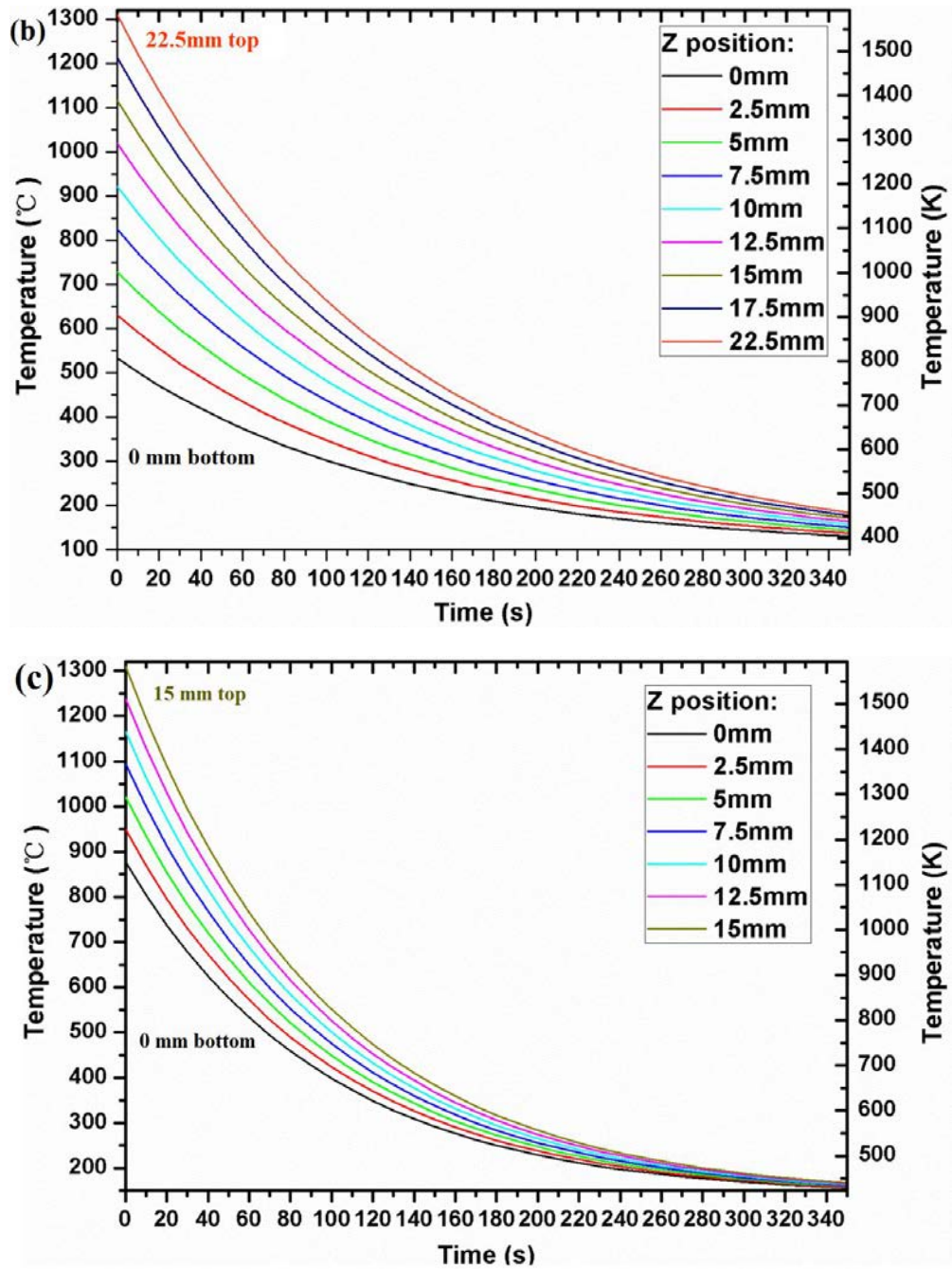


Figure 4.8. Temperature field in the SDA samples during cooling against time with (a) 516 W deposition power, (b) 813 W deposition power and (c) 1312 W deposition power. Temperature field in the sample is linear but the cooling rate is exponential. The fastest cooling rate of these sample is about 5 K/s (300 K/min) at the top of 516 W deposited sample.

4.4 Chemical composition

Since the shape memory properties are sensitive to the chemical composition, especially the oxygen content which is known to reduce the TTs and shape memory performance [28], the oxygen content of the SDA sample was measured by XRF method. The oxygen content in Ti50Ni sample was 0.06 wt.%. The oxygen content in Ti wires is 1200 ppm and in Ni wires is 10 ppm (as provided by the wire supplier). So, the total oxygen content in the wires is $0.12 \times 0.44 \text{ wt.}\% + 0.001 \times 0.56 \text{ wt.}\% = 0.05336 \text{ wt.}\%$. Accordingly, the oxygen pick-up during SDA process in the building chamber is 0.00664 wt.%. As calculated from Equation 1.1, the influence of oxygen pick-up in SDA process on M_s is within the order of -1 K, and the total influence of oxygen content in SDA process is 5.5 K, which is a reasonable range for alloy development. Following a homogenisation treatment for 3 hours at 1273 K heat treatment, the oxygen content in the sample reaches 0.174 wt.%. Again, according to Equation 1.1, the decrease in M_s of the heat treated sample is 16 K.

To assess the chemical homogeneity of the samples, EDS area mapping was used to create a compositional variation contour in the XY-plane of Ti₅₀Ni₅₀ and Ti₅₀Ni₂₅Cu₂₅ samples, using 1 mm × 1 mm area maps, and the XZ-plane of Ti₅₂Ni₄₈ sample, using 0.6 mm × 0.6 mm maps. It was found that the Ti-content varied from 49.0 at.% to 50.7 at.% ($\pm 0.5 \text{ at.}\%$) across the coupon of Ti₅₀Ni₅₀ sample in Figure 4.9 (a), with the edge showing a higher Ti-content at a limited area towards the periphery of the build

(previously referred to as ring 1 and region A). Comparing with the outer area, the central region showed a limited high Ti-content (50.3 at.%). The average Ti-composition for the whole section, however, was 49.9 at.%, which is only 0.1at. % lower than the target content. The Ti-content contour of half of the XZ section in Figure 4.9 (c) indicates the Ti-composition is close to target (52 at.%) and homogeneous in the central part of the build (varied from 51.4 at.% to 53.8 at.%). However, some evidence of remelt pattern with lower Ti-content (light blue regions) at about 0.8 mm distance (the same as Figure 4.3 (c)) can be found in Figure 4.9 (c). Since the melting point of Ti is 1941 K (1668°C), which is 213K higher than the melting point of Ni, this segregation may be induced in the molten droplet as shown in Figure 4.10. The Ti wire is melted slower than the Ni wire. Thus, it stays solid and connects to the unmelted wire in the droplet. This means that the Ti wire stays relatively concentrated at the upper part of droplet rather than distributes homogeneously in the droplet. Unlike gravity segregation in arc melting or induction melting, this small-scale segregation (0.8 mm in size, about 1 at.% in intensity) between layers could be eliminated by a heat treatment.

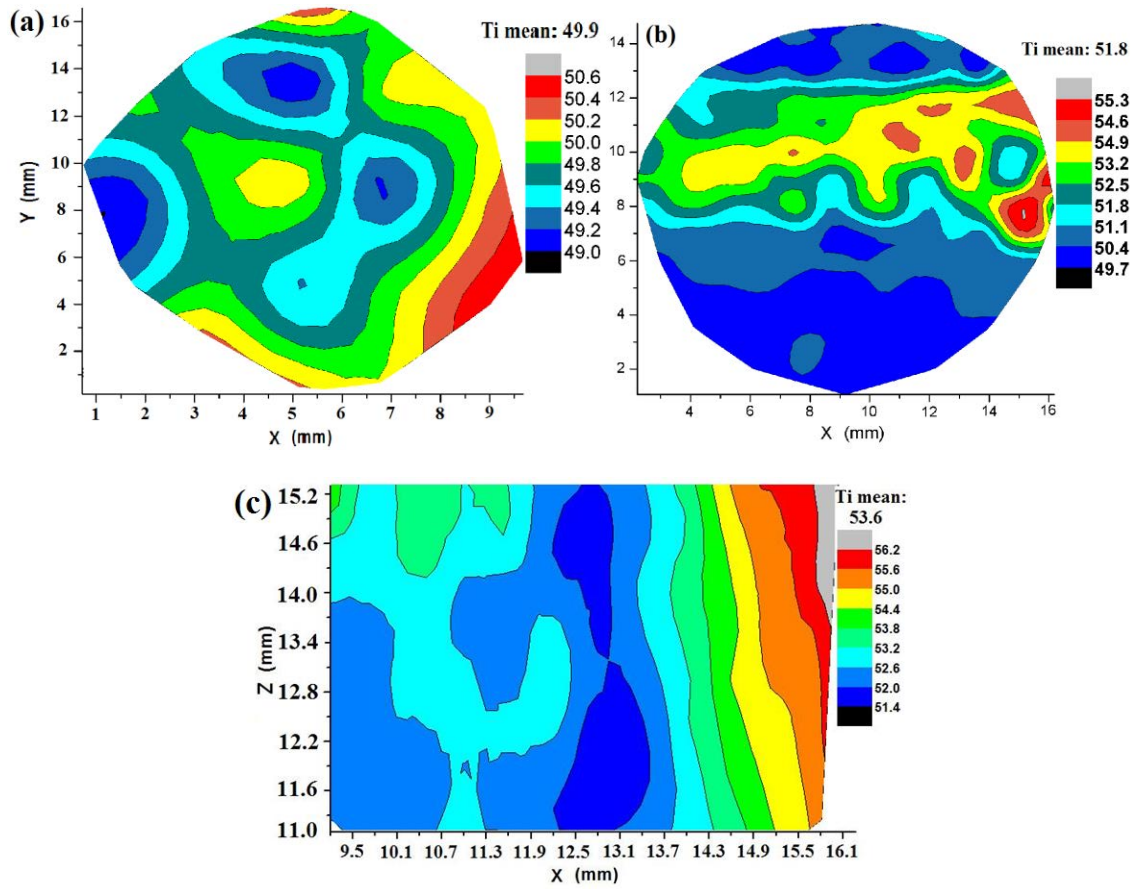


Figure 4.9. Ti-content contour for the XY section of $\text{Ti}_{50}\text{Ni}_{50}$ sample (a) shows the ring structure and the total composition is close to target, the contour for XY section of $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ sample (b) shows the composition variation in ternary sample, and (c) shows XZ section of TiNi_{48} sample with the remelt pattern in the centre.

In the ternary system, the variation in Ti-content was relatively larger (49.7 at.% to 55.5 at.%). Nonetheless, typically the variation does not exceed ± 2 at.% from the target content, except for local variations towards the edge of the samples. It is expected that a post-deposition homogenisation treatment may be required for some of these conditions to eliminate any chemical inhomogeneity in the samples [22].

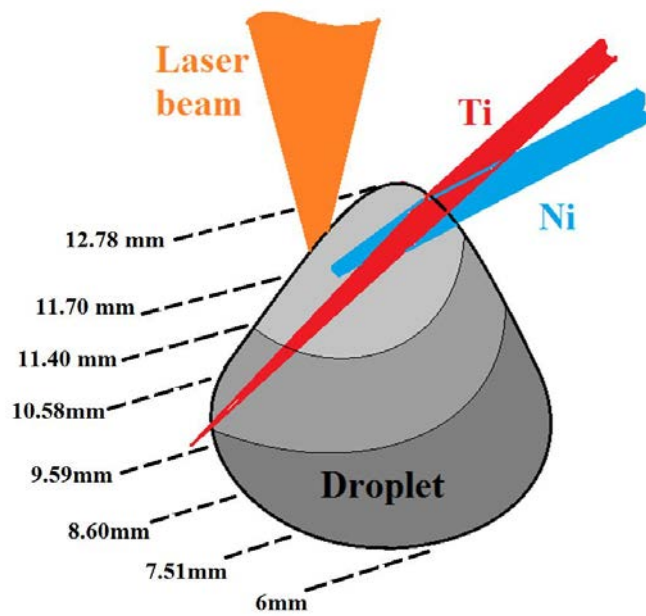
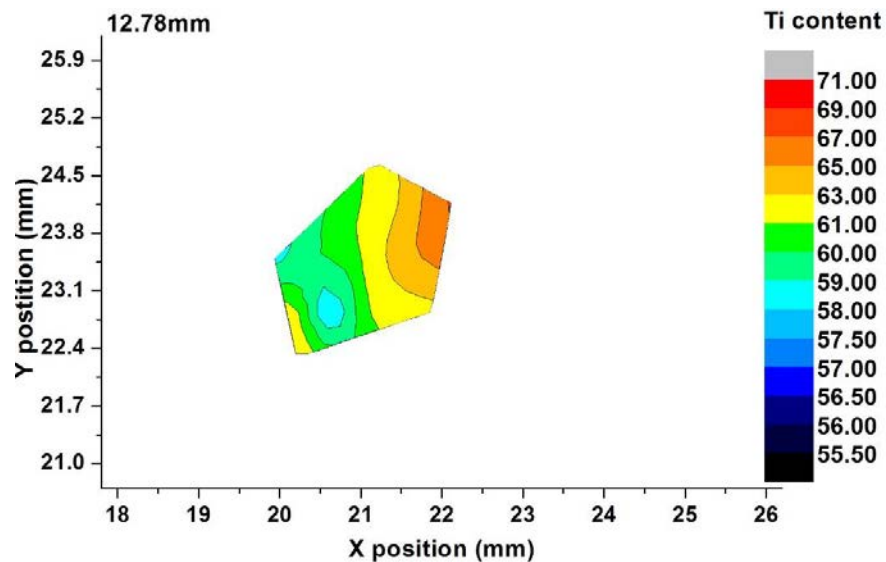
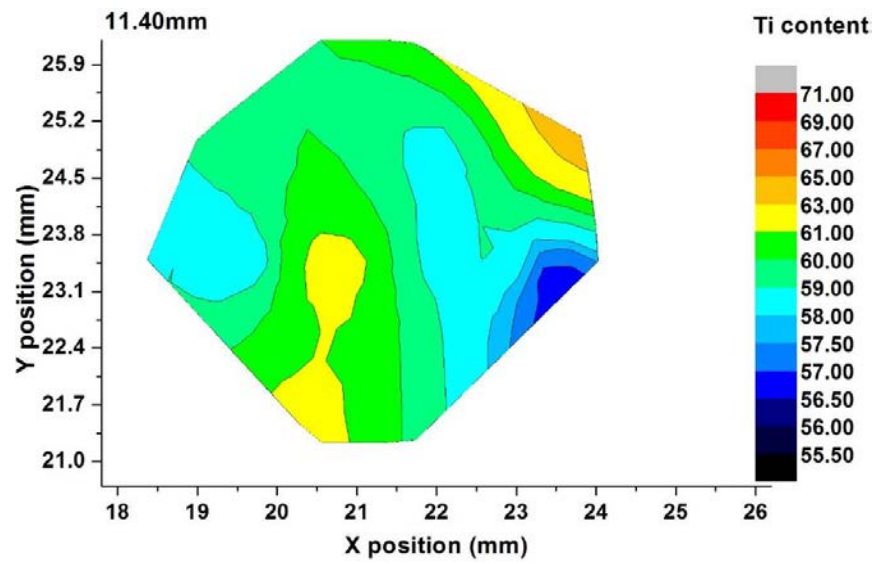
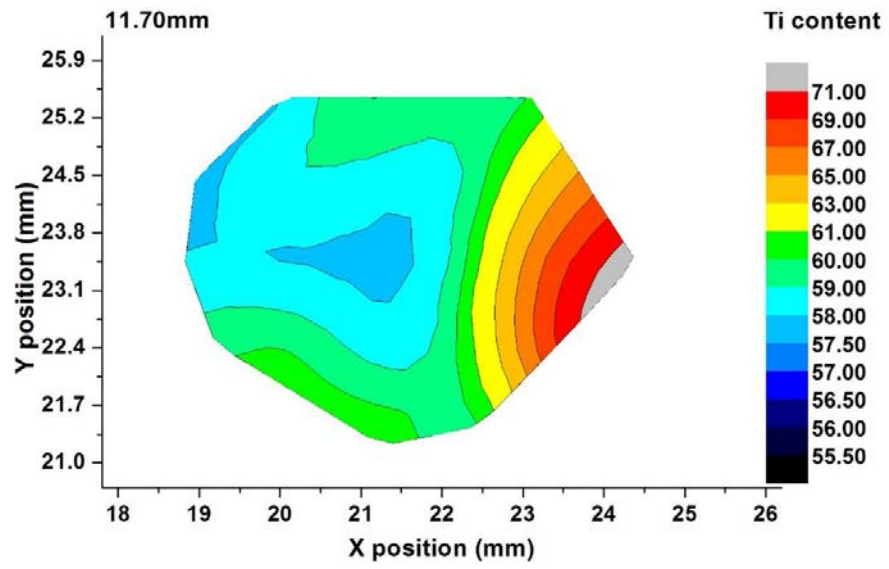


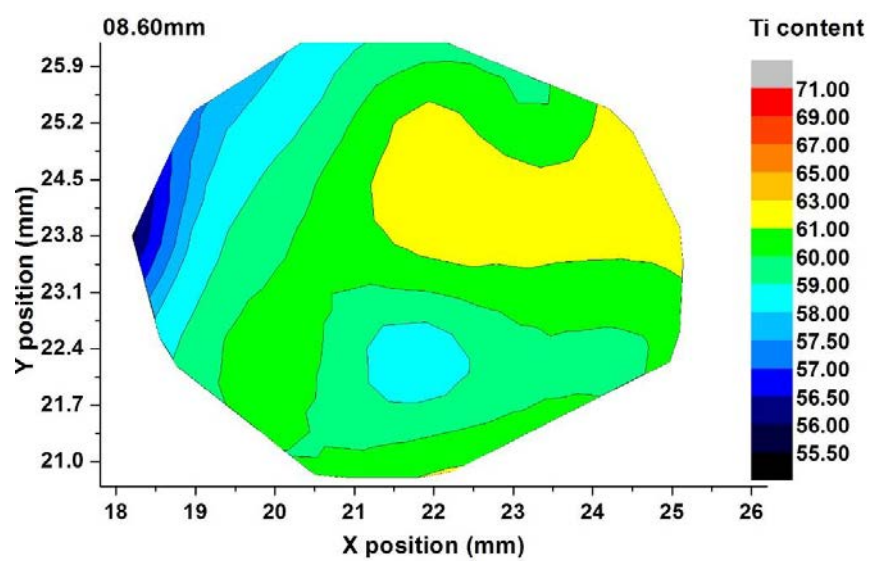
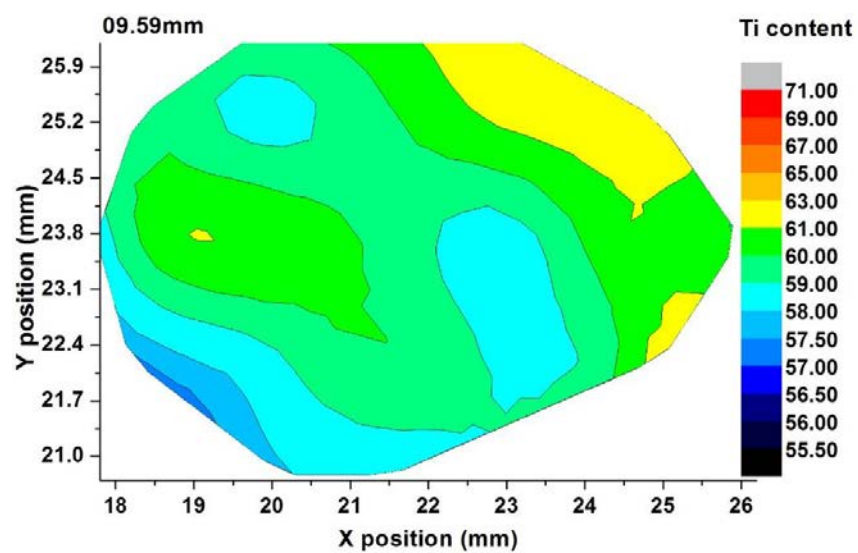
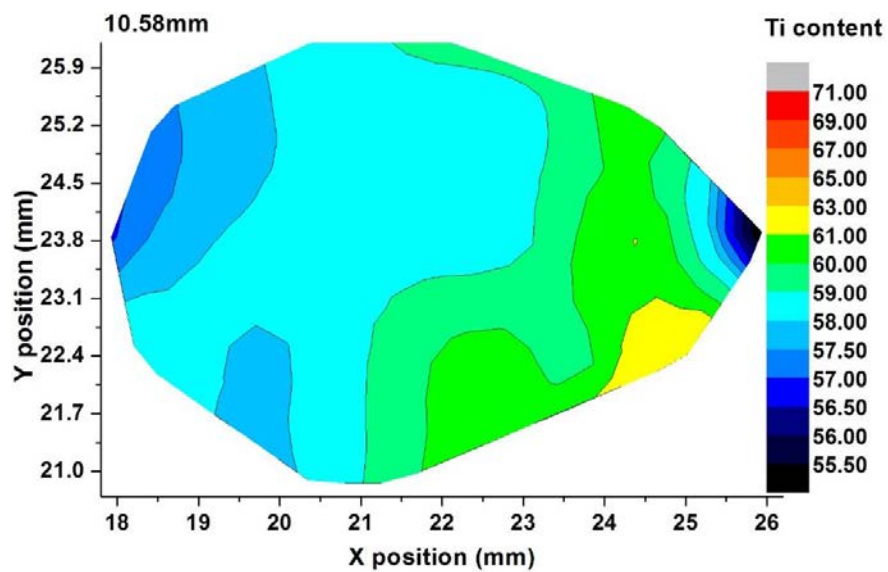
Figure 4.10. A schematic illustration for the interaction of the wires and the droplet during melting in SDA process. The Ti wire melts slower than the Ni wire due to the higher melting point of Ti. In some extreme situations, the high melting point wire may penetrate the droplet during melting.

As shown in Figure 4.11, in order to investigate the chemical composition in the droplet, a droplet with target composition $\text{Ti}_{60}\text{Ni}_{40}$ was made and sectioned for EDS analysis. The laser beam was stopped about 1 s before the droplet fell down (the dropping time of each droplet was measured and showed 32 s consistently) and cut from the wires for analysing. The sample was mounted, with the Ti-wire part facing upwards and the Ni-wire facing downwards, ground and polished down about 1 mm every time for EDS mapping. The EDS mapping was performed using area analysis in a $0.5 \text{ mm} \times 0.5 \text{ mm}$ area and the translational distance between each area is 0.5 mm.

It was found that the Ti-rich area (higher than 60 at. %) is more concentrated than the Ti-poor area. Meanwhile, Ni was mainly concentrated at the left hand side of the droplet (which is the bottom of the droplet during alloying). This is because the Ni has a higher density and lower melting point than the Ti, so the Ti-wire was actually being melted while diffusing into Ni during alloying. As such, the top of the droplet has a higher Ti-content, which also affects the chemical distribution within the sample (i.e. the remelting zone). However, the vibration caused by the droplet dropping into the melt pool helps in mixing the alloying elements, with the top part being exposed to laser beam before the next droplet lands, keeps this part molten and at a high temperature. These factors reduce the heterogeneity of the sample to about 1 at. % within the central area, which can then be used for the characterisation work.







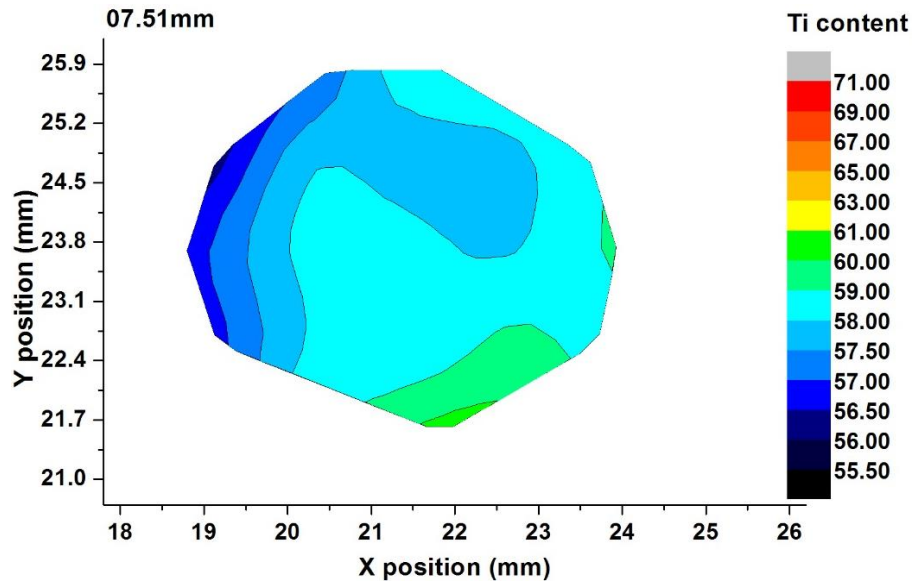


Figure 4.11. EDS mapping of TiNi40 droplet in different sections, showing the chemical composition distribution within the droplet. The Ti content varied from 55 at. % to 71 at.% in the droplet. The position of section is labelled at the top left corner of image as Z position, the sample started from 6 mm to 14 mm in Z axis (section position can be found in Figure 4.10).

4.5 Gradient composition samples

Since the composition of SDA built sample can be adjusted easily by changing the feed rate during building, samples with a compositional gradient, and with a good chemical homogeneity, can be made by SDA. To investigate this process, two compositional gradient samples were produced in the $\text{Ti}_{52-x}\text{Ni}_{48}\text{Hf}_x$ and $\text{Ti}_{52}\text{Ni}_{48-x}\text{Cu}_x$ alloy systems. As shown in Figure 4.12 the composition in the gradient sample varied every 5 mm in the $\text{Ti}_{52-x}\text{Ni}_{48}\text{Hf}_x$ sample. The $\text{Ti}_{52}\text{Ni}_{48-x}\text{Cu}_x$ sample was partially melted during the post-SDA heat treatment, as the melting point of the Cu-containing SMAs is lower than the heat treatment temperature. Therefore, the lower Cu-content part (from 0 to 20 at.%)

has compositional variation very 5 mm, whereas the higher Cu-content section (>20 at.%) melted during the heat treatment.

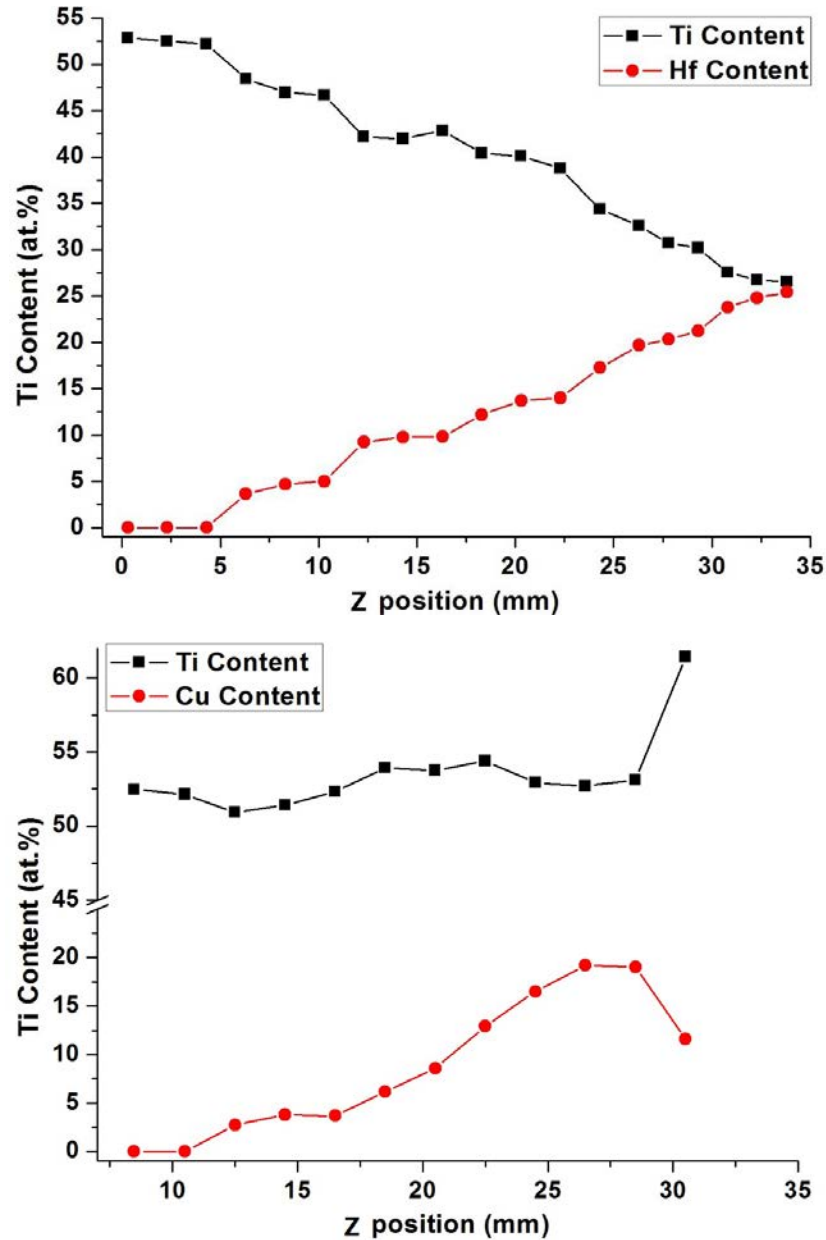


Figure 4.12 Chemical composition in the compositional gradient samples made by SDA process. The EDS results in the vertical section (a) showing the Hf-content varying from 0 at.% to 25 at.% within the $\text{Ti}_{52-x}\text{Ni}_{48}\text{Hf}_x$ sample and (b) showing the Cu-content varying from 0 at.% to 20 at.% within the $\text{Ti}_{52}\text{Ni}_{48-x}\text{Cu}_x$ sample.

4.6 Shape memory properties

Since the chemical composition is critical to the SME, especially in the Ti-Ni system [2, 19], DSC was applied to identify the TTs for SDA built $\text{Ti}_{50}\text{Ni}_{50}$ (actual test area is 51 at. % Ni), compared to $\text{Ti}_{52}\text{Ni}_{48}$ as-built sample, heat treated $\text{Ti}_{52}\text{Ni}_{48}$, and the reference (cast and rolled) sample. As shown in Figure 4.13, the TTs and the heat flow of the SDA alloy was found to match the TTs in the $\text{Ti}_{49}\text{Ni}_{51}$ samples produced by the arc melting method, with a A_s of $\sim 60^\circ\text{C}$ and M_f of $\sim 30^\circ\text{C}$ [19, 140]. The Ti-rich sample has a similar transformation behaviour in terms of TTs and peak width as the reference sample, but the total heat flow is smaller due to the higher Ti-content and Ti_2Ni fraction. The temperature hysteresis slightly reduces from 70°C to 60°C , and the A_f as well as M_s in Ti-rich sample become the same as the reference sample after the heat treatment. This is due to the different cooling rate within the samples during building, which induces segregation, leading to variation in the Ni-content. Additionally, the re-melting when a new alloyed droplet falls causes a rapid temperature variation and compositional change within the re-melt zone.

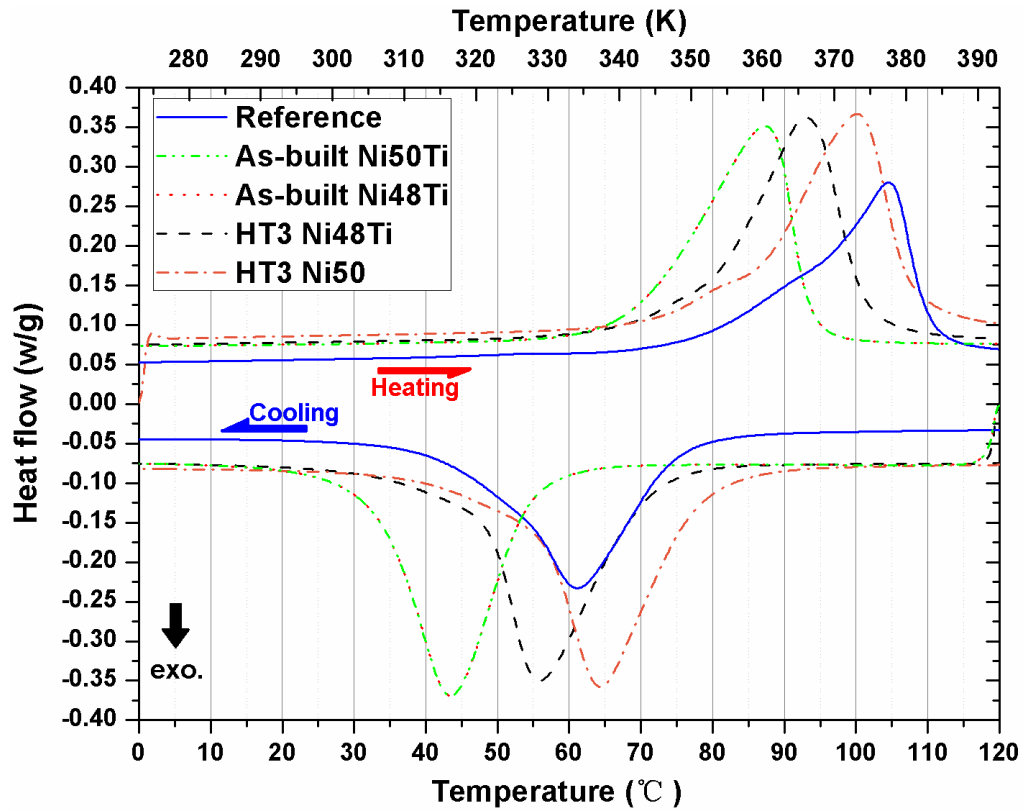


Figure 4.13. DSC trace for hot-rolled reference sample (blue solid), as-built $\text{Ti}_{50}\text{Ni}_{50}$ (green dash dot dot), $\text{Ti}_{52}\text{Ni}_{48}$ (orange dot) SDA samples and heat treated $\text{Ti}_{52}\text{Ni}_{48}$ (black dash), heat treated $\text{Ti}_{50}\text{Ni}_{50}$ (red dash dot).

In order to assess the properties of ternary alloys built by SDA process, a $\text{Ti}_{52}\text{Ni}_{38}\text{Cu}_{10}$ ternary alloy was also produced by SDA process, and compared with the reference hot rolled $\text{Ti}_{50.4}\text{Ni}_{39.6}\text{Cu}_{10}$ sample. The DSC curves of these samples, as shown in Figure 4.14, revealed that the transformation behaviour of SDA samples is the same as the reference. The higher transformation energy per weight in the reference sample is due to the lower Ti-content in this sample. The higher Ti-content means that a larger amount of $\text{Ti}(\text{Ni}, \text{Cu})_2$ precipitates has formed, which is the phase which does not undergo the

martensite transformation, therefore the high Ti-content sample shows lower transformation heat.

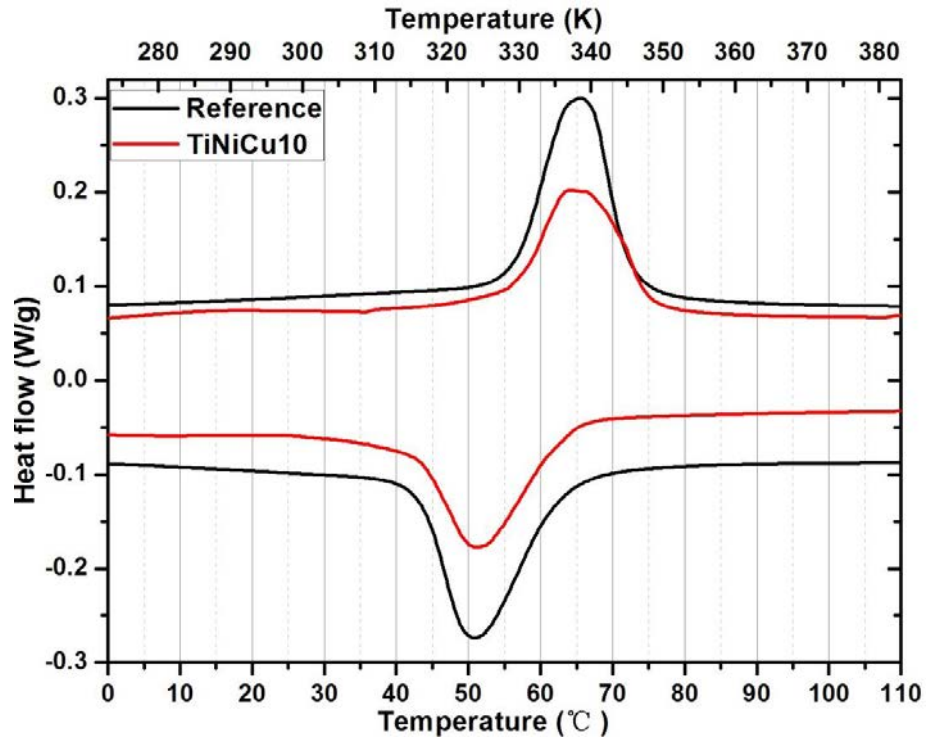


Figure 4.14. DSC trace for hot-rolled $\text{Ti}_{50.4}\text{Ni}_{39.6}\text{Cu}_{10}$ reference sample (black line) and SDA built $\text{Ti}_{52}\text{Ni}_{38}\text{Cu}_{10}$ sample shows the same transformation behavior.

4.7 Heat treatment

The chemical composition distribution of the heat-treated $\text{Ti}_{52}\text{Ni}_{48}$ sample is shown in Figure 4.15. It is clear that the central area has been homogenised by the heat treatment, and the remelting pattern has been reduced by the heat treatment. The Ti-content varies from 52.5 to 53.7 at. % in the centre area. This indicates that the segregation (re-melt zone) in SDA samples can be reduced by a simple one-step heat treatment. The Ti_2Ni percent in the heat-treated sample varies from 3 % to 9 % and the average percent

reduces to 5.4%. Since heat treatment is necessary for full scale samples in any process, especially for SMAs, this SDA samples have the advantage that they required less time as the chemical segregation from the process is lower than that observed in other processes.

The precipitates that occur around the dendrite boundary in the as-built samples convert to a discontinuous shape after the heat treatment. The discontinuous precipitates reduce the stress between the matrix and precipitates. Also, this can improve the mechanical performance of the SMA (e.g. fatigue properties).

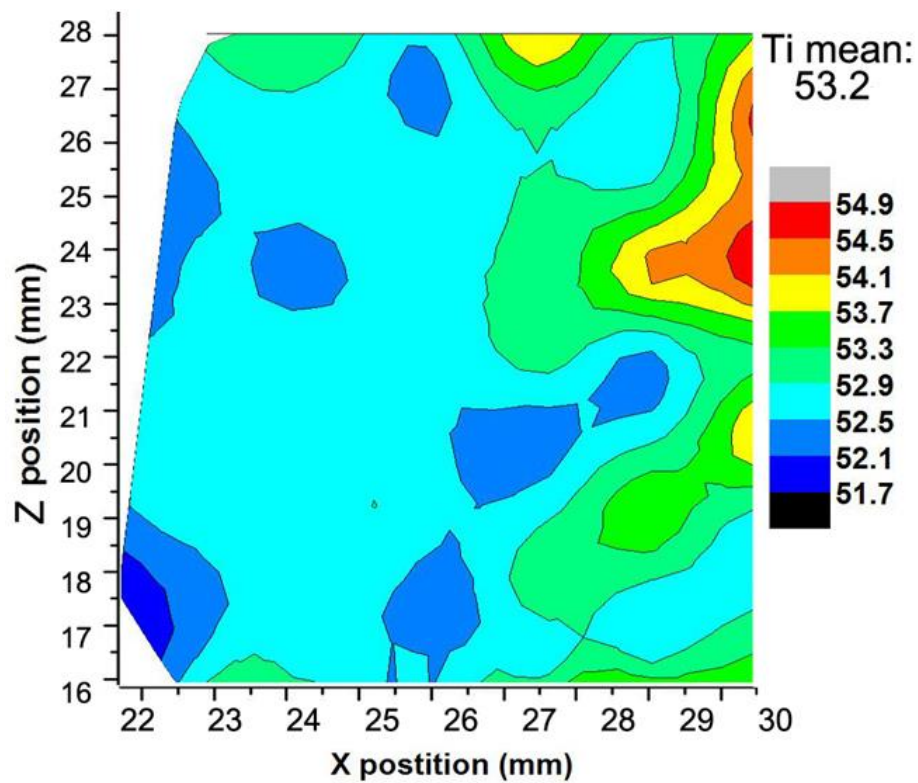


Figure 4.15. Composition contour of XZ section of heat treated $\text{Ti}_{52}\text{Ni}_{48}$ sample with homogeneous composition in the centre.

In order to investigate the influence of heat treatment on SME and homogeneity, a $\text{Ti}_{50.4}\text{Ni}_{49.6}$ (marked as $\text{Ti}_{50}\text{Ni}_{50}$ in the Figure 4.16) sample with 70 mm length was built and cut into 6 sections for heat treatment. The samples were wrapped by Ta wires, sealed in steel tube, evacuated 10^{-5} MPa and be put into muffle furnace at 1273 K for 3 hours, 6 hours, 24 hours, 48 hours and 100 hours, respectively. One of the sections was taken in the as-built condition for comparison, while the other samples were heat treated for the different times. Following the heat treatment, all the samples were water quenched, EDM cut a 5 mm in diameter, 1 mm thick disk from the centre part of the sample for DSC testing. The DSC curves are shown in the Figure 4.16. The as-built sample shows lower transformation temperature ($M_s = 327$ K, $A_f = 366$ K, hysteresis = 39 K) compared with the hot-rolled $\text{Ti}_{50.6}\text{Ni}$ reference sample ($M_s = 348$ K, $A_f = 384$ K, hysteresis = 36 K). This is because of the heterogeneity of the as-built samples (i.e. some parts of the sample have a higher Ni-content, which reduces the transformation temperature). Although the increasing oxygen content after heat treatment would decrease the transformation temperature, the DSC result shows the transformation temperature increases after heat treatment. This is because the heat treatment homogenised the composition and eliminated the Ni-rich areas, therefore increasing the TTs due to homogenisation rather than the decreasing it due to the increase in the oxygen content.

The reference sample shows a two steps transformation, with a small peak before the main transformation peak during heating and after the main transformation peak during cooling. Since it occurs on both heating and cooling process, this small peak refers to the R phase transformation, rather than a pre-martensitic transformation [1]. The heat treated sample shows a similar transformation behaviour as the reference sample, but the austenite transformation temperature is slightly lower and the martensitic transformation is slightly higher ($M_s = 352\text{K}$, $A_f = 380\text{ K}$, hysteresis = 28 K). The transformation temperature and total heat per gram for transformation stay constant between various heat treatment times. The 24 hours treated sample (HT24) shows a higher energy release due to the R phase transformation than the others, while the R phase transformation is the weakest in 100 hours treated sample (HT100). Nonetheless, no relationship was found between the amount of R phase and the heat treatment time.

The variation in the heat treatment time (from 3 hours to 100 hours) in the SDA samples does not significantly affect the shape memory properties. As increasing the heat treatment time could increase the oxygen content and thus, affect the shape memory properties, it was determined that 3 hours treatment was the optimum for SDA built SMA samples.

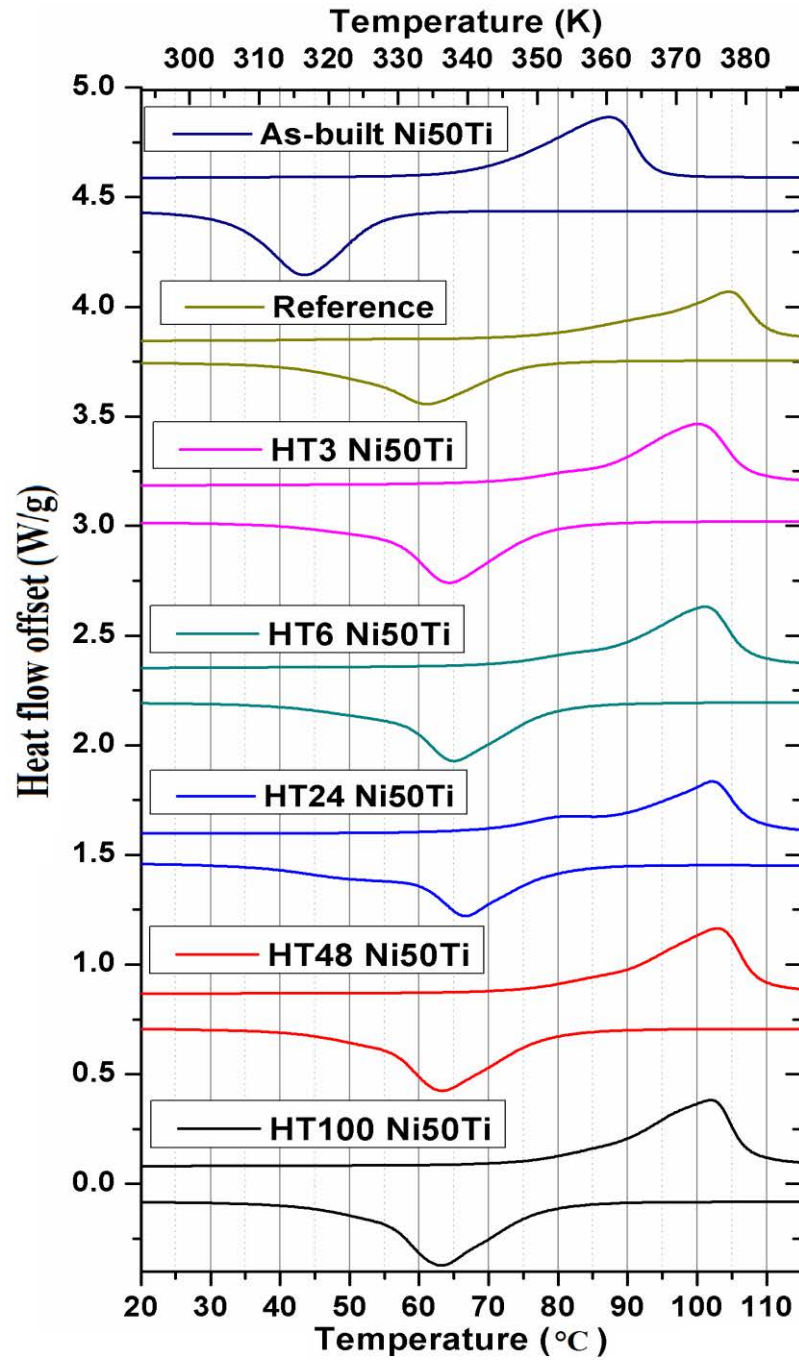


Figure 4.16. DSC curves of reference hot rolled $\text{Ti}_{50.4}\text{Ni}_{49.6}$ sample (golden line marked as reference), As built $\text{Ti}_{50}\text{Ni}_{50}$ sample (dark blue line marked as As-built TiNi_{50}) and 3 h (pink line marked as HT3 Ni_{50}Ti), 6 h (green line marked as HT6 Ni_{50}Ti), 24 h (blue line marked as HT24 Ni_{50}Ti), 48 h (red line marked as HT48 Ni_{50}Ti), 100 h (black line marked as HT100 Ni_{50}Ti) heat treated Ni_{50}Ti samples. The as-built sample has lower transformation temperature while the heat treated samples have the sample transformation behaviour as the reference sample.

4.8 Conclusions and further work

SMAAs produced by SDA were studied to assess their microstructural homogeneity, with respect to the grain structure, Ti_2Ni precipitate, chemical composition, and texture. A mathematical model with a reasonable accuracy was utilised to calculate the temperature fields and cooling rate associated with the SDA process.

1. Some local variations were observed in terms of the grain structure and Ti_2Ni fraction due to different cooling rates in the process.
2. On average, the chemical composition approaches the target composition, despite the local variations (especially in the external surface area). Small scale segregation due to melting point and density differences has been found in SDA samples. Since the mechanical testing will typically be performed after machining the surface, the surface variations are not important.
3. The grains in SDA sample was found preferential to $\langle 001 \rangle$ direction along the building direction. The texture and grain size of SDA sample are similar to arc-melting process.
4. The temperature field in the SDA sample is linear and the sample cools down with a rate of 0.77 K/s for low deposition power and 1 K/s for high deposition power during sample building. The fastest cooling rate of SDA process is less than 5 K/s. A more accurate experimental result could be obtained by using

more thermocouples during building or infrared camera for temperature measurement in the future work.

5. Post-processing heat treatment was generally not essential to obtain an assessment of the utility of the alloy combination (e.g. the phase transformations), but it can be used to improve the microstructural homogeneity and eliminate the small-scale segregation.
6. The heat treatment time at 1273 K for SDA built SMA does not affect the homogeneity and shape memory properties. Thus, the lowest time investigated, 3 hours heat treatment, is chosen for following study.

4.9 Reference

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5 Chapter 5. Mechanical testing

5.1 Introduction

In order to investigate the thermo-mechanical properties of SMA built by SDA process, samples have been produced for testing. The details of the testing method were introduced in Chapter 2. The tests were carried out in a temperature controlled furnace at 573 K, which was 100 K higher than the Ms temperature to ensure that the whole experiment was done in the austenite phase [141]. A reference sample, hot-rolled $\text{Ti}_{50.4}\text{Ni}_{49.6}$, was tested under the same condition for comparison. The tested results of SDA sample were also compared with literature. A heat treated $\text{Ti}_{54}\text{Ni}_{34}\text{Cu}_{12}$ sample, with the same composition to ultralow-fatigue TiNiCu sample reported in literature [142], was tested. Due to the limit of furnace, neither extensometer nor digital image correction was not applied for the experiments in this chapter, so the strain and Young's modulus results can only be compared between the samples within this experiment process.

5.2 Tensile testing at austenite temperature

In order to investigate the thermo-mechanical properties of SMA built by SDA process, samples have been produced for testing. The details of the testing method were introduced in Chapter 2. The tests were carried out in a temperature controlled furnace

at 573 K, which was 100 K higher than the M_s temperature to ensure that the whole experiment was done in the austenite phase [141]. The tensile testing result of the hot-rolled $\text{Ti}_{50.4}\text{Ni}_{49.6}$ reference sample showed the stress-induced martensite transformation starting at 700 MPa, with the permanent plastic strain starting after 757 MPa (strain 6.4%) tensile testing was 0.7 % (Figure 5.1). The stress induced martensitic transformation started at 700 MPa, 2.2 % strain. The Young's modulus in the first stage of deformation (austenite stage) was 3 GPa, while the second stage (martensite stage) was 0.017 GPa. Comparing the hot-rolled dog-bone shape specimen done by other researchers, the stress-induced martensitic transformation stress in this study was much higher, but the Young's modulus in this study was significantly lower. In the study by Maletta *et al.* [143], the sample showed a transformation stress of 450 to 490 MPa for the stress-induced martensitic transformation, and Young's modulus of 68 GPa in the austenite state, 35 GPa in the martensite state). This is due to the extensometer can not be installed on the machine during TMF testing, which leads large error on strain and Young's modulus result.

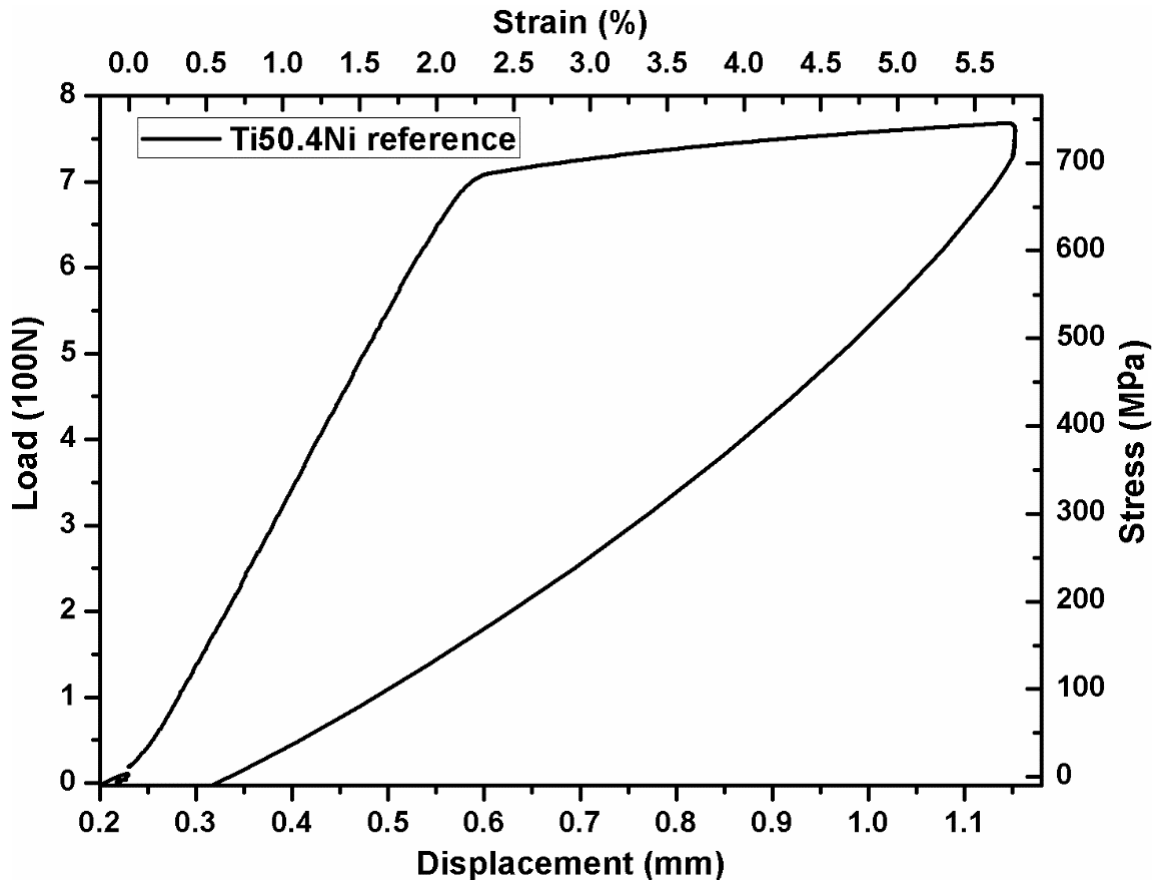


Figure 5.1. Tensile testing curve of Ti_{50.4}Ni_{49.6} reference SMA sample at 573 K (austenite phase). The maximum stress was 757 MPa and the permanent strain after testing was 0.7 %.

The tensile testing of Ti_{50.5}Ni_{49.5} SDA built sample shows similar stress-strain curve to reference sample, but the transformation stress went up to 780 MPa during testing at a strain level of 7.1 %, but recovering to a permanent strain of 1.1 % after testing (Figure 5.2). The stress induced martensite transformation occurred in a wider stress range, compared to the reference sample which started at 650 MPa, 2.5 % strain. This may due to the finer grain structure and the improved microstructural homogeneity of the

reference sample after hot-rolling.

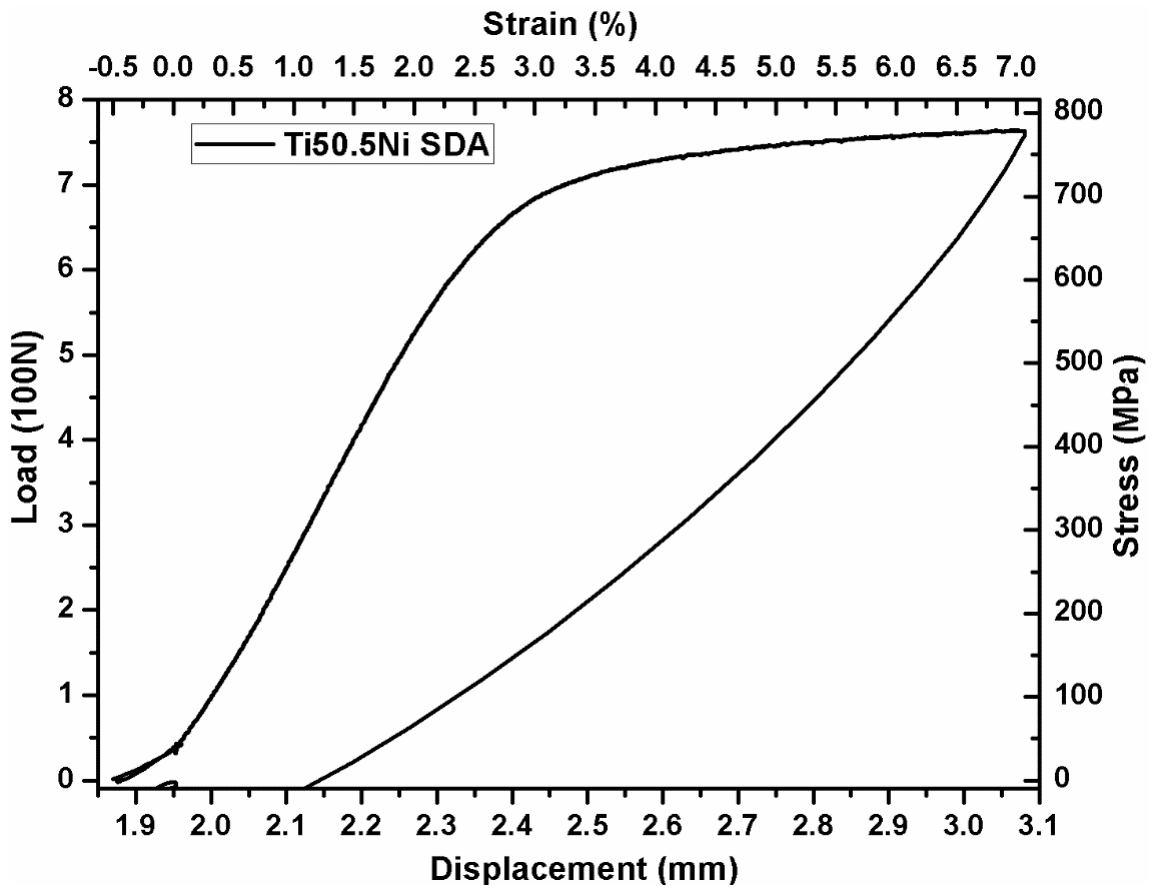


Figure 5.2. Tensile testing curve of Ti_{50.5}Ni_{49.5} SDA built SMA sample at 573 K (austenite condition). The maximum stress was 780 MPa and the permanent strain after testing was 1.1 %.

The Ti₅₄Ni₃₄Cu₁₂ sample built by SDA, however, showed a different deformation behaviour to the Ti-Ni alloys (Figure 5.3). There is no significant stress induced martensite transformation stage before the sample broken and the stress-strain curve of TiNiCu alloys is not linear during tensile testing. The strain in Ti₅₄Ni₃₄Cu₁₂ sample was

3.6%, which is 56.6% of the strain in Ti-Ni sample and the maximum stress was 651 MPa. These could be because of larger amount of brittle $\text{Ti}_2(\text{Ni,Cu})$ precipitate in $\text{Ti}_{54}\text{Ni}_{34}\text{Cu}_{12}$ sample and the precipitates form a continuous layer on the grain boundary after heat treatment, which limits the amount of deformation in the sample. All the samples showed near linear stress-strain relationship before they fractured at about 650 MPa.

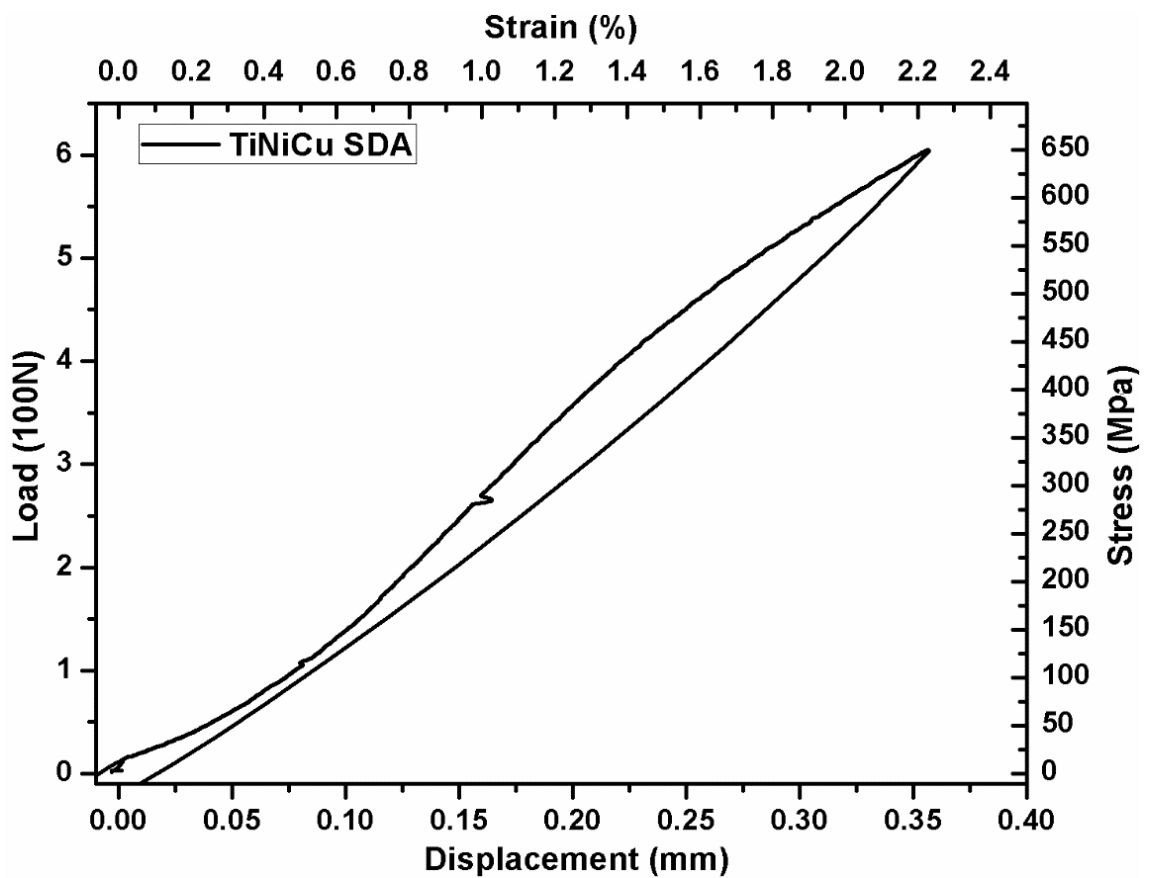


Figure 5.3. Tensile testing curve of $\text{Ti}_{54}\text{Ni}_{34}\text{Cu}_{12}$ SDA built SMA sample at 573 K (austenite condition). The maximum stress was 651 MPa and the permanent strain after testing was 0.013%.

5.3 Thermo-mechanical testing at the austenite temperature

Cycling loading was applied on the test sample and the loading force was determined by the previous tensile test result to ensure the sample reached the SE stage in each loading cycle. Therefore, 800 MPa was selected for Ti-Ni SMA thermo-mechanical fatigue (TMF) testing and 600 MPa was chosen for TiNiCu SMA. The starting strain and residual strain were the strain before the next loading cycle started and after the last loading cycle finished, respectively (loading at 0 N). The test result for the reference sample showed a linear increase in residual strain and maximum strain as the loading cycle increases (Figure 5.4). The permanent strain in the reference sample after testing (40th loading cycle) was 1.9 %. However, the recoverable strain (maximum strain – residual strain) was stable at 0.7% during the TMF testing. Due to the stress concentration and the tensile testing condition, the sample fractured after 40 testing cycles.

The Ti_{50.5}Ni_{49.5} SDA built sample was also tested in the same condition as the reference sample (Figure 5.5). The residual strain and starting strain varied a lot during the first 20 cycles but the strain at maximum load was stable. This may be due to the stability and control accuracy of the machine. In general, the recoverable strain was stable, but smaller than the recoverable strain in the reference sample (0.55% in SDA sample). The permanent strain in SDA Ti-Ni sample, however, was ~0.2% which was much smaller

than the reference sample. Since the plateau part of stress-strain in SDA sample tensile testing was slightly higher than the reference sample, there was more plastic deformation introduced in reference sample during TMF testing. Additionally, the machine was set as load control mode for TMF testing, but the Young's modulus at SE stage (plateau part in stress-strain curve) is very small, which means a small error of loading force could bring large strain in this stage. Comparing to the stress cycling testing in austenite phase done by Jiang *et al.* (~0.8% permanent strain), the permanent strain of reference sample was 1 % higher but the SDA sample was much smaller [132]. Comparing to the work done by Maletta *et al.* [143] the permanent strain (0.02 to 1.24%) and residual strain (0.68% to 3.26%) were similar.

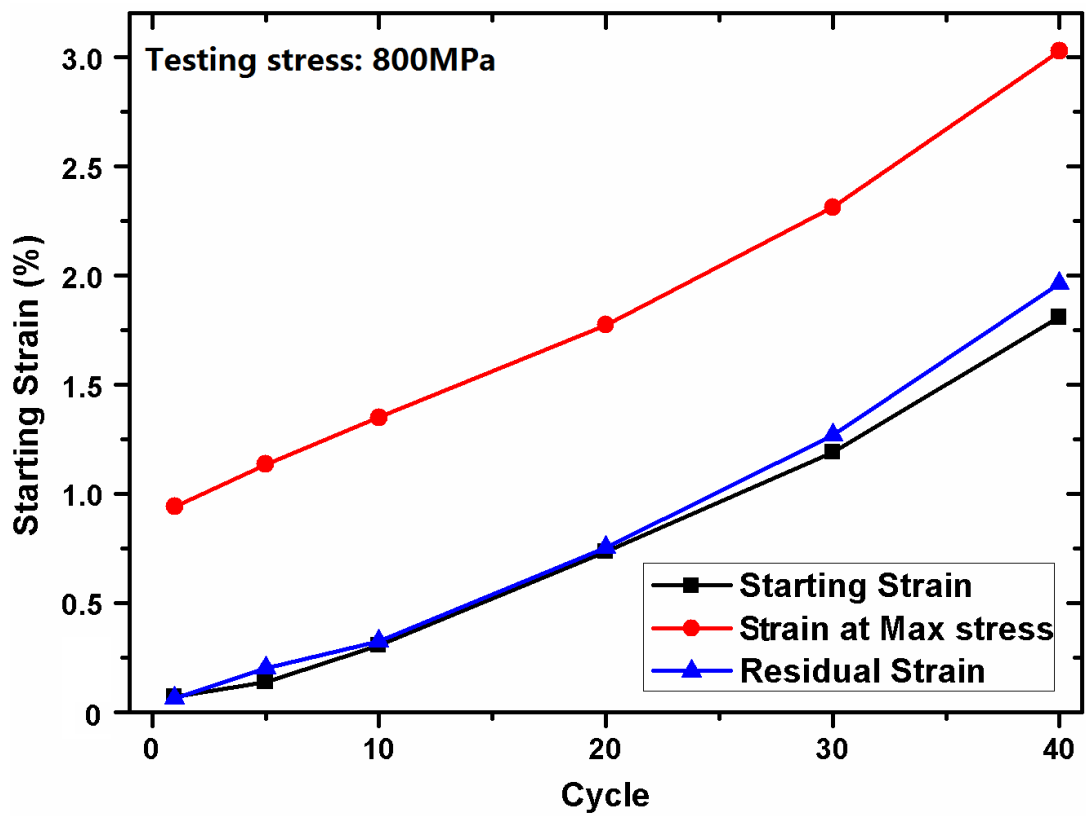


Figure 5.4. TMF testing result of $\text{Ti}_{50.4}\text{Ni}_{49.6}$ reference sample. The testing temperature was 573K, maximum stress was 800MPa and the sample was broken after 40 test cycles. The starting strain and residual strain are the strain before and after each cycle loading.

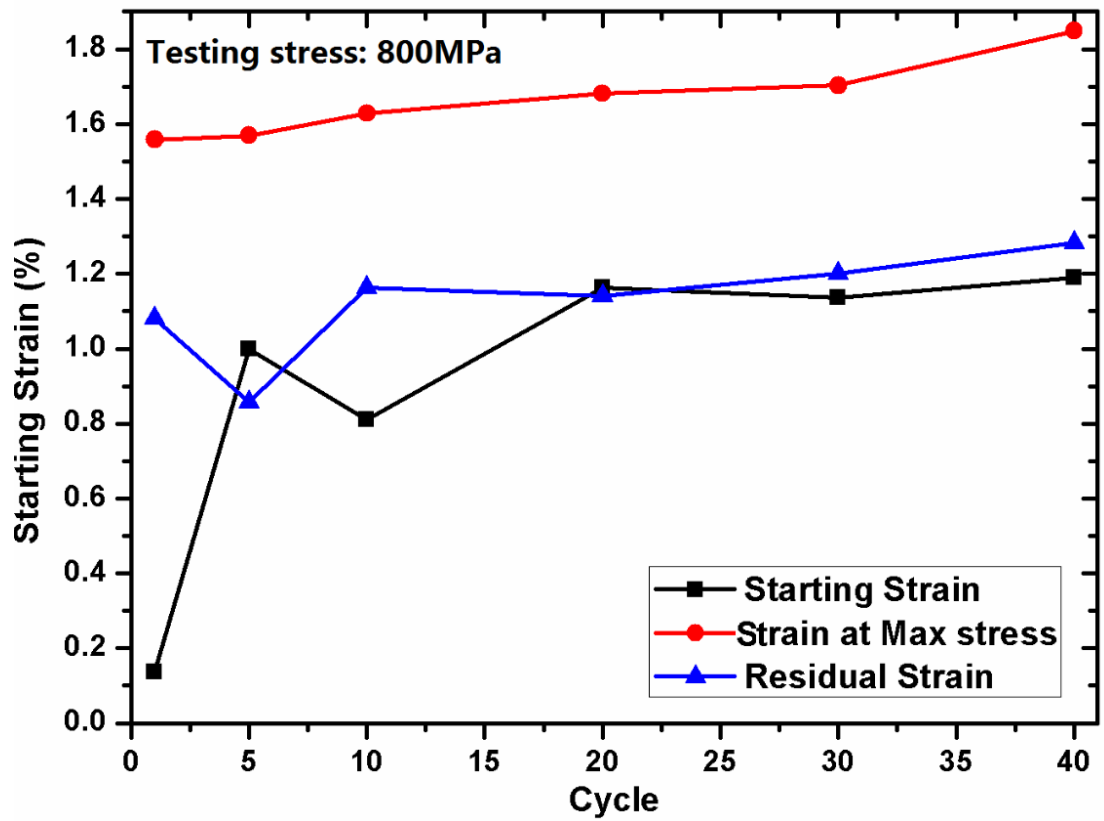


Figure 5.5. TMF testing result of $\text{Ti}_{50.5}\text{Ni}_{49.5}$ SDA sample. The testing condition is the same as the reference sample and the sample was also broken after 40 cycles.

The TMF testing of $\text{Ti}_{54}\text{Ni}_{34}\text{Cu}_{12}$ SDA sample showed better thermo-mechanical cycling stability than Ti-Ni sample, but there was no clear SE stage can be found in the testing curve (Figure 5.6). In order to compare the $\text{Ti}_{54}\text{Ni}_{34}\text{Cu}_{12}$ with $\text{Ti}_{50.5}\text{Ni}_{49.5}$ sample, a low stress (400 MPa) TMF testing was also applied on $\text{Ti}_{50.5}\text{Ni}_{49.5}$ SDA sample. The residual strain in TMF tested $\text{Ti}_{54}\text{Ni}_{34}\text{Cu}_{12}$ sample was varied from 0.07% to 0.125% during testing and the recoverable strain was about 0.45%, which were both smaller than the Ti-Ni sample. Comparing to the low stress TMF testing on Ti-Ni SDA sample (Figure

5.7), the recoverable strain in Ti-Ni sample was ~0.1% and the residual strain varied from 0.05% to 0.18% (44% larger than residual strain in TiNiCu sample).

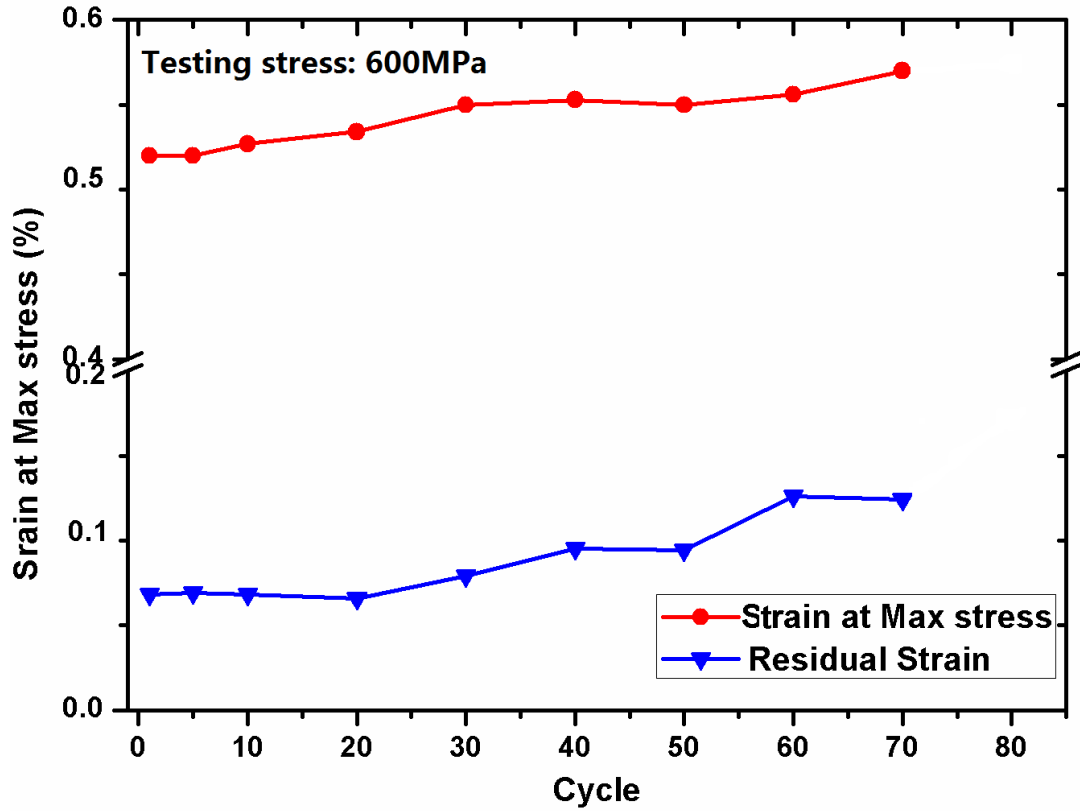


Figure 5.6. TMF testing on $\text{Ti}_{54}\text{Ni}_{34}\text{Cu}_{12}$ SDA sample at 573K, 600MPa. Due to the starting strain in this testing were all the same as residual strain, the starting strain was not plotted here.

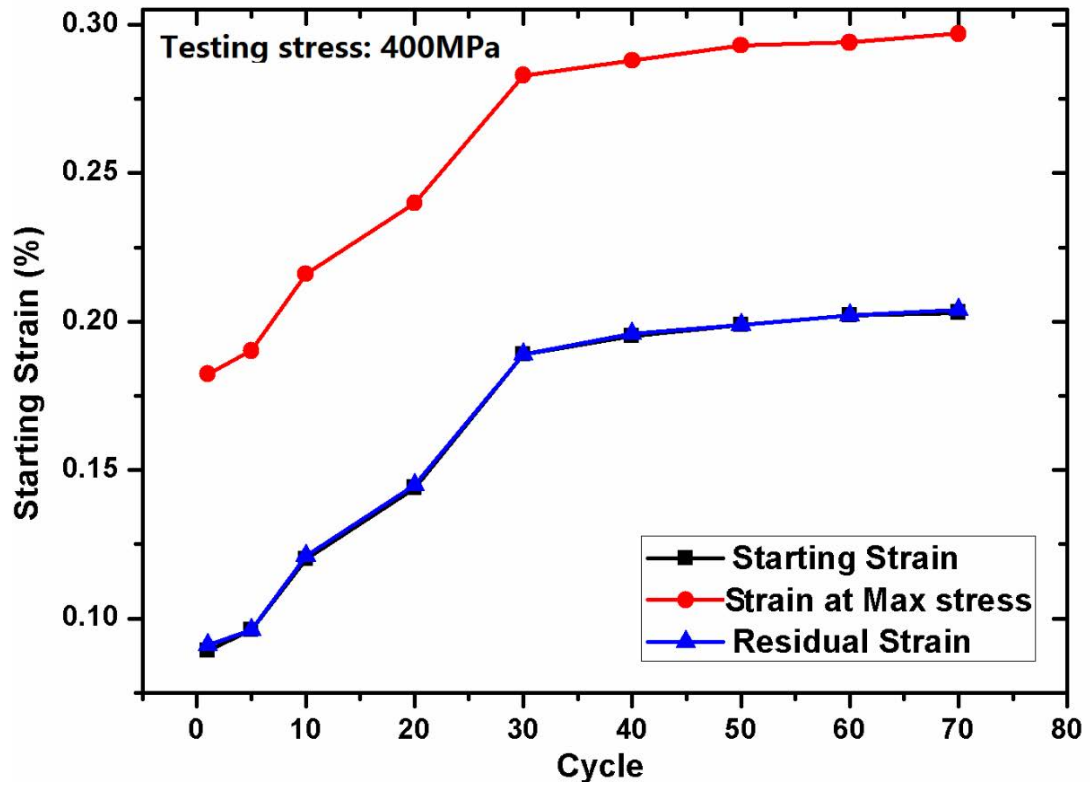


Figure 5.7. Low stress (400MPa) TMF testing on $\text{Ti}_{50.5}\text{Ni}_{49.5}$ SDA sample. The residual strain became stable after 30 cycles.

5.4 Fracture surface analysis

The fracture surface of TMF tested sample was observed under the SEM. The Ti-Ni sample showed ductile fracture while the $\text{Ti}_{54}\text{Ni}_{34}\text{Cu}_{12}$ sample showed flat brittle fracture due to the high percentage of Ti-rich precipitates. On the bottom-right corner of the fracture surface of $\text{Ti}_{50.4}\text{-Ni}$ reference sample, a crack was found which could refer to the crack started from the corner (Figure 5.8) due to stress concentration. The fracture surface of the reference sample (Figure 5.9) and SDA Ti-Ni sample (Figure 5.10) showed similar ductile fracture surface, with dimple fracture surface, but the structure in

the reference sample was finer. The SDA sample also showed cleavage facets, which indicated this sample had brittle-ductile mixed fracture. A few pores can be found in the fracture surface which refers to the Ti_2Ni precipitates. Comparing to the fracture surface of Ti-Ni tensile testing in literature, the fractograph of these samples were similar [144]. The cracks nucleated from the corner in these samples which may due to stress concentration in the flat dog-bone shape sample.

The fracture surface of $\text{Ti}_{54}\text{Ni}_{34}\text{Cu}_{12}$ sample, however, shows brittle fracture with a large amount of micro-cracks (Figure 5.11). Most cracks were growing in the brittle $\text{Ti}_2(\text{Ni,Cu})$ phase along the grain boundary. Therefore, the mechanism of Ti_2Cu precipitates improving shape memory properties and TMF life does not exist in bulk materials for the size and morphology of precipitate is hard to be controlled in bulk materials [142]. Addition of the other elements to alter the size, morphology and composition of precipitates is necessary for developing new Ti-Ni-based SMA with better TMF resistance.

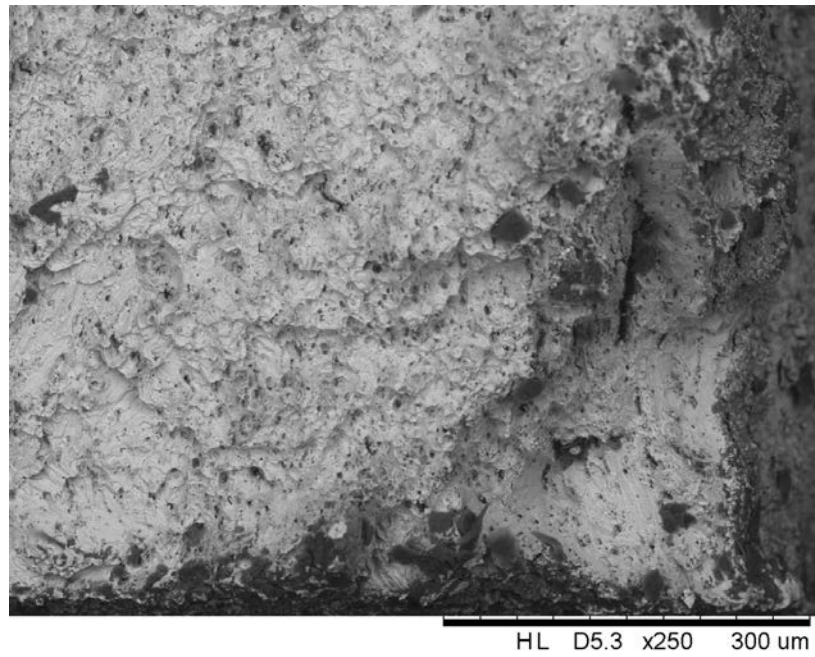


Figure 5.8. BSE image of fracture of bottom-right corner of Ti_{50.4}Ni_{49.6} reference sample showed a crack around the corner.

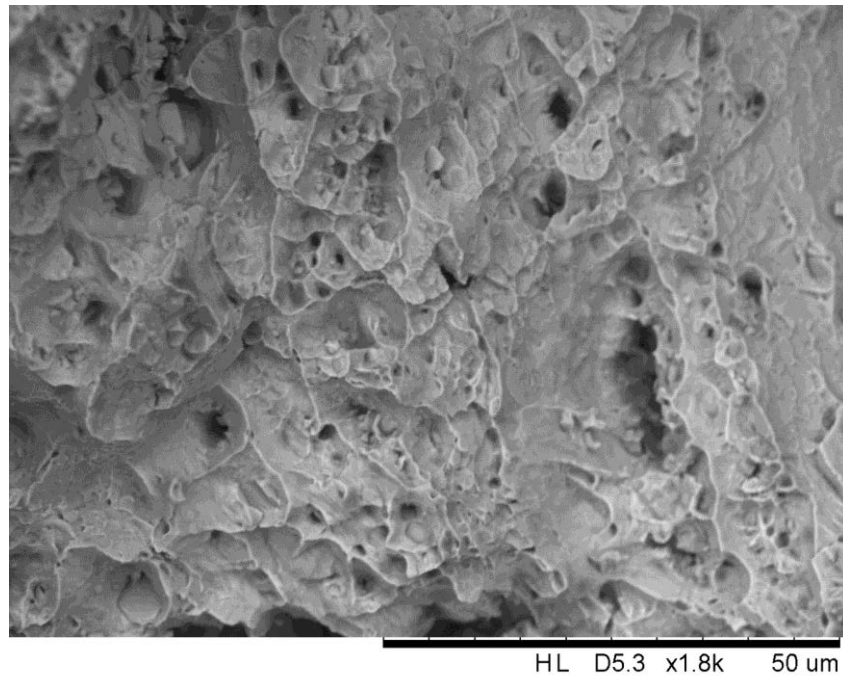


Figure 5.9. Fracture surface of Ti_{50.4}Ni_{49.6} reference sample showed dimpled structure and the holes were Ti-rich precipitates.

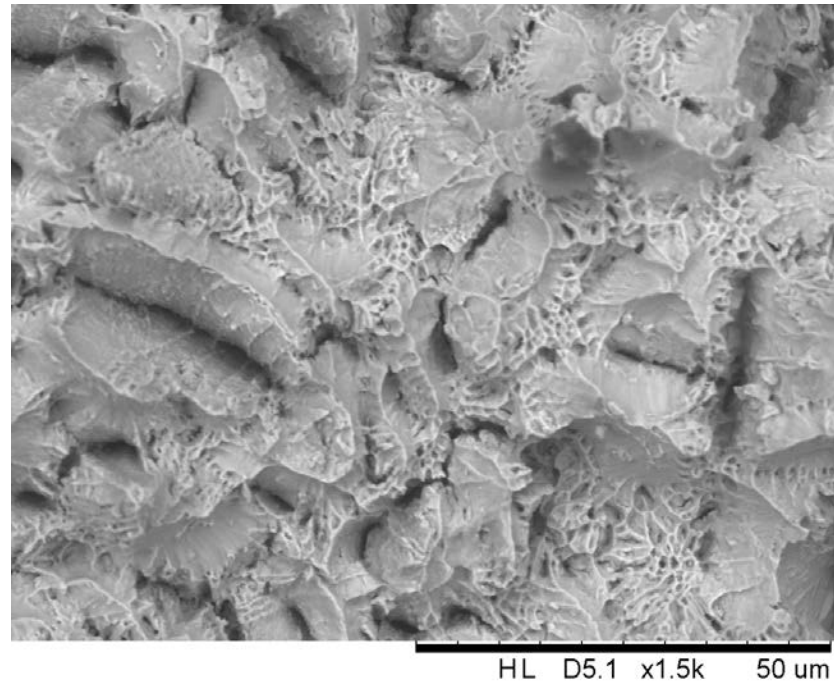


Figure 5.10. Fracture surface of $\text{Ti}_{50.5}\text{Ni}_{49.5}$ SDA sample showed larger dimpled structure and cleavage facets comparing to reference sample.

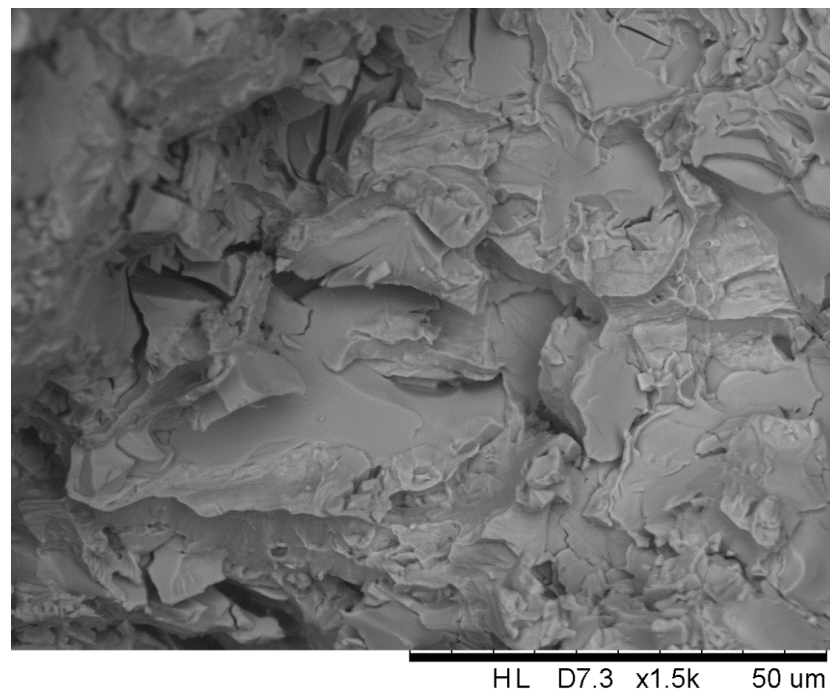


Figure 5.11. Fracture surface of $\text{Ti}_{54}\text{Ni}_{34}\text{Cu}_{12}$ SDA built SMA shows a generally brittle fracture surface, with large amount of micro-cracks along the cell boundary.

5.5 Conclusions and further work

The SDA built $\text{Ti}_{50.5}\text{Ni}_{49.5}$, $\text{Ti}_{54}\text{Ni}_{34}\text{Cu}_{12}$ SMA flat dog-bone samples were tested using cyclic-loading within the austenite phase field to investigate the TMF properties of SDA built samples. A $\text{Ti}_{50.4}\text{Ni}_{49.6}$ hot-rolled SMA sample was also tested under the same condition for comparison.

Although the TMF testing results of SMA sample reported in literature varied a lot due to several factors, apart from Young's modulus, the result of reference sample done in this research was within the range reported by literature except for Young's modulus.

Comparing the reference sample with SDA built sample, the permanent strain and transformation stress in SDA sample was slightly higher (~4% and 36% higher in stress and strain respectively).

The $\text{Ti}_{54}\text{Ni}_{34}\text{Cu}_{12}$ SDA sample showed different behaviours to Ti-Ni sample due to higher precipitate fraction, which indicated the mechanism of Ti_2Cu improving TMF performance in thin film does not work in bulk materials.

To alter the size and morphology of precipitates, the use of other alloying elements is necessary for to develop new SMA, with a good TMF resistance.

5.6 Reference

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6 Chapter 6. Selective Laser Melting of Negative Poisson's Ratio Shape Memory Alloy

6.1 Introduction

In this chapter, high negative poisson's ratio (NPR) structure has been made using Ti-riched TiNi shape memory alloys (SMA), enabling improved performance and on demand manufacturing of smart and functional systems. The main objectives of this chapter were to design, model, fabricate and to mechanical testing NPR structures made from TiNi-SMA by additive manufacturing, to combine the outstanding mechanical properties of NPR and the shape change recovery of TiNi-SMA. It is important to mention that the response of these types of structures depends on the microstructure of the material as well as the macroscopic (structural or design). Therefore, a special emphasis is dedicated on the additive manufacturing (AM) and optimisation, microstructural development, and influence of post-processing, because of their significant importance for the overall response of the NPR-SMA concept. By optimising the process parameters, stress-induced cracks and porosity in selective laser melting (SLM) built SMA could be minimised. Nonetheless, the morphology of Ti_2Ni intermetallics, which affects the matrix chemistry, and hence alters phase transformation temperatures and mechanical properties, can be improved by post-processing homogenisation. Finally, compression testing has been used to calculate the Poisson's

ratio of the NPR-SMA and to characterise the ductility of the samples after post-processing.

6.2 Design of negative Poisson's ratio structure

Over the past years, several different types of structures, which geometrical cause NPR response, have been studied and tested. As Chapter 2 discussed, two types of re-entrant structures, which are conventional re-entrant structure and AM modified structure, were employed in this chapter.

Finite element analysis (FEA) using ABAQUS software is used for predicting the mechanical behaviour of the NPR structures. The 8-node quadrilateral elements method was applied to mesh the NPR structure. The setting of boundary conditions was as follows: a compressive force was applied on the top edges while the bottom was fixed to simulate the compression test.

The influence of the re-entrant angle (θ) in both designs were calculated. The 2D struts were used to reduce FEA meshing. The theoretical values for Poisson's Ratio (ν) were calculated by Equation 6.1, which is the vertical dimensions strain ($\epsilon_{\text{vertical}}$) divided by obtained FEA transverse direction strain ($\epsilon_{\text{transverse}}$).

$$\nu = - \frac{\epsilon_{\text{transverse}}}{\epsilon_{\text{vertical}}}$$

Equation 6.1

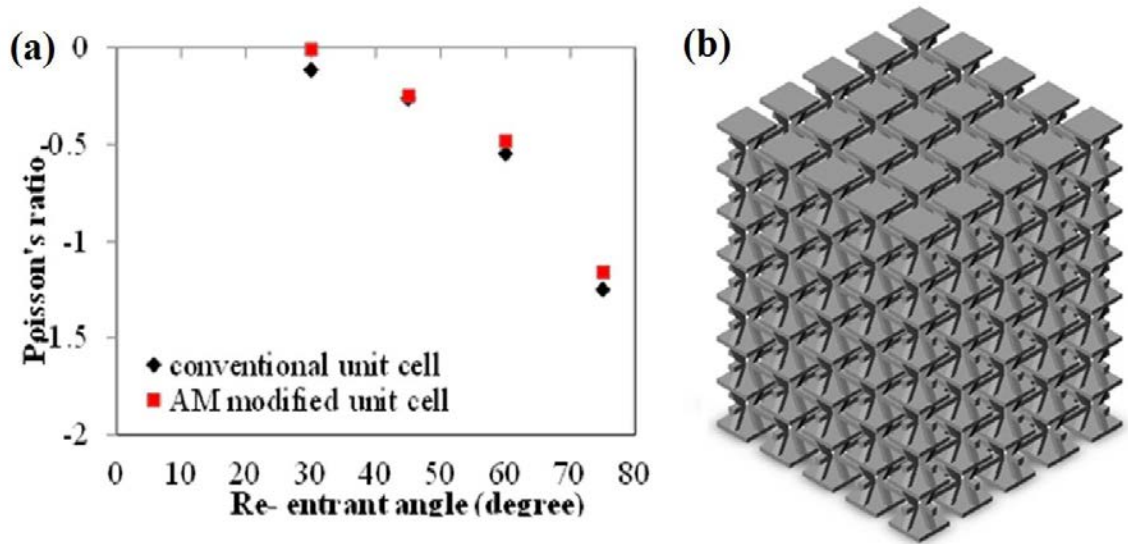


Figure 6.1: (a) Influence of re-entrant angle on Poisson's ratio in two different model, (b) 3D construction of AM modified re-entrant design [145].

Figure 6.1 shows the calculated structures' Poisson's ratios for the two designs under compressive loading with varied re-entrant angles ($^{\circ}$). Figure 6.1 (a) shows the calculated Poisson's ratio on different re-entrant angle (30° to 80°). The predicted Poisson's ratio is increased with increasing re-entrant angle for both designs. The conventional configuration, however, shows a higher Poisson's ratio than the modified design. The AM modified design shows a Poisson's ratio of about -1.3 when re-entrant angle of 75° and therefore, the 3D model in Figure 6.1 (b) is the developed NPR model for SLM manufacturing and testing.

6.3 Material and Experiment Methods

The Ti-Ni SMA powder used in this chapter was argon atomised by TLS Technik GmbH&Co (Germany) from a casted, homogenised and forged Ti₅₆Ni₄₄ ingot with 55.7 at.% Ti content. The powder was sieved down to 60 µm before SLM processing. A Leco TC436AR ANALYSER was applied to measure the O-content of the as-received powder and was found to be 1000 ppm. A CoulterLS230 laser diffraction particle size analyser was applied to measure the particle size distribution of the powder. Samples dimensions (x,y,z) of stl file was 5×5×10 mm³ and the build was carried out by a laser powder bed system, Concept Laser M2 Cusing® SLM. The building chamber filled with Ar atmosphere (O-content <0.1%). A continuous wave fiber laser with 60µm spot size and track width about 150µm was used in the system uses and the power output was variable up to 400W. In order to achieve defect-free builds the process parameters including laser power, scan speed, and scan spacing were optimised within the range of 50-120 W, 100-300 mm/s, and 45-150µm. The layer thickness was fixed as 20µm and the scanning strategy was using the M2 system island strategy [129, 146], with an 5mm island size, with 30 build conditions in total. Following the process parameters optimisation, the optimum parameters were applied to build auxetic structures.

Two different homogenisation treatments, which were HT1: 950°C/3h and HT2: 1000°C/2h, both followed by water quench, were applied to these samples. The

characterisation including microstructure and TTs were characterised using microscopy and DSC respectively. Auxetic structure samples with both as-fabricated (AF) and HT2 heat treated conditions were used for room temperature compression test by Zwick/Roell 1484 mechanical test machine for the mechanical properties and the Poisson's ratio investigation.

6.4 Results and Discussion

6.4.1 Microstructural assessment of the powder and of SLMed samples

Figure 6.2 (a) shows the shape of as-received powder was generally spherical with limited amount of irregular or satellites morphologies. This suggested a good powder flowability, which was evident in the 1.12 value from Hausner ratio measurement, which was determined by the ratio between tapped density of powder and freely settle density of powder (good flowability < 1.25). Entrapped gas pores (during atomisation) were infrequently observed in the powder particles section, as shown in Figure 6.2 (b). Since it is known that the entrapped gas pores presented in powder contributes to the porosity in AM builds, the results above suggests that the powder quality is suitable for SLM [147]. The d_{50} (average particle size) is about 22 μm as shown in powder size distribution in Figure 6.2 (c), with a limited percentage in the sub-10 μm range. It was also worth to mention that, despite the rapid cooling during gas atomisation, the cross section of powder particles in Figure 6.2 (b) shows Ti_2Ni intermetallics formed within the martensitic interdendritic regions, which indicates the susceptibility of this alloy to

micro-segregation. As discussed in Chapter 2, according to the Ti-Ni phase diagram [2], there are two phases at room temperature with this alloy's composition, which are the Ti_2Ni phase precipitate and the B19' TiNi matrix monoclinic phase [131].

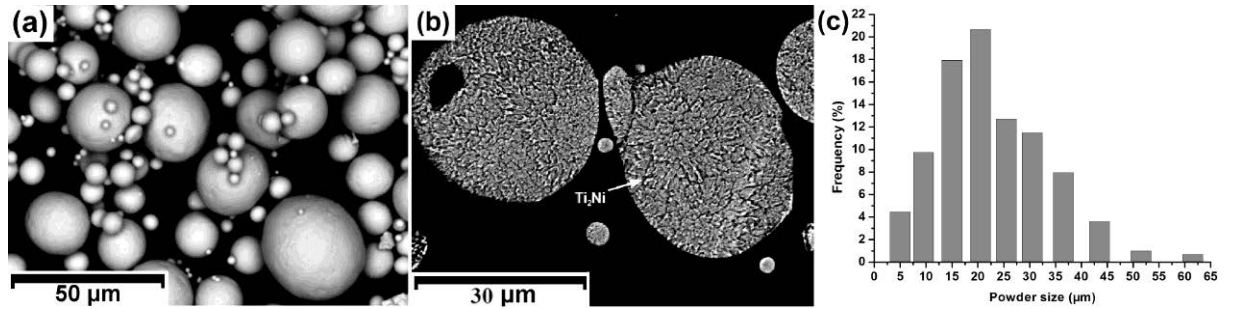


Figure 6.2. The Ti-Ni powder in as-received condition; a) morphology of powder, b) dendritic microstructure and an entrapped gas pore in particles section and c) powder size distribution [145].

6.4.2 Process Optimisation

Previously Bormann *et al.* [100, 104] studied a correlated parameter called volumetric energy density with the TTs in Ni-rich Ti-Ni, whereby:

$$E_v = \frac{P}{v \times h \times t} \quad \text{Equation 6.2}$$

where E_v is volume energy density (J/mm^3), v is scan speed (mm/s), h is scan spacing (mm), and t is layer thickness (mm). No reports using the E_v to control the development of porosity fraction or cracking density in Ti-Ni were found in the literature, although it is a standard approach in fabricating other alloys [89, 148]. Typically, the percentage of porosity decreases with the increasing energy density until a threshold level is achieved

alloy systems (e.g. Al-alloys) [150]. By plotting the E_v versus the measured porosity area percentage, no obvious trend was observed, as the data points in Figure 6.3 shows a large scatter. The area energy density (E_s) and linear energy density (E_L) can also be used for analysis.

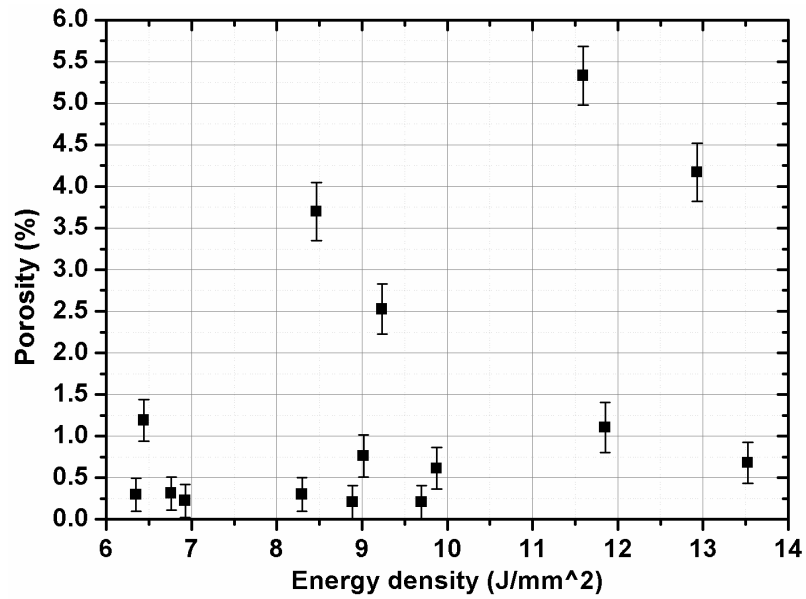


Figure 6.3. The plot of energy density vs porosity, showing the porosity fraction variation in Ti-Ni SLM [145].

It is important to note that the investigated energy density range exceeded the range investigated in previous studies on Ni-rich TiNi [99]. It is worth mentioning that the samples processed at energy density $E_s < 300 \text{ J/mm}^2$ demonstrated excessive cracking and lack of consolidation, Figure 6.3, whereas the majority of the builds beyond 300 J/mm^2 achieved porosity fraction $< 1\%$, yet with cracks present in some conditions. Alternatively to the energy density approach, the porosity fraction and cracking density (crack length/area, mm/mm^2) were plotted against the linear energy density ($E_L = P/v$,

J/mm), Figure 6.3-(a,b). Contour plots were constructed, showing the variation in the porosity fraction and cracking density as a function of both the scan spacing and E_L . By correlating both contours, processing windows to achieve low porosity fraction and low cracking density were identified, albeit separately in most conditions, since each defect type appeared to be reduced at a different parameters range. By choosing $P/v = 0.67$ J/mm and scan spacing = 0.065 mm, a good compromise can be obtained in terms of the cracking density and porosity fraction. Still, a very narrow processing range showed low levels of both the porosity fraction and cracking density, as shown in Figure 6.4-(c,d,e). Since the lattice and mesh structures (including auxetics) typically have thin struts of diameter <3 mm, thermal cracks are known to be lower in those structures than in cubic/bulk specimens due to the differences in the level of thermal stresses experienced [151]. An interesting correlation can be found from Figure 6.5. It is obvious that low porosity can be achieved via a combination of low E_L (Figure 6.5-a), whereas low cracking density is obtained at high E_L (Figure 6.5-b). This suggests that the cracking density tends to be reduced as the melt pool temperature increases (assuming that the melt pool temperature is proportional to E_L). Evidence on the possibility of this hypothesis is the observation that high E_L resulted in high porosity fraction, since high melt pool temperatures result in turbulence[147].

6.4.3 Build Microstructure

The build microstructure exhibited three features; residual pores, cracks, and a dendritic solidification microstructure. The size of the pores in the high E_L samples varied between 10 to 60 μm without any powders trapped inside, Figure 6.6-a. This suggests that they were formed as a result of melt pool turbulences leading to gas entrapment, rather than from the porosity within the powder. The lowest porosity in the investigated parameters range was 0.09%, which is lowest ever found on studies on AM of TiNi, although the solidification behaviour (including porosity formation and susceptibility to macro and micro-cracking) would be expected to be alloy-dependent [9, 10, 13]. The microstructure was primarily dendritic, with Ti_2Ni present along the interdendritic regions. The dendritic structure was finer in the low E_L conditions (e.g. Figure 6.6-(b,c)), compared to the high E_L conditions (Figure 6.6-a), which suggests that slower cooling rates occurred in the high E_L conditions. The high E_L condition consisted of 20-60 μm columnar and 5-10 μm equiaxed dendrites (Figure 6.6-a), compared to fine columnar dendrites of 10-40 μm in length in low E_L condition (Figure 6.6-b). The Ti_2Ni content was quantified using ImageJ[®] image analysis, revealing an area fraction of $31 \pm 4\%$ (18 ± 4 vol.%) in the high E_L condition (90 W, 115 mm/s, 0.0675 mm), compared to $27 \pm 4\%$ (14 ± 4 vol.%) in the low E_L condition (60 W, 120 mm/s, 0.056 mm).

The coarse dendritic structure in high E_L sample is result from higher energy input during fabrication reduced the cooling rate. Since the laser beam reheated the materials

when it was scanning the next few paths, the energy input will significantly affect the thermal conditions during building. Comparing with the low EL sample, the high EL sample received more energy during melting and reheating. Hence, the cooling rate of high EL sample was smaller.

The high Ti_2Ni content suggests that a heat treatment is necessary to improve the homogeneity, mechanical properties, and shape memory behaviour of SLM-built SMA.

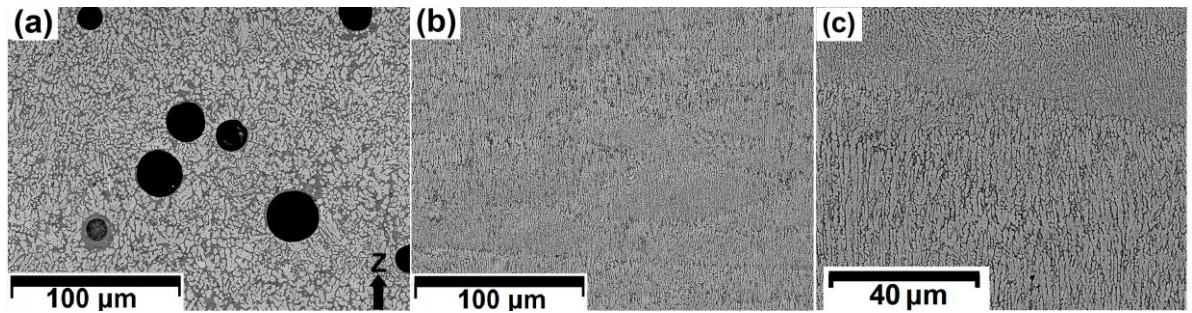


Figure 6.6. BSE micrographs taken along the X-Z plane showing (a) the residual porosity in high E_L samples (90 W, 115 mm/s, 0.0675 mm), (b) the dendritic structure and the melt pool beads in the low E_L condition (60 W, 120 mm/s, 0.056 mm), and (c) high magnification micrograph for the low E_L condition [145]

It was worth to mention that more Ti_2Ni was found around the pores as shown in Figure 6.6 a. The Ti_2Ni area fraction around a few pores have been analysed by ImageJ with the same threshold, the results show that around most pores the Ti_2Ni fraction decreases as the distance increases, Figure 6.7. However, some of them remain the same level as

the distance increases, which may be affected by the pores under investigated sections or the pores are formed by the other reasons. In addition, the fractions at the edge of some pores may be affected by grinding during which the brittle Ti_2Ni could break and peel off. This could be due to the locally nickel vaporisation during melting, which was also reported by Meier et al [152]. Because the vapourisation temperature of nickel (3003K) is 530K lower than titanium, the microstructural variations above might be because of the nickel evaporation in higher energy sample. However, there is not enough evidence to prove the nickel evaporation in the sample. Because the high porosity high EL sample prepared by twin-jet polishing lacks of thin area for TEM analysis and the EDS analysis in SEM did not show significant change in chemical composition. Due to the distribution of energy in laser beam and the island scan strategy, the temperature higher than nickel evaporation temperature might occur locally (the corner of the island, for example). On the other hand, the poor accuracy of EDS in SEM and influence of the area around could affect the testing results. Hence the EDS failed to detect the locally compositional variation with small amount.

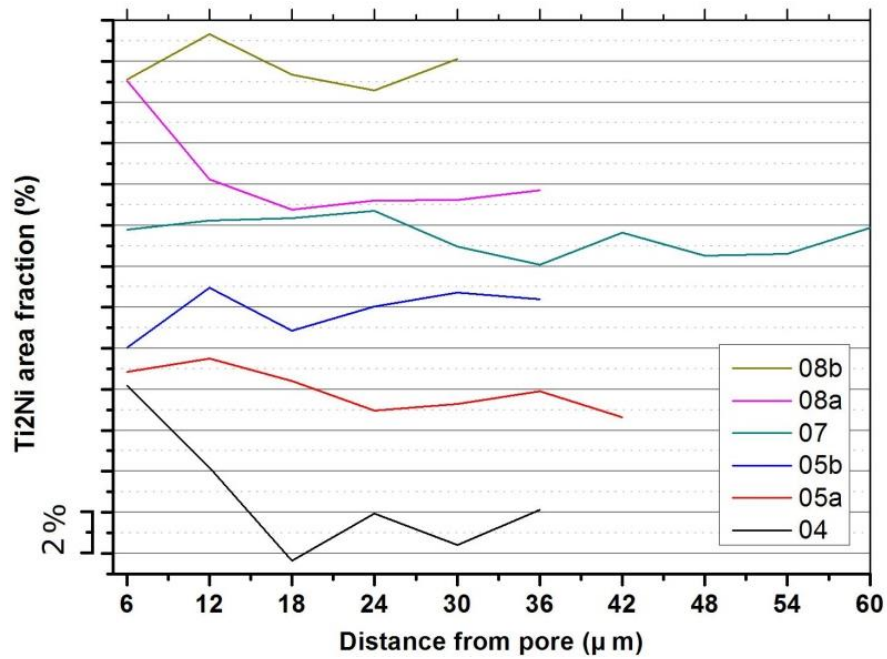


Figure 6.7. Ti_2Ni area fraction around the pores in high E_L sample. Most pores show decreasing Ti_2Ni area fraction as the distance increasing but some of them show different variation.

Although the critical stress of NiTi is rather low (about 300MPa in the martensite phase and about 400MPa in the austenite phase), the strain can be higher than 20% during tensile tests, thus the matrix should not sensitive to cracks [133]. Since Ti_2Ni is very brittle, cracks appeared to stem from the continuous Ti_2Ni phase present in the interdendritic regions, Figure 6.8-(a, b). As a result, it is believed that the ductility of the as-built samples is going to be poor due to the propagation and growth of the existing micro-cracks. The majority of the macro-cracks cracks were horizontal (i.e. normal to the build direction), Figure 6.8-a. The vertical cracks appeared to form only after

sectioning, and presumably occur as a mechanism to relax the residual stresses. As the cracking density variation contour suggests (Figure 6.5-b), despite the high porosity fraction present in the high E_L conditions, it seems also that the porosity allows more deformation within the samples, which potentially reduces the cracking density. Mechanical testing of porous Ti-Ni structures also suggests this behaviour [153, 154].

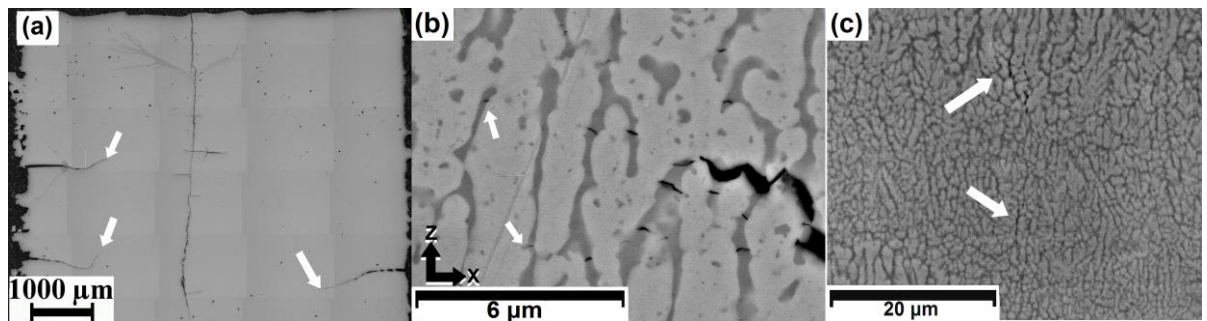


Figure 6.8. Horizontal thermal cracks shown by white arrows at the edge of near fully dense sample and vertical cracks appeared after sectioning in (a) optical microscope image, cracks grow through the cell and Ti_2Ni (b) and cracks are initiated on Ti_2Ni in (c) back-scatter images of XZ section [145].

XRD result of the powder and as-fabricated samples (built using the low E_L and high E_L parameters) confirmed the presence of two phases only; Ti_2Ni and B19', Figure 6.9. The XRD indicates that the as-fabricated samples of various build conditions have similar peaks, but the peaks intensities are different, while the powder has random orientations.

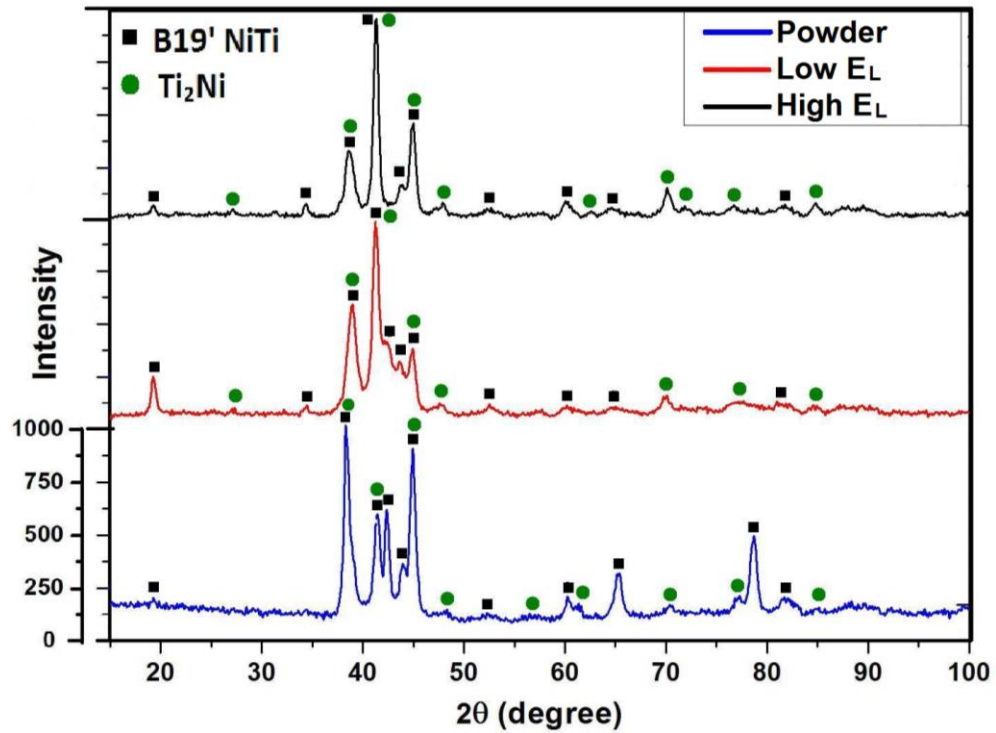


Figure 6.9. XRD result for SLM built Ti-Ni and powders reveal the presence of B19' and Ti₂Ni. The high E_L sample has larger amount of Ti₂Ni than the low E_L sample), while the powder (blue) has random orientations [145].

6.4.4 Post SLM Heat Treatments

One of the concerns with the presence of Ti₂Ni intermetallics is that it disturbs the chemistry of the matrix by depleting the matrix from Ti, resulting in a drop in the TTs. As a result, a heat treatment is essential to improve the homogeneity, SME, and mechanical properties. According the Ti-Ni binary phase diagram, Ti₂Ni phase melts at 964°C. However, this temperature can be affected by the presence of O and other minor elements. As such, DSC was used to determine the melting temperature of Ti₂Ni. The DSC revealed that Ti₂Ni melting initiates at ~1000°C, Figure 6.10.

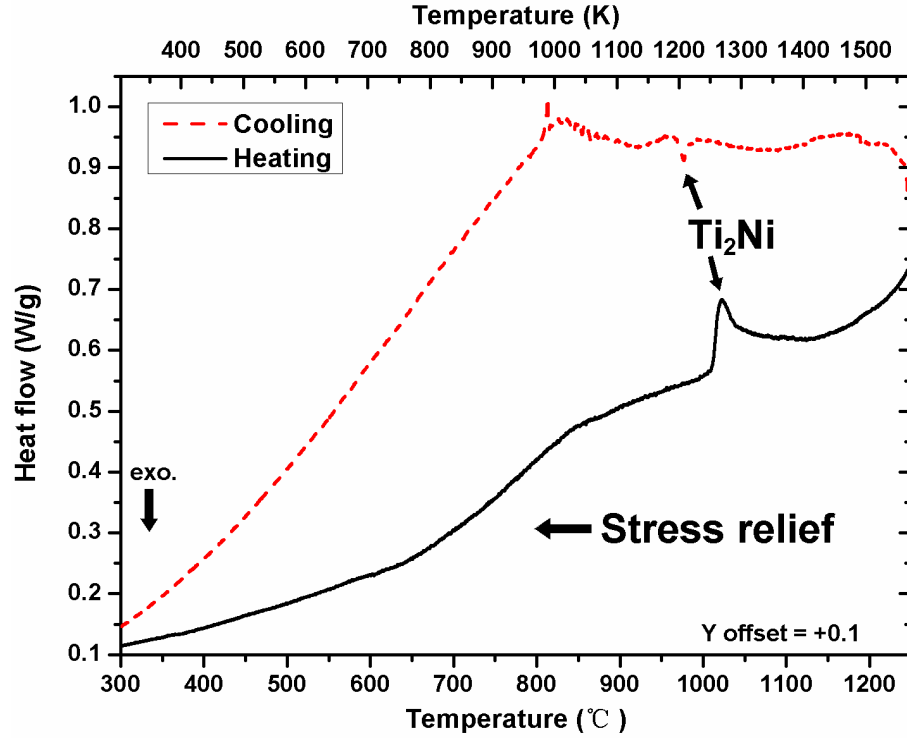


Figure 6.10. DSC trace of the low E_L AF condition shows Ti_2Ni melts around $1000^{\circ}C$ and solidified about $980^{\circ}C$ during cooling [145].

Thus two heat treatments (HT1 and HT2) were applied to the optimum build condition. HT2 ($1000^{\circ}C$, 2h, water quench) is just on the melting point of Ti_2Ni in this is alloy, which was intended to potentially consolidate the microcracks in Ti_2Ni by melting and re-solidification. HT1 ($950^{\circ}C$, 3h, water quench) appeared to break most of Ti_2Ni , whereas HT2 eliminated the continuous Ti_2Ni interdendritic morphology altogether.

The Figure 6.11 a and b show the XY and ZX sections of HT2 treated sample, the Ti_2Ni precipitation separates from each other into 0.5 to 1 μm spots or 10 μm short bars. The precipitation percentage of HT2 treated sample calculated by ImageJ is $26 \pm 4\%$ (13 ± 4 vol.%), which indicates the Ti_2Ni fraction does not change during heat treatment.

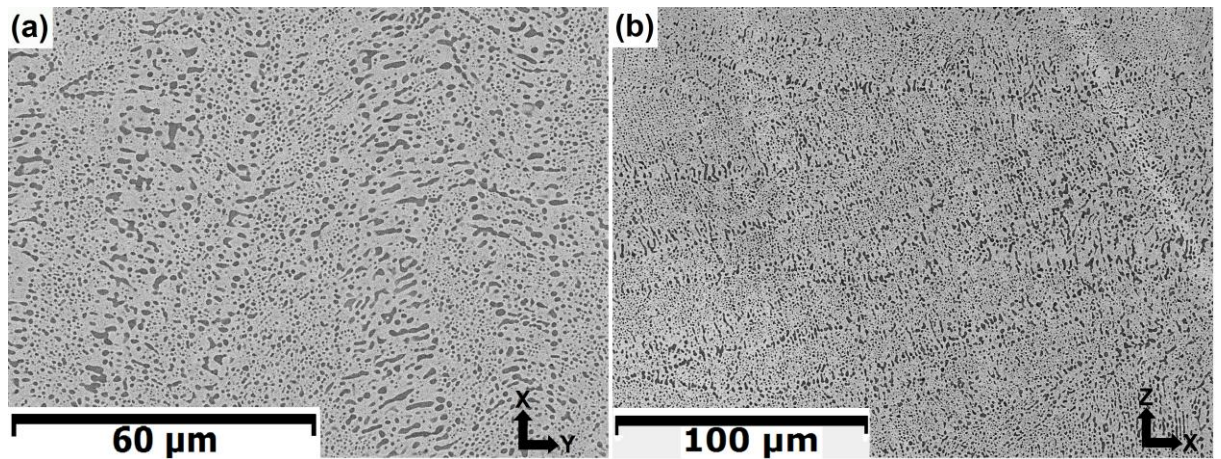


Figure 6.11. Back-scatter images of 1000°C 2h solution treated (HT2) sample in (a)XY plane and (b) ZX plane show the precipitations separated into small spot or short bar after heat treatment [145].

6.4.5 The Phase Transformation Behaviour

The phase transformation behaviour and TTs of the builds were studied using DSC for the as-fabricated and HT2 conditions. Initially, the samples were thermally cycled in their transformation range to stabilise their behaviour [2, 155], before recording their phase transformation behaviour using DSC, Figure 6.12. It appears that the heat treatment resulted in an increase in the TTs due to dissolution of the excess Ti_2Ni formed during fabrication, and a narrower phase transformation range (i. e. $M_s - M_f$). The dissolution of Ti_2Ni increases the Ti at. % content within the matrix, which will lead to an increase in the M_s . Only one-step transformation was observed. The narrowness of the peak in the heat-treated sample shows that the heat treatment has homogenised the samples, eliminating chemical segregation within the matrix [20].

By calculating the energy release during the martensitic transformation from the peak area in DSC curve, the energy release was found to be 19.5 J/g for the low E_L condition, 17.9 J/g for the high E_L build (~10% lower than low E_L sample), and 19.3 J/g for the HT2 low E_L condition. The change in the energy release can be correlated to the fraction of TiNi matrix present in the sample. As such, this suggests that the low E_L condition and the heat-treated condition generally contain more TiNi fraction (and lower Ti_2Ni fraction) than in the high E_L condition, which can be verified from Figure 6.6-(a,b). The Ti_2Ni fraction (P_{Ti_2Ni}) is calculated by the integrated intensity of the XRD patterns (Figure 6.9) with the equation below:

$$P_{Ti_2Ni} = \frac{\sum C_j}{\sum C_i} \quad \text{Equation 6.3}$$

where the C_j is the intensity of Ti_2Ni peak and C_i are the peak intensity for all phases, it was found that the total intensity of Ti_2Ni in high E_L sample is $33 \pm 2\%$, which is about 10% higher than the low E_L sample ($23 \pm 2\%$), which confirms the previous hypothesis. The high E_L condition introduces more heat input to the materials which increases the melt pool temperature and reduce the cooling rate, hence showing larger dendrite size. In addition, the boiling point of Ni is $2732^\circ C$ ($555^\circ C$ lower than Ti), which could introduce Ni evaporation during fabrication and increases Ti_2Ni fraction.

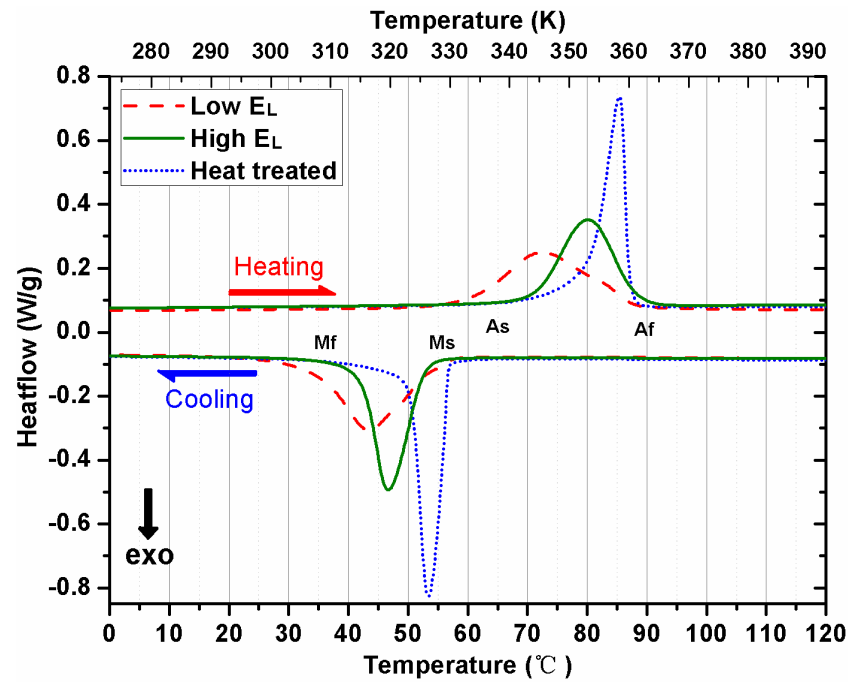


Figure 6.12. DSC traces for the as-built low E_L , as-built high E_L and heat-treated low E_L samples. The low E_L sample (noted as Low E_L with dash line) has the widest martensitic transformation peak from 56 to 30 $^{\circ}\text{C}$, the high E_L sample (note as Low Energy with solid line) has narrower peak than low E_L sample with the 4 $^{\circ}\text{C}$ lower martensite start temperature (M_s), while the heat-treated sample (dot line) has the narrowest peak with M_s at 56 $^{\circ}\text{C}$ [145].

The peak width is related to the inhomogeneity of the TiNi matrix. If the TiNi displays chemical inhomogeneities in the Ti-content, it is possible that the TTs range will end up being extended over a wider area. The energy release, however, is related to the TiNi fraction. As a result, the heat-treated sample has the most homogeneous B19' chemistry, which results in the narrowest TTs range. Interestingly, the A_f does not appear to differ in the three conditions, and the M_s shows only some slight differences. The heat-treated

sample has the most homogenous microstructure, which leads to narrowest peak.

Although rising of austenite transformation temperature and martensite transformation temperature dropping as stress or strain increase have been reported, the DSC samples are very thin and small, most stress is released during sample preparation [10, 156]. Furthermore, there is no austenite finish temperature increase observed in these samples. For porous samples, the residual stress may be partially released so the peak width decreased. The residual stress in these samples needs further research by other methods. Another reason for peak width variation in DSC curves could be the compositional variation in the sample, for the TTs is very sensitive to Ni content in Ti-Ni SMAs [19]. By using TEM and EDS, some Ni-rich areas in TiNi matrix are found in low E_L sample. As shown in Figure 6.13, the Ti-rich or near equiatomic matrix with martensite twinning microstructure are indicated by black arrow. The area near Ti_2Ni indicated by white area shows 51 at.% Ni in EDS investigation. This may indicate the wider DSC peak, which means larger TTs range, of low E_L is because of greater compositional heterogeneous in the low E_L than high E_L sample. This means even the material is Ti-riched, some Ni-riched area could occur during rapid cooling. Thus, heat treatment is necessary for homogenising the sample.

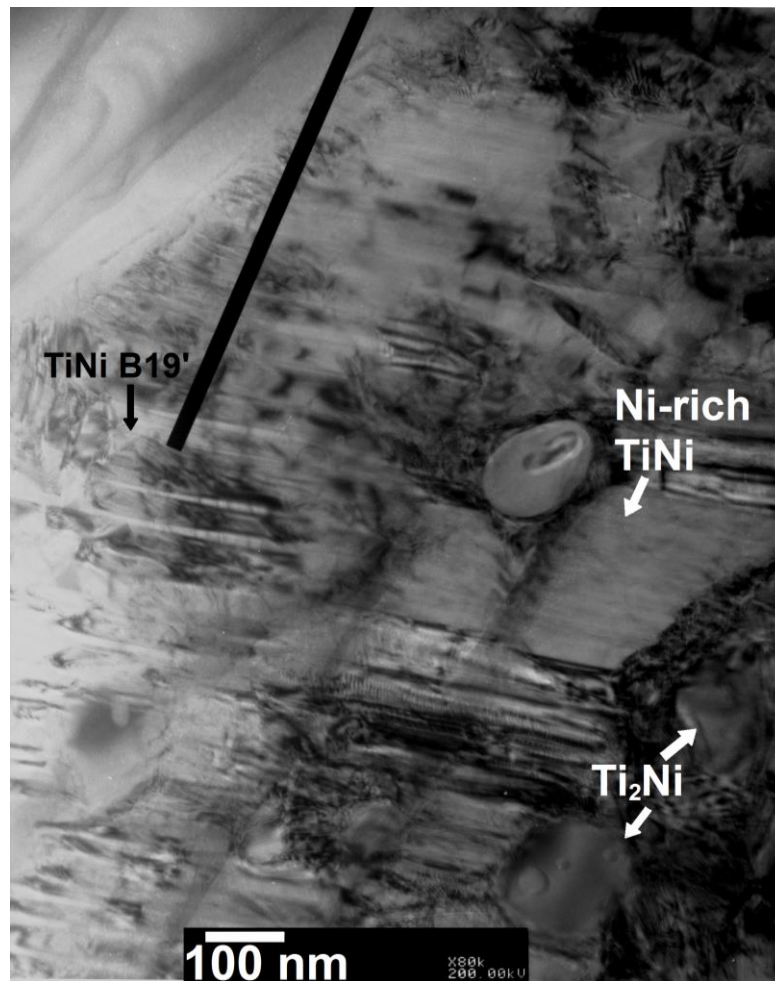


Figure 6.13. Dark field TEM image of low E_L sample showing Ti_2Ni and $TiNi$ matrix. The EDS result shows the martensite area indicated by black arrow is Ti-riched (51 at.% Ti), while the area near Ti_2Ni indicated by white arrow is Ni-riched (49 at.% Ti) [145].

6.4.6 NPR Structure Morphology and Performance

Conventional re-entrant structure samples with a dimension (26×26×36 mm) were built with the low E_L parameters. The geometry of sample is shown in Figure 6.14-b. As shown, the designed beam thickness in stl file is 0.3 mm while the beam thickness in actual fabricated samples is about 1 mm and a 0.8 mm ball forms at the corner. These

defects are induced by following natural characteristics of SLM: first, although the low E_L parameter was selected for auxetic structure fabrication, the energy of laser beam still penetrated a certain distance below each layer. Second, the heat input from laser beam sintered some of the powders around melt pool, which sticks these powders on the samples. Third, the geometry size of corner is smaller than the other area while the scan path at the corner does not change, this means more energy input at the corner. Fourth, the amount of solid/fabricated metal at the corner is less than the other area, which leads variations of heat transferring rate. It can be clearly see the poor underside surfaces due to the overhangs structures of the conventional design. These defects are reasonably improved when building the modified AM re-entrant structure, see Figure 6.14 (b).

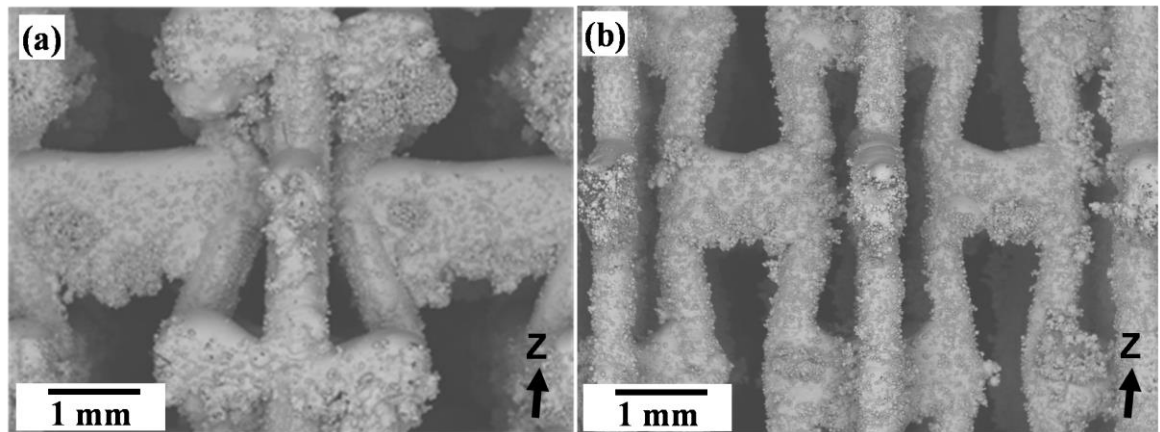


Figure 6.14. The morphology of NPR cells investigated by SEM (a) conventional re-entrant design, (b) modified AM re-entrant design [145].

Mechanical tests were carried on before and after HT2 treatment for comparison.

Lubrication grease was applied on the contact surface between samples and machine to reduce radial friction. A 50N preload was applied before testing and the displacement rate during compression test is 1 mm/min. Vertical displacement during compression test was recorded by the machine displacement and the horizontal displacement was measured during loading by using Digital caliper. The force-displacement curves of as-fabricated sample and heat treated sample are showed in Figure 6.15 with blue and red curves respectively. The as-fabricated sample shows steeper force/displacement curves than heat treated sample and the load is 12% higher than heat treated sample. The as-fabricated sample also shows linear curves before being broken while the heat treated sample shows two step deformation. This two-step deformation is due to the friction on contact surface deformed the cells at the bottom. However, the deformation of the as-fabricated sample is 46% lower than the heat treated sample, which indicates the ductility improved after heat treatment. The as-fabricated sample includes continually Ti_2Ni in the sample which has higher yield stress, which provides a stronger support within the structure, while the yield stress in Ti-Ni is much lower [133, 157]. However, the defects on the surface of these samples make cracks start easily and the cracks grow along the low ductility Ti_2Ni as shown in Figure 6.5, which reduces the ductility of as-fabricated samples. The separated Ti_2Ni in heat treated samples, however, allows the material have larger deformation.

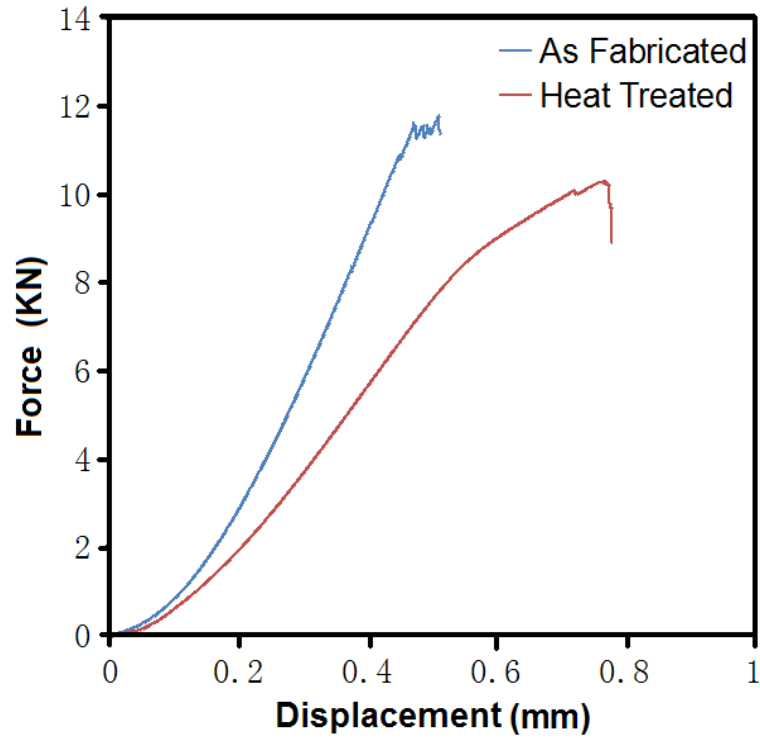


Figure 6.15. Force-displacement curve shows the as-fabricated sample (blue) has higher strength but lower ductility than the heat treated sample (red) [145].

Force-displacement data were used to calculate Poisson's ratio using Equation 5.1. The Poisson's ratio of heat treated NPR structure is -2.01 as shown in Figure 6.16, which is similar to the Ti-6Al-4V NPR structure fabricated by electron beam melting [158].

After compressive testing, the heat treated sample was heat up to 573K on a hot plate and the dimension of sample was recovered 0.4 mm in total, however this included the broken and bended corner of sample. It proved that the SMA NPR structure can recover after deformation.

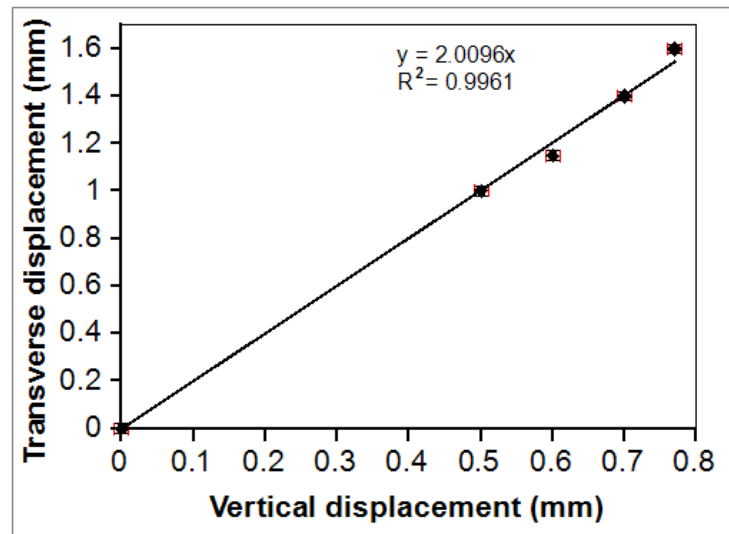


Figure 6.16. The Poisson's ratio ν_{tz} (-2.01) was calculated as the negative ratio between the transverse and vertical deformation from the best fit of force-displacement data of heat treated sample [145].

6.5 Conclusions and further works

Selective laser melting of Ti-Ni shape memory alloys has been successfully optimised for porosity and crack density. Fully dense (99.9%) solid and NPR structures from Ti-Ni was built.

Heat treatment can improve microstructural homogeneity, shape memory effect and ductility of Ti-Ni shape memory alloys by improving the morphology of Ti_2Ni precipitates and chemical homogeneity.

High energy input parameter in selective laser melting process could vary the chemical composition of Ti-Ni shape memory alloys by vaporisation, which affects shape memory effects. Unfortunately, the limit experimental method can not prove

this assumption. This could be further investigated by using focused ion beam (FIB) and TEM.

The heat treated Ti-Ni auxetic structure has comparable Poisson's ratio to Ti-6Al-4V auxetic structure.

The reason of peak width changing as well as residual stress in different energy input samples need to be further studied.

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7 Chapter 7. Development of TiNiHfCuNb shape memory alloys

7.1 Introduction

Since shape memory alloys (SMA) with comparable transformation behaviour to arc-melting can be produced by suspended droplet alloying (SDA) process, this process was applied to manufacture SMAs with different composition and develop new SMA. Samples were built to study the influence of Hf and Cu content on the TTs of Ti-Ni SMA and Nb content on the TTs of TiNiCu and TiNiHfCu alloys. As shown in Chapter 6, the mechanical testing results indicated that altering the size and morphology of precipitates by alloying is necessary for the development of SMAs with improved performance. Two alloys with similar chemical composition were found to have different transformation behaviour and the microstructure of these alloys were analysed by SEM and XRD.

7.2 Influence of Hf and Cu content on transformation temperature of TiNi-based shape memory alloys

Since the highest martensitic transformation start temperature (M_s) of binary Ti-Ni SMA is below 363K (90°C) [2], the demand for higher TTs for Ti-Ni based shape memory alloys has not been satisfied. As shown in Figure 7.1, Hf has been known as an effective element for increasing the M_s of TiNi-based SMA. The figure shows the

difference between M_s (ΔM_s) of $Ti_{51-x}Ni_{49}Hf_x$ SMA and M_s of Ti-Ni SMA from literature [35], the ΔM_s of $Ti_{51}Ni_{49-x}Hf_x$ SMA produced by SDA process. The effect of Hf on M_s can be simplified as a linear function, which is M_s (K) = $16x$ (at.%) + 333, where x is the at.% of Hf content and M_s is the martensite start temperature in K. However, the addition of Hf increases the hysteresis of transformation (up to 200K at 30 at.% Hf content), as shown through (Figure 7.1) the change in the martensite transformation finish temperature M_f and the austenite transformation finish temperature A_f with the difference between them being the hysteresis.

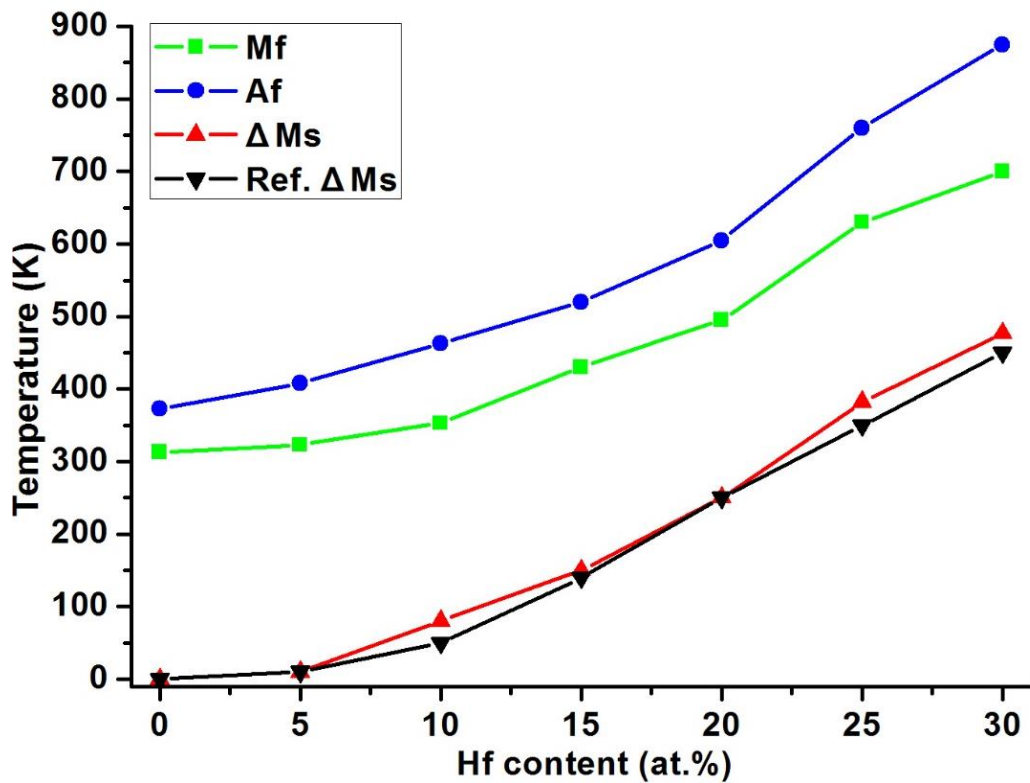


Figure 7.1. Improvement of Martensitic transformation start temperature (ΔM_s) of TiNiHf SMA according to the Hf content.

Also, as shown in Figure 7.2, the addition of Hf reduces the thermal stability (i.e. the M_s decreases as the number of thermal cycle increases) of SMA. The M_s of $Ti_{51}Ni_{49}$ alloys decreases by 12 K after 8 cycles while the M_s of $Ti_{46}Ni_{49}Hf_5$ alloys decreases by 18 K after 8 cycles. However, adding Cu into the Ti-Ni alloys significantly improves the thermal stability as both the $Ti_{51}Ni_{39}Cu_{10}$ and $Ti_{51}Ni_{24}Cu_{25}$ alloys show constant M_s after 3 cycles. Since TiNiCu SMA are known to have a very good thermal stability, alloying Hf and Cu into Ti-Ni SMA can potentially produce SMA with high M_s and good thermal stability (e.g. $Ti_{36}Ni_{44}Hf_{15}Cu_5$) as shown in Figure 7.2. The M_s of this alloys decreases by about 8 K in 8 cycles, which is slightly better than Ti-Ni SMA and much better than TiNiHf SMA. On the other hand, the strain recovery of TiNiCu and TiNiHf are poorer than Ti-Ni SMA, so the shape memory behaviour of TiNiHfCu SMA is not good enough for applications.

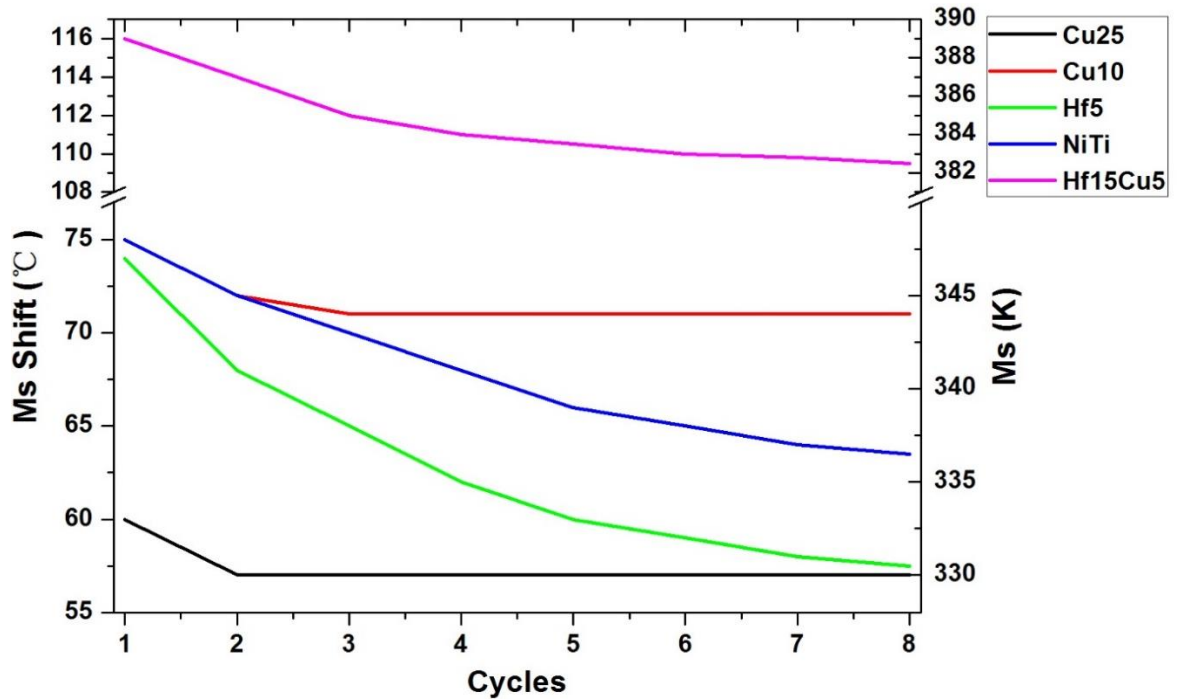


Figure 7.2. Decreasing of martensitic transformation start temperature (M_s) of some TiNi based SMA as the increasing of thermal cycles. The TiNiCu alloys have very good thermal cycle stability and the TiNiHf-Cu alloy has higher M_s and better thermal cycle stability than TiNi alloy.

As reported by the other researchers, TiNiCu alloys with Ti_2Cu precipitates have very good thermal stability and thermo-mechanical stability, a $Ti_{54}Ni_{34}Cu_{12}$ thin film has recently been reported as showing ultralow-fatigue SMA [142]. It was reported that the low fatigue of this alloys was because of the B19 and B2 phases were epitaxially related to Ti_2Cu precipitates and to each other. As such, the misfit of the matrix and precipitates is reduced, and the transformation is complete reversible. In bulk materials, however, the Ti-rich precipitates cannot be distributed as good as in thin film materials and it is

very hard to obtain Ti_2Cu precipitates. As discussed in chapter 5, the Ti_2Cu was not presented in the bulk materials and the $\text{Ti}_{54}\text{Ni}_{44}\text{Cu}_{12}$ sample (which had the same composition to the Ultralow-fatigue sample reported in literature [142]) was brittle during mechanical testing, which indicated this method does not work in bulk materials. Nonetheless, Nb has been known as an element that is able to increase the thermo-mechanical stability for fine β -Nb particles distributes around the precipitates [32]. On the other hand, adding Nb into Ti-Ni SMA increases the hysteresis of transformation (the hysteresis increases by 100 K with 10 at.% Nb) which is harmful for actuator applications. However, this is related to the Nb-content and Cu is able to reduce the hysteresis, which means the shape memory properties can be controlled by adjusting the content of Nb and Cu. As such, Ti-rich TiNiCuNb and TiNiHfCuNb alloys were produced by SDA process for developing high transformation temperature and good thermo-mechanical stability (ultralow-fatigue) SMA.

Before producing quaternary alloys and beyond, it is necessary to find out the influence of different elements (Cu, Hf, and Nb) content on M_s and hysteresis. Both the literature and experimental results of SDA samples showed that Hf increases the M_s significantly, while Cu slightly decreases the M_s , as the elements content increases, see Figure 7.3.

The variation of M_s caused by adding Cu into $\text{Ti}_{51}\text{Ni}_{49}$ alloys can be described as:

$$M_s (\text{K}) = -0.67x (\text{at.}\%) + 344 \quad \text{Equation 7.1}$$

where x is Cu at. % content and M_s the martensitic transformation start temperature in K.

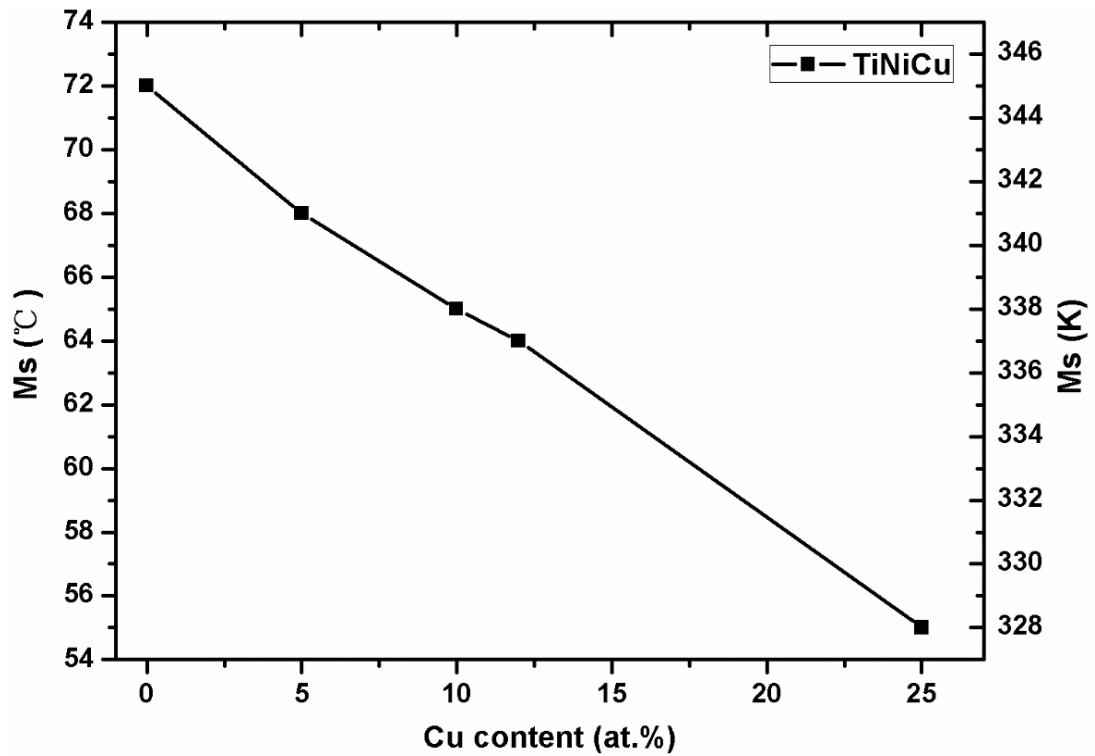


Figure 7.3. Influence of Cu content on martensite transformation temperature (M_s) of Ti-Ni shape memory alloys shows linear M_s decreasing as the Cu content increase.

For quaternary TiNiHfCu alloy, however, Cu has greater influence than in ternary alloys. Although some researchers have reported the martensite structure and transformation behaviour of $Ti_{36}Ni_{49-x}Hf_{15}Cu_x$ alloys, some compositions including $Ti_{36}Ni_{39}Hf_{15}Cu_{10}$, $Ti_{41}Ni_{49-x}Hf_{10}Cu_x$ have not been reported. As such, $Ti_{36}Ni_{44}Hf_{15}Cu_5$, $Ti_{36}Ni_{39}Hf_{15}Cu_{10}$ and $Ti_{41}Ni_{49-x}Hf_{10}Cu_x$ system were made by SDA process and compared with the literature. The influence of Cu content on martensite transformation start temperature

M_s of TiNiHfCu system are shown in Figure 7.4. As shown in the literature and experimental results, the Hf and Cu have negative influence with each other [39]. The decrease in M_s (temperature drop per Cu at. %) becomes greater as the Hf content increase. For 15 at. % Hf TiNiHfCu sample, the influence of Cu content on M_s can be described as below:

$$M_s \text{ (K)} = -5.7x \text{ (at. \%)} + 445 \quad \text{Equation 7.2}$$

Although the M_s of $\text{Ti}_{36}\text{Ni}_{44}\text{Hf}_{15}\text{Cu}_5$ alloy reported by literature is 420 K as-built, and 363 K after annealing, which does not follow the rule above. However, the result from SDA sample shows linear relation. In literature, the $\text{Ti}_{36}\text{Ni}_{44}\text{Hf}_{15}\text{Cu}_5$ sample was thin film manufactured by melt spun, which has different transformation characteristic to the bulk materials [38, 159]. The alloys with 10 at. % Hf also have linear decreasing M_s as the Cu content increase and the SDA sample agreed with the literature results [41], the relation can be described as below:

$$M_s \text{ (K)} = -5.1x \text{ (at.\%)} + 380 \quad \text{Equation 7.3}$$

Hence the Hf and Cu have a negative influence to each other on TTs, as the M_s decrease in $\text{Ti}_{41}\text{Ni}_{49-x}\text{Hf}_{10}\text{Cu}_x$ SMA (-5.7 K/at. %) is much greater than $\text{Ti}_{51}\text{Ni}_{49-x}\text{Cu}_x$ SMA (-0.67K/at.%).

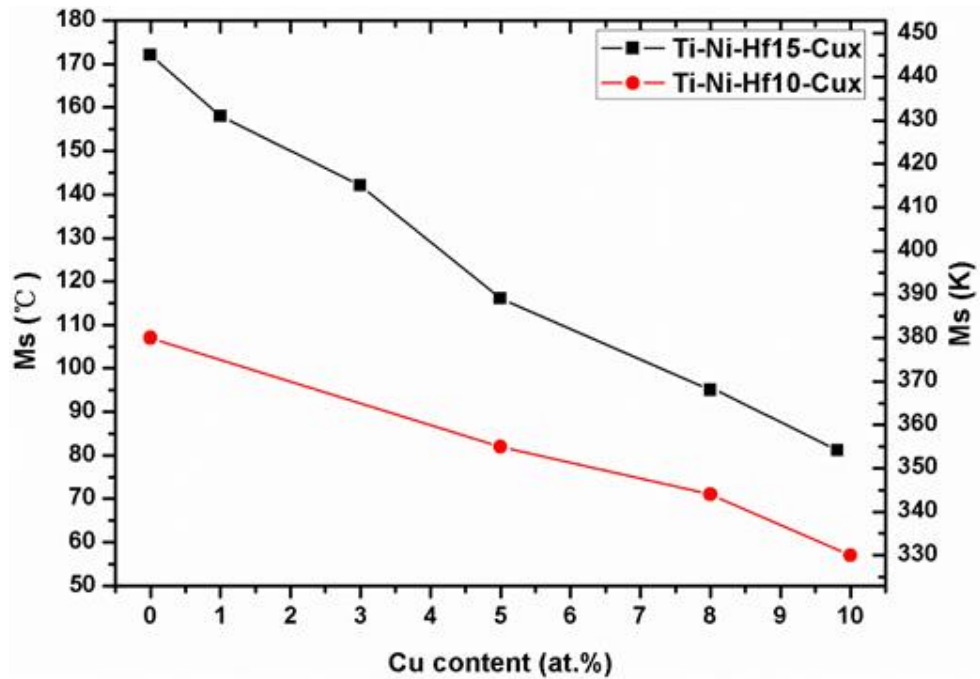


Figure 7.4. Both $\text{Ti}_{36}\text{Ni}_{49-x}\text{Hf}_{15}\text{Cu}_x$ (labelled as Ti-Ni-Hf15-Cux) and $\text{Ti}_{41}\text{Ni}_{49-x}\text{Hf}_{10}\text{Cu}_x$ (labelled as Ti-Ni-Hf10-Cux) alloys shows linear decreasing Ms as the Cu content increase in TiNiHfCuNb alloys. The influence of Cu become stronger in higher Hf content alloys.

7.3 Improving stability of quaternary and quinary shape memory alloys

From literature, the austenitic transformation start temperature (A_s) of TiNiNb alloys is affected, not only by the Nb content but also the deformation strain [32, 33]. The the A_s increases from 308 K to 364 K as the Nb content increases from 3 at. % to 20 at.% and the hysteresis increases up to 175 K as the Nb content reaches 20 at.%. As shown in Figure 7.5, the Nb-content reduces the Ms significantly which can be described as

below:

$$Ms \text{ (K)} = -6.3x \text{ (at. \%)} + 343 \quad \text{Equation 7.4}$$

The influence of Nb content on Ms of $\text{Ti}_{51-0.5x}\text{Ni}_{49-0.5x}\text{Nb}_x$ alloys is slightly stronger than Cu on Ms of Ti-Ni-Hf-Cu alloys (-6.3 K/at. % for Nb and -5.7 K/at. % for Cu).

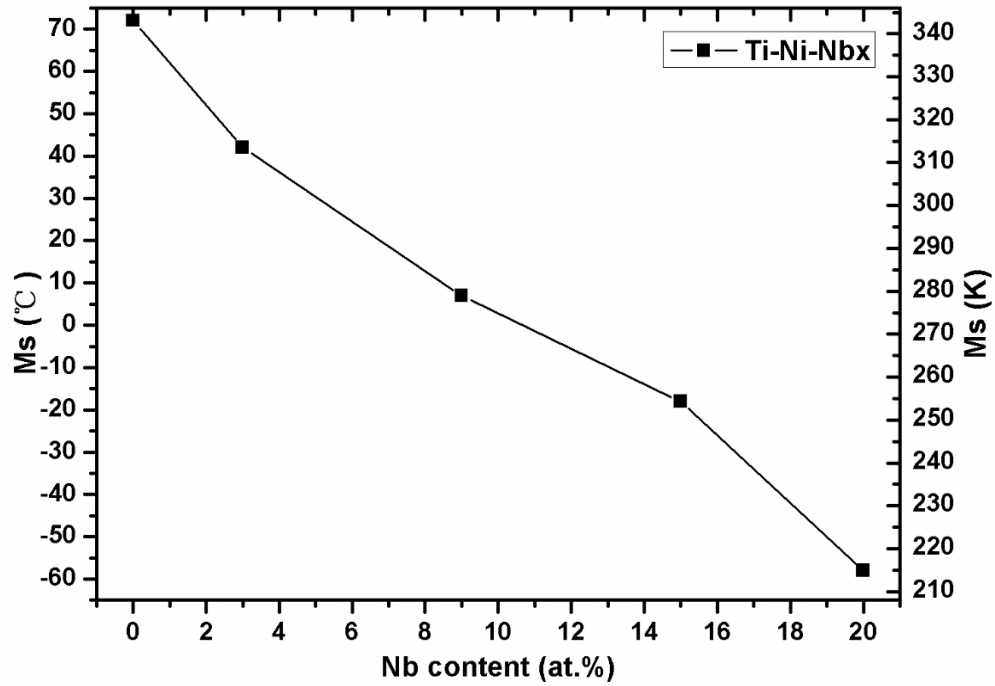


Figure 7.5. Nb decreases the Ms of Ti-Ni SMA and slightly increases the As, which leading large temperature hysteresis in TiNiNb SMA. The Nb content and Ms shows near linear relation in TiNiNb alloys [33].

In order to compare the results with ultralow-fatigue thin film sample in literature [142], a Ti-rich SMA with $\text{Ti}_{54}\text{Ni}_{34}\text{Cu}_{12}$ composition has been chosen for alloying, see Figure 7.6. Except for having a good thermal stability as TiNiCu alloys, this alloys (i.e. $\text{Ti}_{54}\text{Ni}_{34}\text{Cu}_{12}$) has a very narrow transformation peak and small hysteresis compared with the $\text{Ti}_{51}\text{Ni}_{39}\text{Cu}_{10}$ SMA produced by SDA process. By adding Nb from 1 at. % to 3

at.%, the M_s of alloys decreased from 338K to 283K, but the thermal stability stayed as good as the base alloy. Hence, we can conclude that the Nb decreases the M_s , but does not negatively affect the thermal stability of $\text{Ti}_{51-0.5x}\text{Ni}_{39-0.5x}\text{Cu}_{10}\text{Nb}_x$ SMA when the Nb content is lower than 3 at.%. The influence of Nb on M_s can be described as below:

$$M_s (\text{K}) = -19x (\text{at. \%}) + 338 \quad \text{Equation 7.5}$$

Compared to the influence of Nb content on M_s of TiNiNb SMA, the M_s decreases faster in $\text{Ti}_{51-0.5x}\text{Ni}_{39-0.5x}\text{Cu}_{10}\text{Nb}_x$ alloys (-6.3 K/at. % in $\text{Ti}_{51-0.5x}\text{Ni}_{49-0.5x}\text{Nb}_x$ SMA). Cu and Nb also have a negative influence to each other on transformation temperature. As such, the addition of Nb-content will be limited in further alloy development.

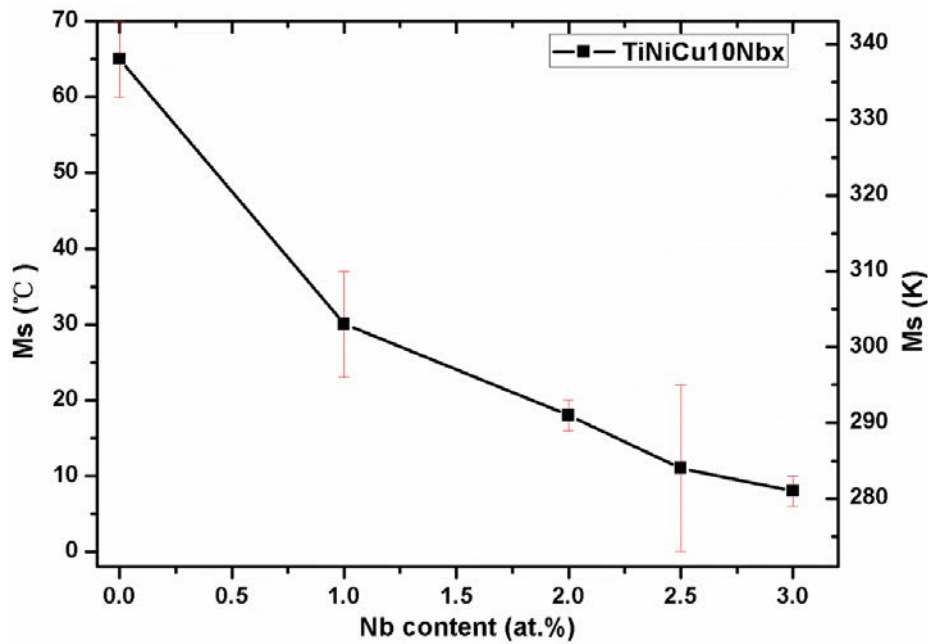


Figure 7.6. $\text{Ti}_{51-0.5x}\text{Ni}_{39-0.5x}\text{Cu}_{10}\text{Nb}_x$ produced by SDA process shows Nb decreases the M_s but the hysteresis remains the same level as Ti-Ni alloys and the thermal stability is as good as TiNiCu SMA.

From the microstructure of these alloys, it can be found that the β -Nb particles occurs around the precipitates and the EDS results shows the Nb content in the matrix does not excess 1 at. % as the overall Nb content of the alloys increases. The Figure 7.7 shows the backscatter images of TiNiCuNb samples. The average spacing between $\text{Ti}_2(\text{Ni,Cu})$ precipitates (dark contrast particles) are around $20\mu\text{m}$ and the area fraction of white particles (Nb-rich) increases as the Nb content increasing. Most Nb-rich particles appear around the $\text{Ti}_2(\text{Ni,Cu})$ precipitates and the typical Nb content around $\text{Ti}_2(\text{Ni,Cu})$ precipitates is 2 to 4 at.% from EDS results (marked as 2 in Figure 7.7), while the Nb content in the matrix varied from 0.5 at.% to 1.6 at.% as the Nb increases from 1 to 3 at.% (marked as 1 in Figure 7.7). No Ti_2Cu precipitates were found in these sample and the $\text{Ti}_2(\text{Ni,Cu})$ precipitates contents more Ni than Cu, which is totally different from the thin film materials. The EDS point analysis on the β -Nb particles shows 6 to 67 at.% Nb content (marked as 3 in Figure 7.7), but considering the size of the these particles (the size of Nb-rich particles is less than $5\mu\text{m}$ while the index area of EDS in SEM is about $10\mu\text{m}$), the accuracy of EDS results in SEM is limited. This indicates that the Nb affects the transformation behaviour by changing the misfit between the matrix and precipitates, instead of altering the lattice parameters of matrix like Cu and Hf. In order to alter the amount of Nb-rich particles, the Nb content has to be about 2 at. % in TiNiCuNb alloys and TiNiCuHfNb alloys. The low magnification image Figure 7.7 (d) shows the TiNiCuNb samples built by SDA have homogeneous microstructure and fine

precipitates.

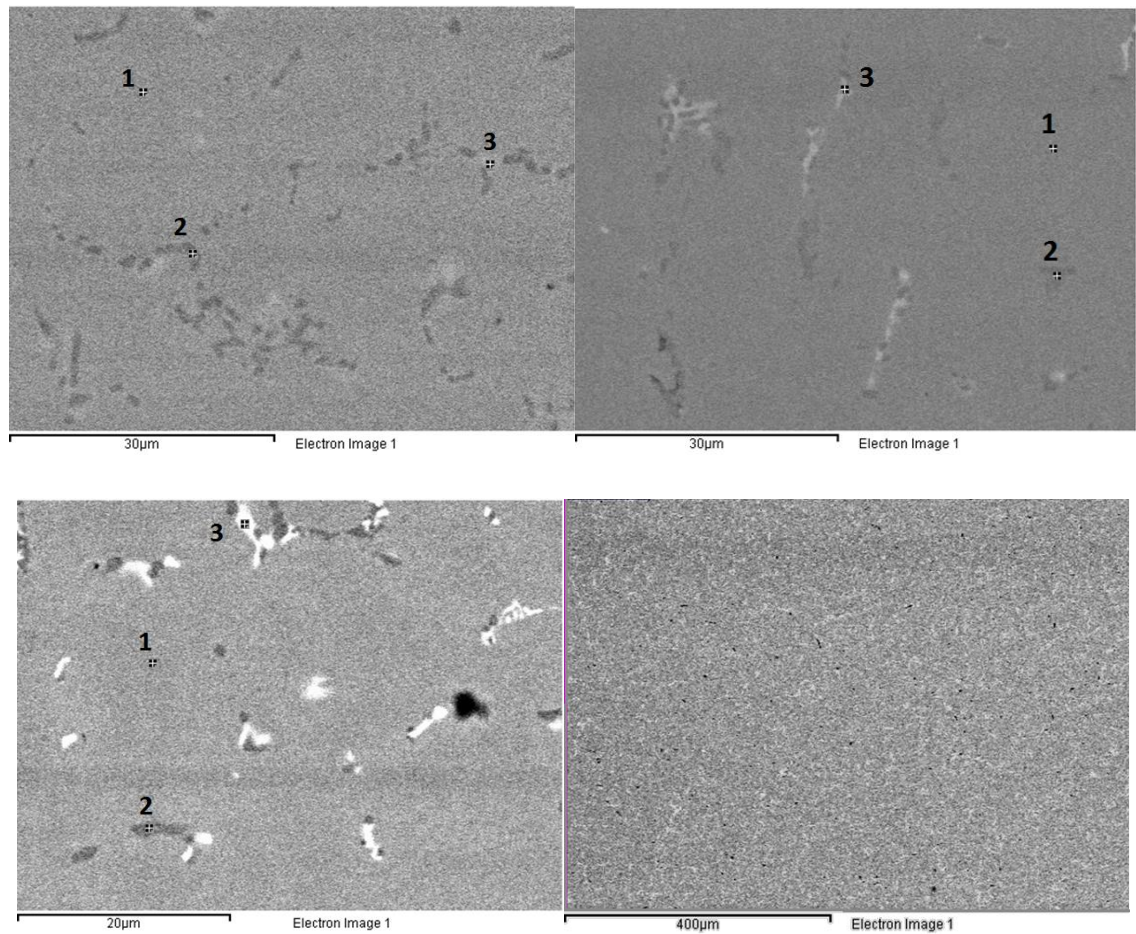


Figure 7.7. Backscatter image of $\text{Ti}_{51-0.5x}\text{Ni}_{39-0.5x}\text{Cu}_{10}\text{Nb}_x$ samples produced by SDA. The sample with 1 at. % Nb (a) has a few Nb-rich particles (white) around the $\text{Ti}_2(\text{Ni,Cu})$ precipitates. The sample with 2 at. % Nb (b) has larger Nb-rich particles around the precipitates. The sample with 3 at. % Nb (c) shows more Nb-rich particles with 2 to 3 μm size around the $\text{Ti}_2(\text{Ni,Cu})$. (d) shows low magnification backscatter image of $\text{Ti}_{49.5}\text{Ni}_{37.5}\text{Cu}_{10}\text{Nb}_3$ SMA.

Table 7.1. EDS analysis results of TiNiCuNb samples

Sample	Ti ₅₀ Ni ₃₉ Cu ₁₀ Nb ₁	Ti ₅₀ Ni ₃₈ Cu ₁₀ Nb ₂	Ti ₅₀ Ni ₃₇ Cu ₁₀ Nb ₃
1 (matrix)	Ti ₅₀ Ni ₄₂ Cu ₈	Ti ₅₀ Ni ₄₂ Cu ₇ Nb ₁	Ti ₅₀ Ni _{41.5} Cu _{7.5} Nb ₁
2 (precipitate)	Ti ₅₅ Ni ₃₂ Cu ₁₁ Nb ₂	Ti ₆₃ Ni ₂₈ Cu ₆ Nb ₂	Ti ₆₀ Ni ₂₈ Cu ₉ Nb ₃
3 (precipitate)	To ₅₀ Ni ₃₈ Cu ₁₁ Nb ₁	Ti ₅₅ Ni ₁₄ Cu ₅ Nb ₂₆	Ti ₆₀ Ni ₂₈ Cu ₈ Nb ₄
Area analysis	Ti ₅₀ Ni ₃₉ Cu ₁₀ Nb ₁	Ti ₄₉ Ni ₃₉ Cu ₁₀ Nb ₂	Ti ₅₀ Ni ₃₇ Cu ₁₀ Nb ₃

Since the Nb does not affect the thermal stability of TiNiCu alloys and the decrement of M_s is acceptable, the next step is adding Hf into the alloys to alter transformation temperature and assess the thermal stability of TiNiCuHfNb alloys. Since the TiNiHfCu alloys with 5% Cu has higher M_s , two different series alloys were produced, which are $Ti_{41-x}Ni_{44-x}Cu_5Hf_{10}Nb_{2x}$ and $Ti_{41-x}Ni_{39-x}Cu_{10}Hf_{10}Nb_{2x}$ respectively. Some of the composition showed two peaks transformation before heat treatment but the all of them showed single peak transformation after 1273 K 3 h heat treatment and the transformation temperature were similar before and after heat treatment. Six and eleven cycles DSC testing were applied to investigate the thermal stabilities of TiNiCuHfNb samples. It indicated the increasing of Nb content decreased the M_s of these alloys but the thermal stability stayed the same level (decreased from 10 K for 1 at.% Nb alloys and 13 K for 3 at.% Nb alloys). The M_s of $Ti_{41-x}Ni_{44-x}Cu_5Hf_{10}Nb_{2x}$ alloys was slightly higher than the 10 at.% Cu alloys (22K higher), but the thermal stability of 10 at.% Cu

sample was better than the alloy with 5 at.% Cu. The hysteresis of these samples were lower than 40 K, which was close the the Ti-Ni binary alloys (40 K). Therefore, Nb can be applied to TiNiCu and TiNiCuHf alloys for improving thermal-mechanical fatigue properties.

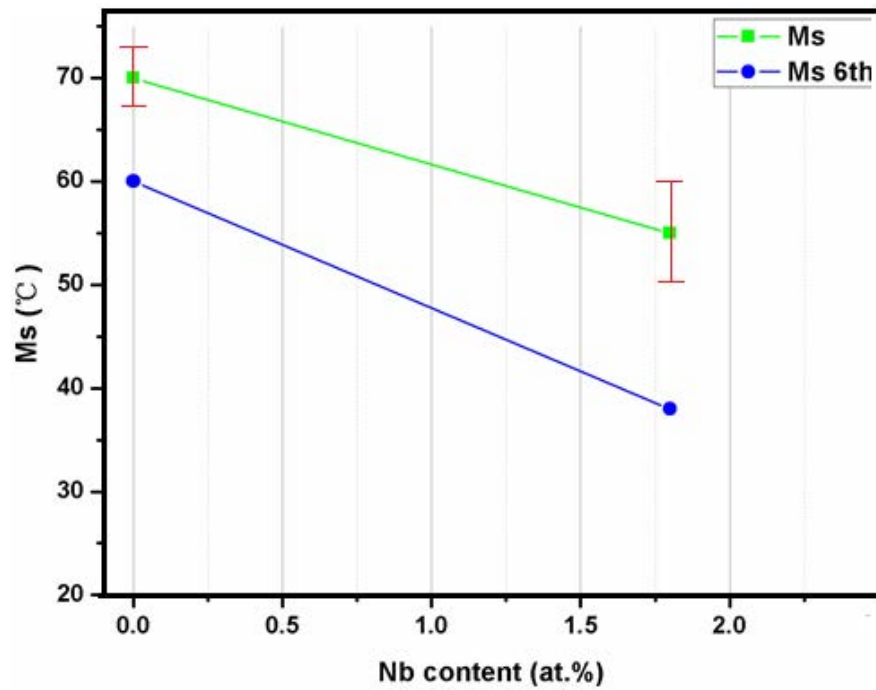


Figure 7.8. Transformation temperature and thermal cycle stability of $\text{Ti}_{41-x}\text{Ni}_{44-x}\text{Cu}_5\text{Hf}_{10}\text{Nb}_{2x}$ SMA.

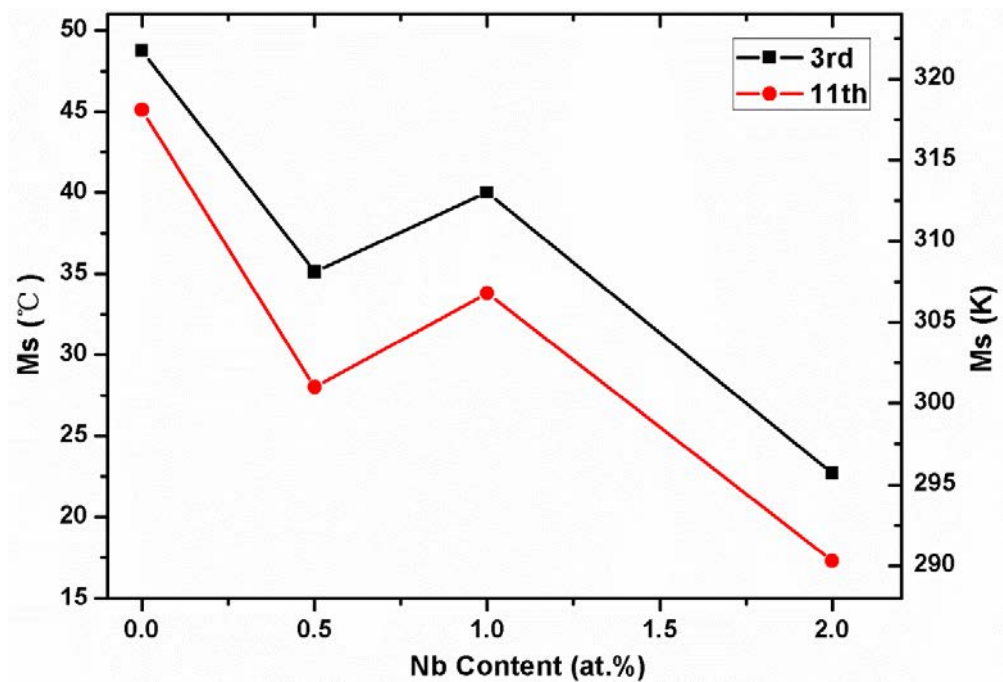


Figure 7.9. Transformation temperature and thermal cycle stability of $\text{Ti}_{41-x}\text{Ni}_{39-x}\text{Cu}_5\text{Hf}_{10}\text{Nb}_{2x}$ SMA. The alloy with 1 at.% Nb has higher Ms than the others but the thermal stability is the worst.

The decrease in Ms per cycles increased as the Nb content increased from 0.5 at.% to 1 at.% but decreased as the Nb content reached 2 at.%, see Figure 7.10. Although the 1 at.% Nb alloy has higher Ms than the others, the thermal cycle stability was the poorest among these compositions. As such, 2 at.% Nb addition was chosen for further research. The variation of transformation heat increased as the Nb content increased see Figure 7.11. Since the Nb content in matrix stays constant when Nb content higher than 1%, the transformation heat significantly affected by Nb-rich particles around the precipitates. There is some research using dH (ΔH), which is the transformation heat

between austenite and martensite transformation, to analyse the transformation behaviour, but the dH in $\text{Ti}_{40}\text{Ni}_{43}\text{Hf}_{10}\text{Cu}_{10}\text{Nb}_2$ sample shows no clear relation between the other transformation parameters (Figure 7.12).

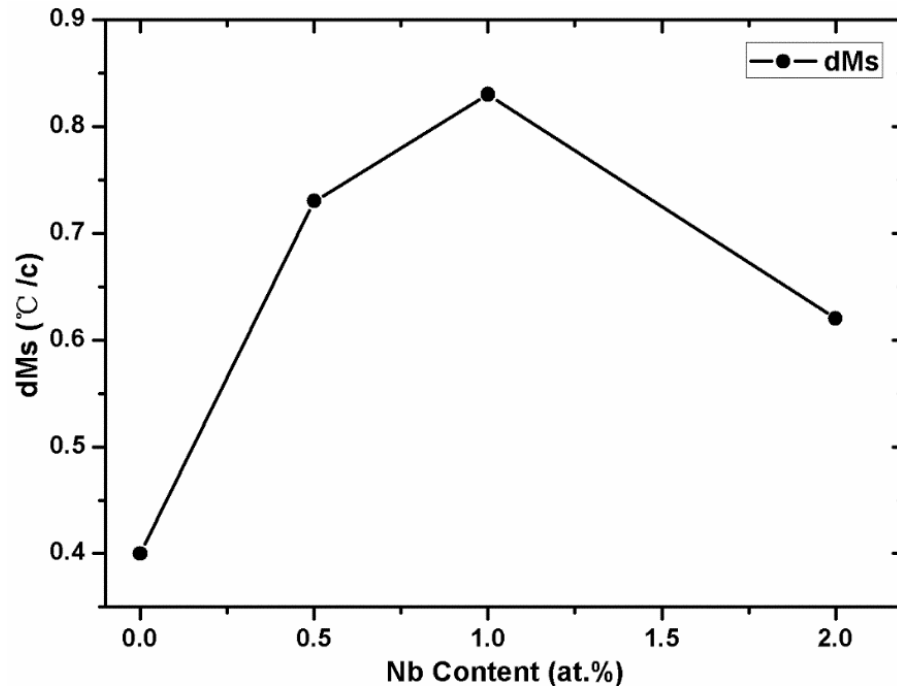


Figure 7.10. Influence of Nb content on thermal cycle stability of TiNiCuHfNb SMA shows the thermal stability increases until the Nb content raises up to 1 at.% and the 2 at.% Nb alloy has the best thermal cycle stability.

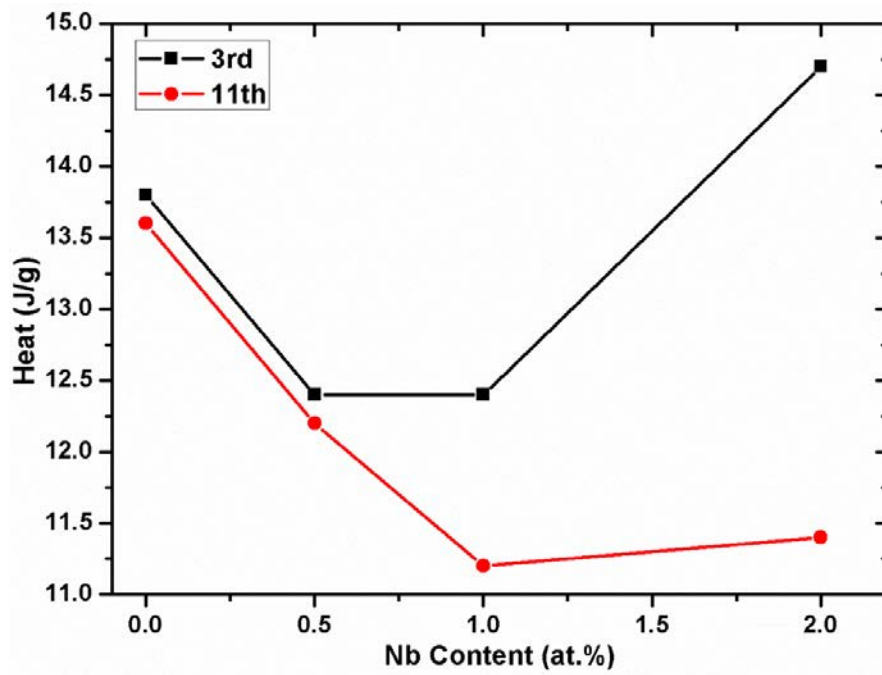


Figure 7.11. Influence of Nb content on transformation heat during the third and the eleventh thermal cycle. The transformation heat increases as Nb content increasing.

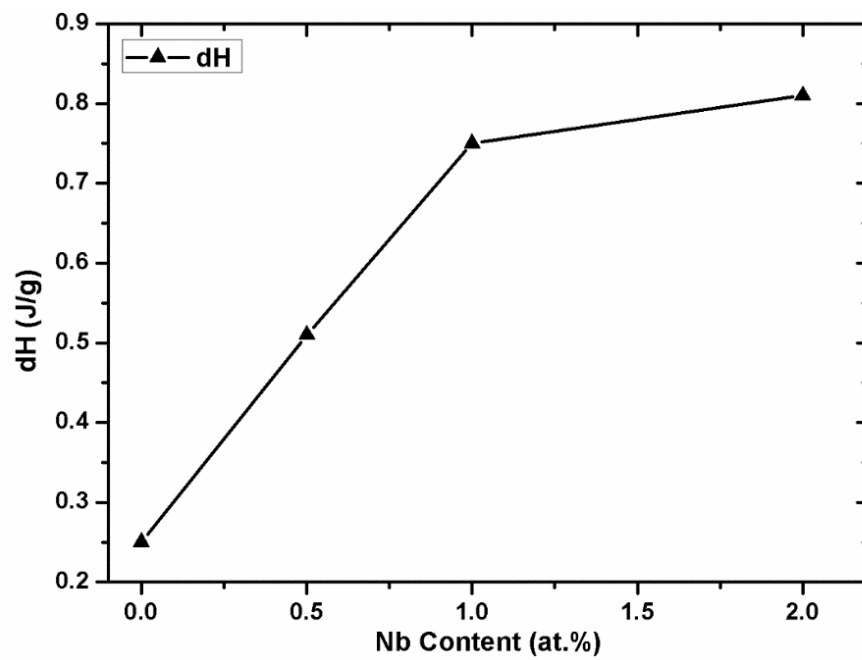


Figure 7.12. Transformation heat difference between austenite and martensite transformation

7.4 Precipitates controlled by chemical composition in TiNiHfCuNb

alloys

7.4.1 Different performance in TiNiHfCuNb SMAs with similar composition

Two alloys with similar composition, which were $\text{Ti}_{43}\text{Ni}_{33}\text{Hf}_{10.5}\text{Cu}_{11}\text{Nb}_{2.5}$ and $\text{Ti}_{44}\text{Ni}_{34}\text{Hf}_{10}\text{Cu}_{10}\text{Nb}_2$, were produced. However, the DSC result showed these alloys have completely different transformation behaviours under thermal cycle as shown in the Figure 7.13 and Figure 7.14. The top one was $\text{Ti}_{43}\text{Ni}_{33}\text{Hf}_{10.5}\text{Cu}_{11}\text{Nb}_{2.5}$ alloys which has low transformation temperature ($M_s = 251 \text{ K}$ or $-22 \text{ }^\circ\text{C}$), but the transformation curves had no difference between thermal cycles (there were 3 cycles in the figure and all of them were overlapped) and the peak width for transformation was very big. The Figure 7.14 was $\text{Ti}_{44}\text{Ni}_{34}\text{Hf}_{10}\text{Cu}_{10}\text{Nb}_2$ alloys in 7 thermal cycles, the transformation temperature was higher ($M_s = 305 \text{ K}$ or $32 \text{ }^\circ\text{C}$), but the thermal stability of this alloy was worse than the other (M_s dropped from 305 K to 298 K in 7 cycles). The EDS area analysis result showed the average composition of these alloys were $\text{Ti}_{44.8}\text{Ni}_{34}\text{Hf}_{10}\text{Cu}_{8.5}\text{Nb}_{2.7}$ and $\text{Ti}_{42}\text{Ni}_{33}\text{Hf}_{10.5}\text{Cu}_{12}\text{Nb}_{2.5}$ respectively, which were close to target composition.

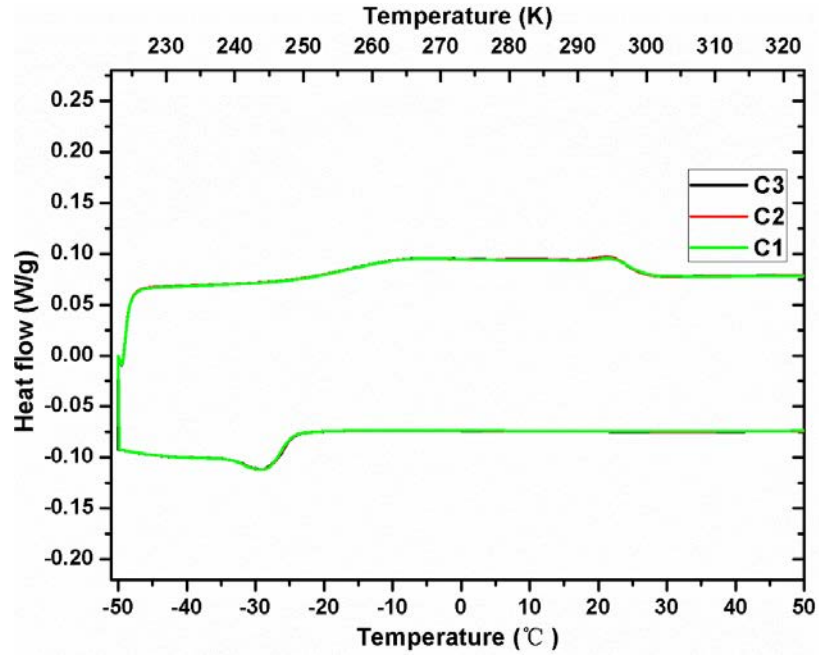


Figure 7.13. DSC curve of $\text{Ti}_{43}\text{Ni}_{33}\text{Hf}_{10.5}\text{Cu}_{11}\text{Nb}_{2.5}$ sample showed low M_s (251 K), wide transformation peak (50 K) and good thermal cycle stability (three cycles overlapped).

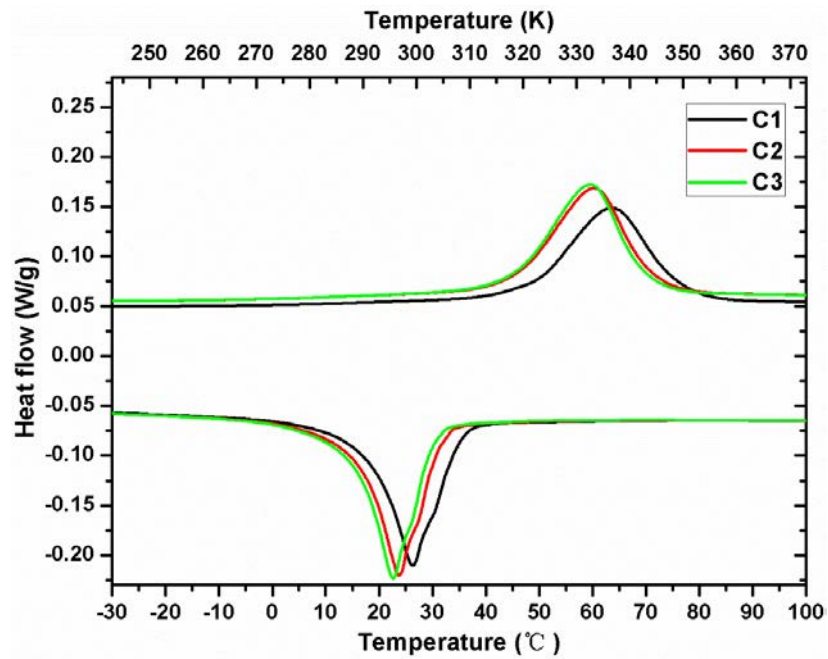


Figure 7.14. DSC curve of $\text{Ti}_{44}\text{Ni}_{34}\text{Hf}_{10}\text{Cu}_{10}\text{Nb}_2$ sample showed high M_s (305K), narrow transformation peak (30K) and poor thermal cycle stability.

7.4.2 Microstructure of TiNiHfCuNb SMAs

From the backscatter images (Figure 7.15 and Figure 7.16), they showed different microstructure in these samples. The low transformation temperature sample had finer precipitates distribution and smaller grains size, while the high transformation temperature sample had coarser grains and a few different type of precipitates. This consist with the theory of ultralow-fatigue TiNiCu sample which was the $Ti_2(Ni,Cu)$ particles reduced the stress field of martensitic lattice around them and improved the thermal-mechanical stability. However, comparing with the size of precipitates in bulk materials (5-10 μm) and thin film, the size in bulk materials was much bigger. Hence, there must be another reason for the improvement of stability (for example the small particles around precipitates and different precipitates present in the samples). In order to investigate the particles in our bulk materials, EDS mapping has been done (see Figure 7.17). The yellow frames showed the mapping area and different colour indicated different elements. It shows that the precipitates are Ti-rich, but it did not show high Hf content in the precipitates. The Nb concentrated as spots within and around the precipitates. The point EDS analysis showed the darkest contrast area was $Ti_{60}Ni_9Cu_5Hf_5Nb_{21}$, the medium contrast part of precipitates was $Ti_{57}Ni_{28}Cu_5Hf_8Nb_2$ while the matrix was $Ti_{39}Ni_{38}Cu_{11}Hf_{11}Nb_1$. The line scan in Figure 7.19 showed lower Hf, Cu and Ni content near the precipitates while the Nb content increased.

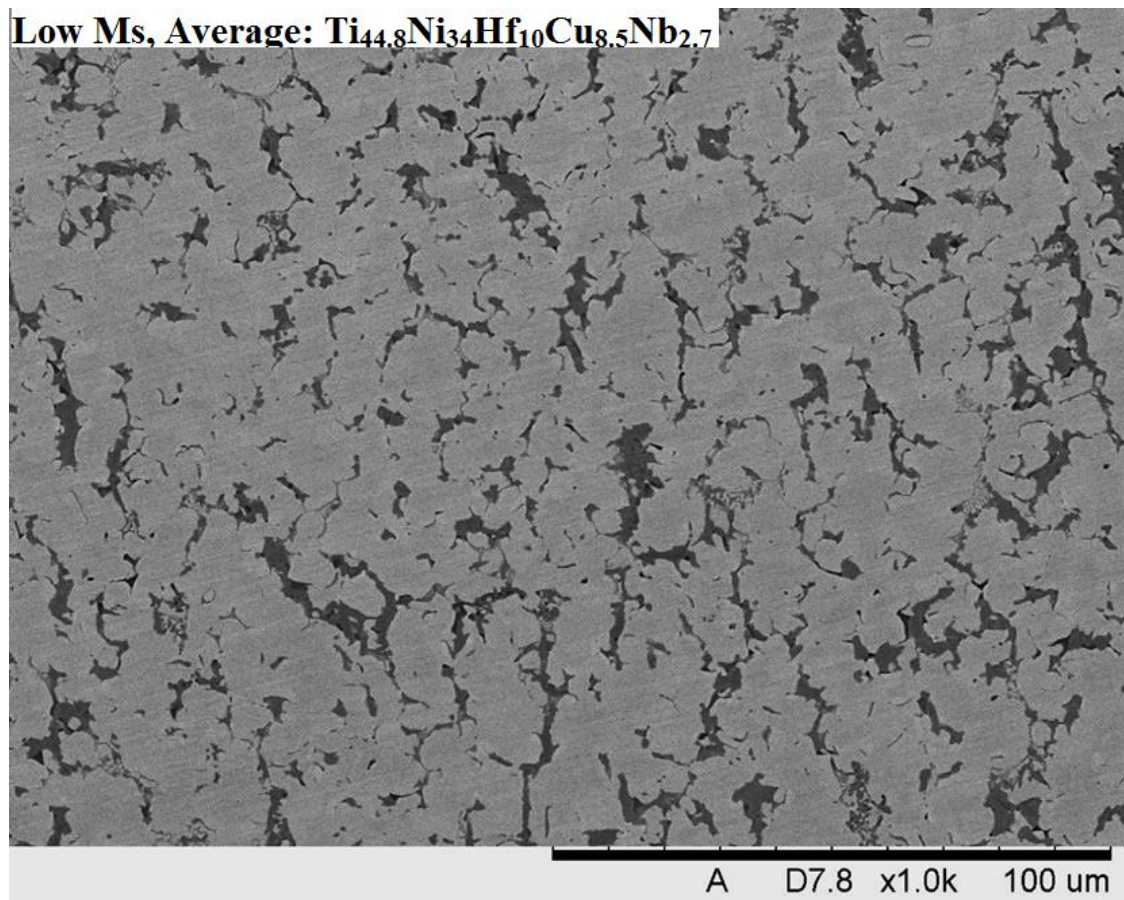


Figure 7.15. Backscatter image of low Ms $\text{Ti}_{43}\text{Ni}_{33}\text{Hf}_{10.5}\text{Cu}_{11}\text{Nb}_{2.5}$ sample shows fine dendrite and Ti(Hf)-rich precipitates around dendrite boundary. The EDS area analysis result show the composition of sample is $\text{Ti}_{44.8}\text{Ni}_{34}\text{Hf}_{10}\text{Cu}_{8.5}\text{Nb}_{2.7}$.

Comparing the matrix composition between these samples (Table 7.2. Chemical composition in $\text{Ti}_{43}\text{Ni}_{33}\text{Hf}_{10.5}\text{Cu}_{11}\text{Nb}_{2.5}$ and $\text{Ti}_{44}\text{Ni}_{34}\text{Hf}_{10}\text{Cu}_{10}\text{Nb}_2$ samples analysed by EDS), we found that the Ti content in low Ms sample was 2 at.% lower than the high Ms, but the Hf content in low Ms one was 1 at.% higher. Moreover, the Cu content in low Ms sample was 2 at.% higher than high Ms sample. The total element content of Ti and Hf in the matrix of low Ms sample was 50 at.% which was 1 at.%

lower than the matrix composition of high Ms sample. Although the lower Ti+Hf content and higher Cu content decreased the Ms, these elements increased the thermal mechanical stability in Ti-Ni-based SMA. The results shown in these specified alloys were much higher than the influence mentioned in section 7.3. Hence, there might be the other mechanism affects the transformation behaviour in these samples.

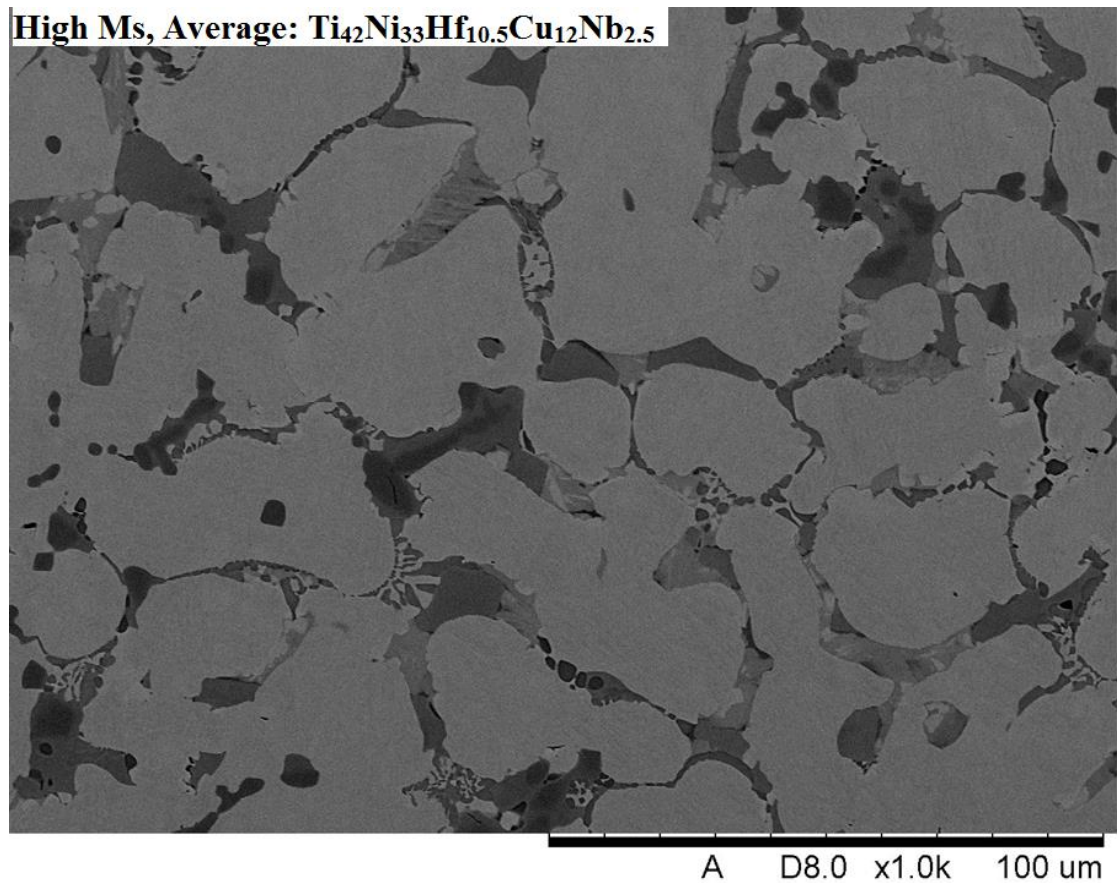


Figure 7.16. Backscatter image of high Ms $\text{Ti}_{44}\text{Ni}_{34}\text{Hf}_{10}\text{Cu}_{10}\text{Nb}_2$ sample shows larger dendrite size and 4 different type of precipitates, which are dark contrast, medium contrast, light contrast and flower shape. The EDS area analysis result shows the sample composition is $\text{Ti}_{42}\text{Ni}_{33}\text{Hf}_{10.5}\text{Cu}_{12}\text{Nb}_{2.5}$

Table 7.2. Chemical composition in $\text{Ti}_{43}\text{Ni}_{33}\text{Hf}_{10.5}\text{Cu}_{11}\text{Nb}_{2.5}$ and $\text{Ti}_{44}\text{Ni}_{34}\text{Hf}_{10}\text{Cu}_{10}\text{Nb}_2$ samples analysed by EDS

Sample	$\text{Ti}_{43}\text{Ni}_{33}\text{Hf}_{10.5}\text{Cu}_{11}\text{Nb}_{2.5}$	$\text{Ti}_{44}\text{Ni}_{34}\text{Hf}_{10}\text{Cu}_{10}\text{Nb}_2$
Matrix	$\text{Ti}_{39}\text{Ni}_{38}\text{Cu}_{11}\text{Hf}_{11}\text{Nb}_1$	$\text{Ti}_{41}\text{Ni}_{38}\text{Cu}_9\text{Hf}_{10}\text{Nb}_1$
Precipitate (Dark)	$\text{Ti}_{60.5}\text{Ni}_9\text{Cu}_{4.5}\text{Hf}_5\text{Nb}_{21}$	$\text{Ti}_{60}\text{Ni}_{27}\text{Cu}_4\text{Hf}_7\text{Nb}_2$
Precipitate (light)	$\text{Ti}_{57}\text{Ni}_{28}\text{Cu}_5\text{Hf}_8\text{Nb}_2$	$\text{Ti}_{55}\text{Ni}_{28}\text{Cu}_7\text{Hf}_8\text{Nb}_2$
Area average	$\text{Ti}_{44.8}\text{Ni}_{34}\text{Hf}_{10}\text{Cu}_{8.5}\text{Nb}_{2.7}$	$\text{Ti}_{42}\text{Ni}_{33}\text{Hf}_{10.5}\text{Cu}_{12}\text{Nb}_{2.5}$

In the high transformation temperature (Ms) sample, the large precipitate in the center was Ti-rich with lower Hf and Cu content comparing with the lighter contrast particles on the left and right. Those finer particles on the top had much higher Nb content than the other area. The point analysis showed the center particles were $\text{Ti}_{60}\text{Ni}_{27}\text{Cu}_4\text{Hf}_7\text{Nb}_2$ and the matrix is $\text{Ti}_{41}\text{Ni}_{38}\text{Cu}_{10}\text{Hf}_{10}\text{Nb}_1$. Unfortunately, the small particles were too small for SEM EDS analysis. The line scan in Figure 7.21 did not show clear reduction of Hf or Cu around the precipitates but the Nb content increased and Ti content decreased at the small spots (flower shape) precipitates area. This indicated that the gap between flower shape precipitates contained Nb-rich particles.

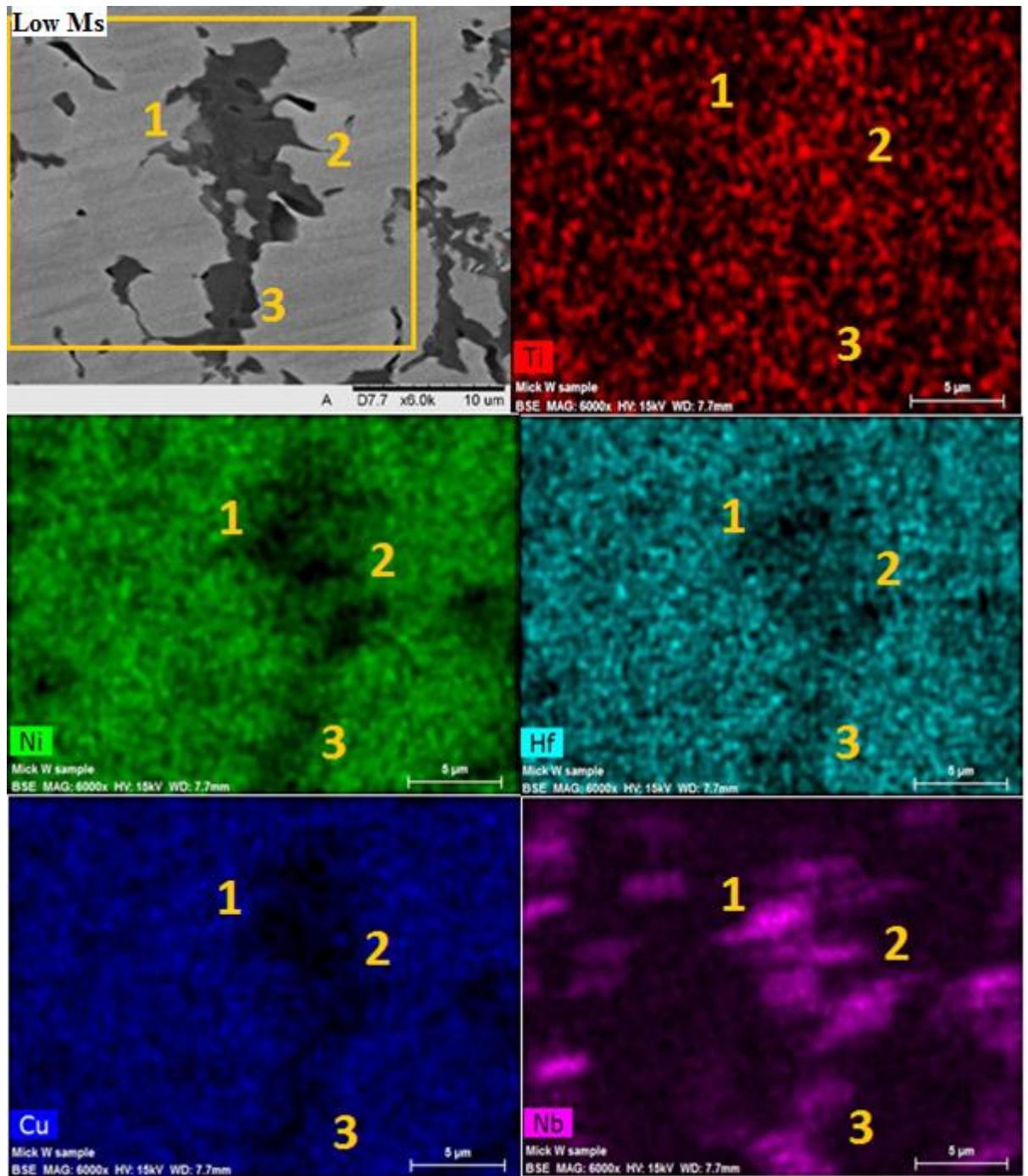


Figure 7.17. EDS mapping around the precipitates in $\text{Ti}_{43}\text{Ni}_{33}\text{Hf}_{10.5}\text{Cu}_{11}\text{Nb}_{2.5}$ low Ms sample shows three different types of precipitates.

The EDS mapping around the precipitates in low Ms sample (Figure 7.17 and Figure 7.18) showed significant higher Nb and slightly higher Ti content in the precipitates in low Ms sample but the Nb-rich area was not continuously. Also it showed three different precipitates which were light contrast area marked as 1 in Figure 7.17, medium contrast area near mark 2, dark contrast area marked as 3 and the lightest contrast precipitates marked as 4. The precipitate marked as 1 has lower Ni and Cu content as dark area can be found in these element map, and the Hf content was lower than matrix but higher than the precipitate regions with dark contrast, so it could be Ti-rich and Nb-rich $(\text{Ti,Hf,Nb})_2(\text{Ni,Cu})$ with some Hf replacing Ti. The low Hf content area on the right was the center of the precipitate, which shows a few pattern in backscatter image. The dark contrast precipitate below mark 2 had the lowest Ni, Cu and Hf content, so it might be Ti-rich and Nb-rich $(\text{Ti,Hf,Nb})_2(\text{Ni,Cu})$ without Hf and Cu. Comparing to area 2, precipitate on the left of mark 3 and 3' with dark contrast had higher Hf and Cu content, so it could be $(\text{Ti,Hf})_2(\text{Ni,Cu})$ precipitates with Hf and Cu and less Nb. The light contrast precipitates beside mark 4 had lower Hf, Cu content and slightly lower Ni content than matrix area. But the Nb content was lower than the other precipitates. In addition, the EDS mapping shows a slightly higher Cu content in matrix around the precipitates which also indicated by the lighter contrast around precipitates in backscatter image.

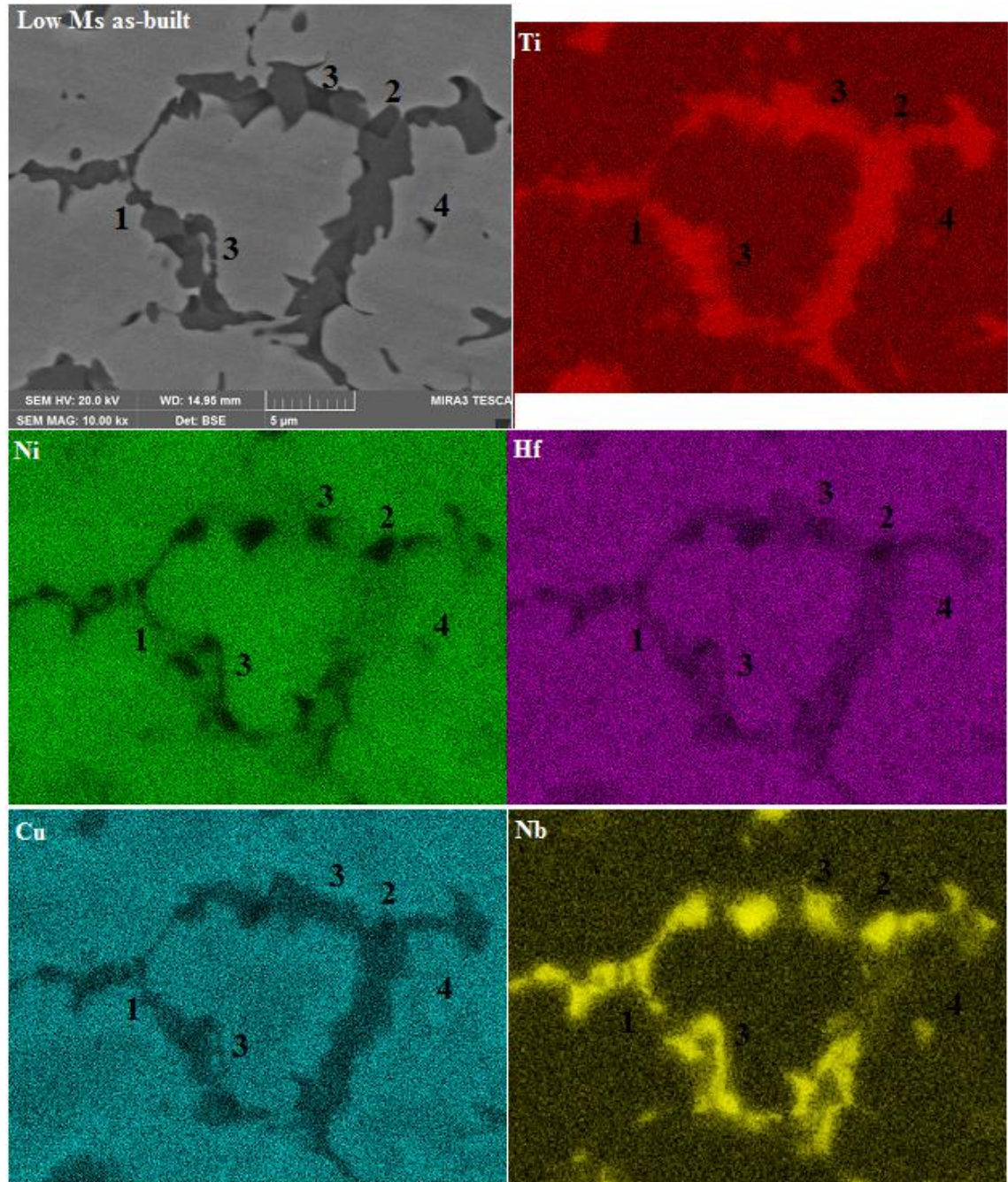


Figure 7.18. EDS mapping around the precipitates in $\text{Ti}_{43}\text{Ni}_{33}\text{Hf}_{10.5}\text{Cu}_{11}\text{Nb}_{2.5}$ low Ms as-built sample shows high Nb content in the precipitates with the darkest contrast. The precipitates generally have higher Ti and Nb content.

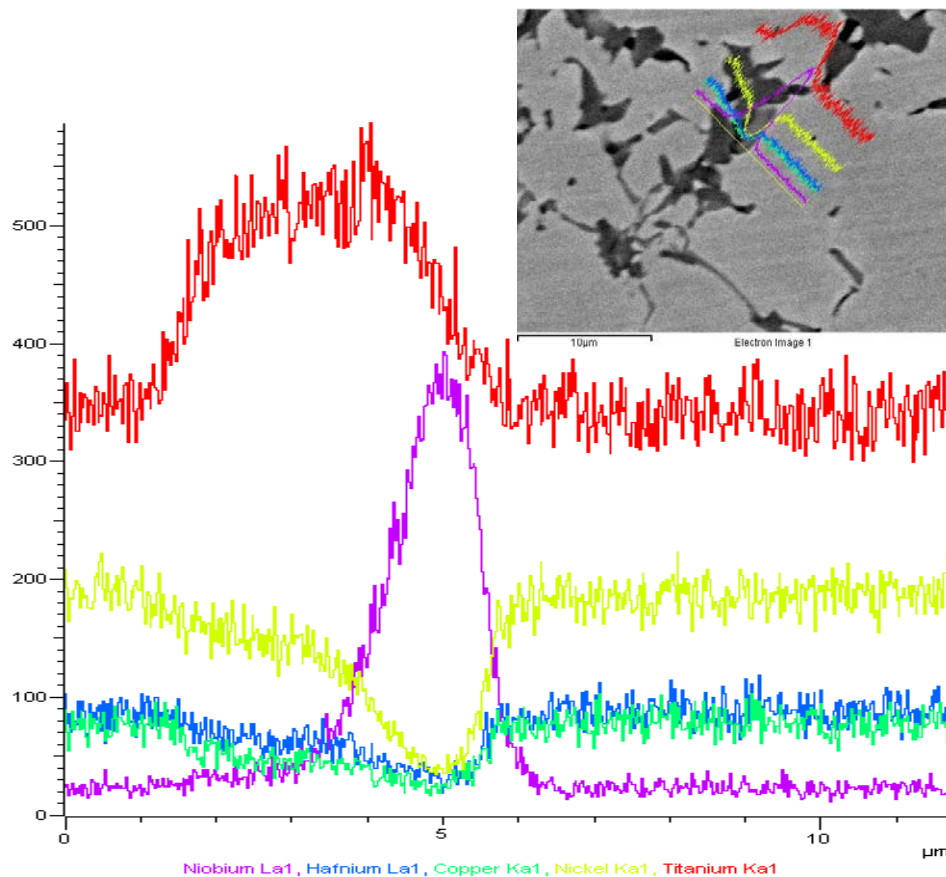


Figure 7.19. EDS line analysis cross precipitates in $\text{Ti}_{43}\text{Ni}_{33}\text{Hf}_{10.5}\text{Cu}_{11}\text{Nb}_{2.5}$ low Ms sample shows high Ti content in precipitate but the Ti content start decreasing at the darkest contrast area while the Nb content increases. The Ni content is slightly higher near the precipitates.

The EDS mapping in high Ms sample (Figure 7.20) showed the Nb-rich areas were around the fine separated precipitates marked as 1 in Figure 7.20. Both Ni, Cu and Hf show low concentration in these area but the Ti content was slightly higher than matrix area and Nb content was higher. The medium contrast precipitate in the center marked as 2 has lower Ni and Cu content than matrix but less than the other precipitates. The Hf content was slighter lower than the matrix while Nb content was similar to matrix. The

light contrast precipitates on both sides (marked as 3) had lower Ni content while Cu content was slightly higher. Again, these patterns within the precipitates were too small to be investigated by SEM. The matrix around these precipitates also showed slightly higher Cu content in EDS mapping which indicated Cu segregation within the sample.

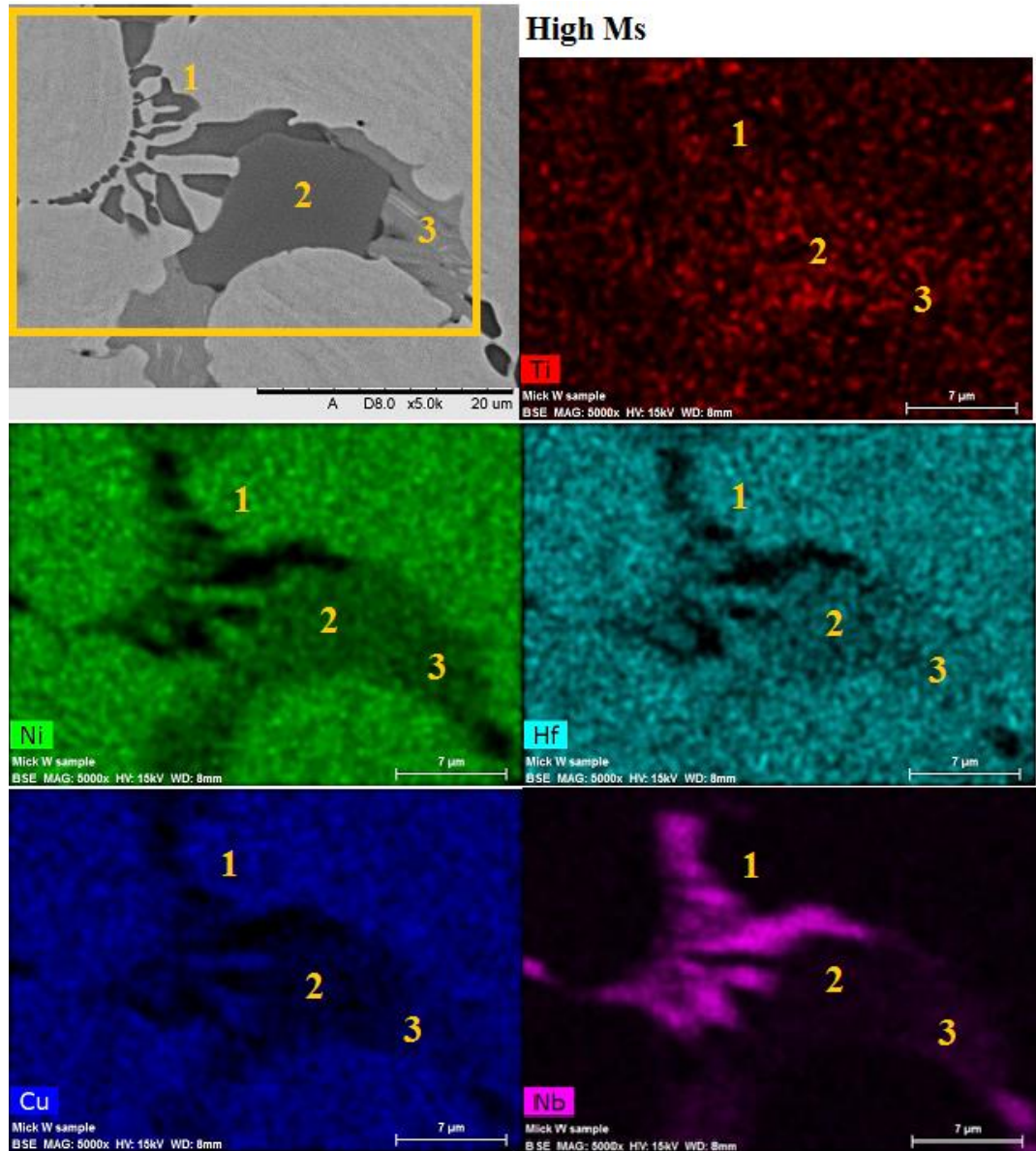


Figure 7.20. EDS mapping around the precipitates in $\text{Ti}_{44}\text{Ni}_{34}\text{Hf}_{10}\text{Cu}_{10}\text{Nb}_2$ high Ms sample shows three different types of precipitates.

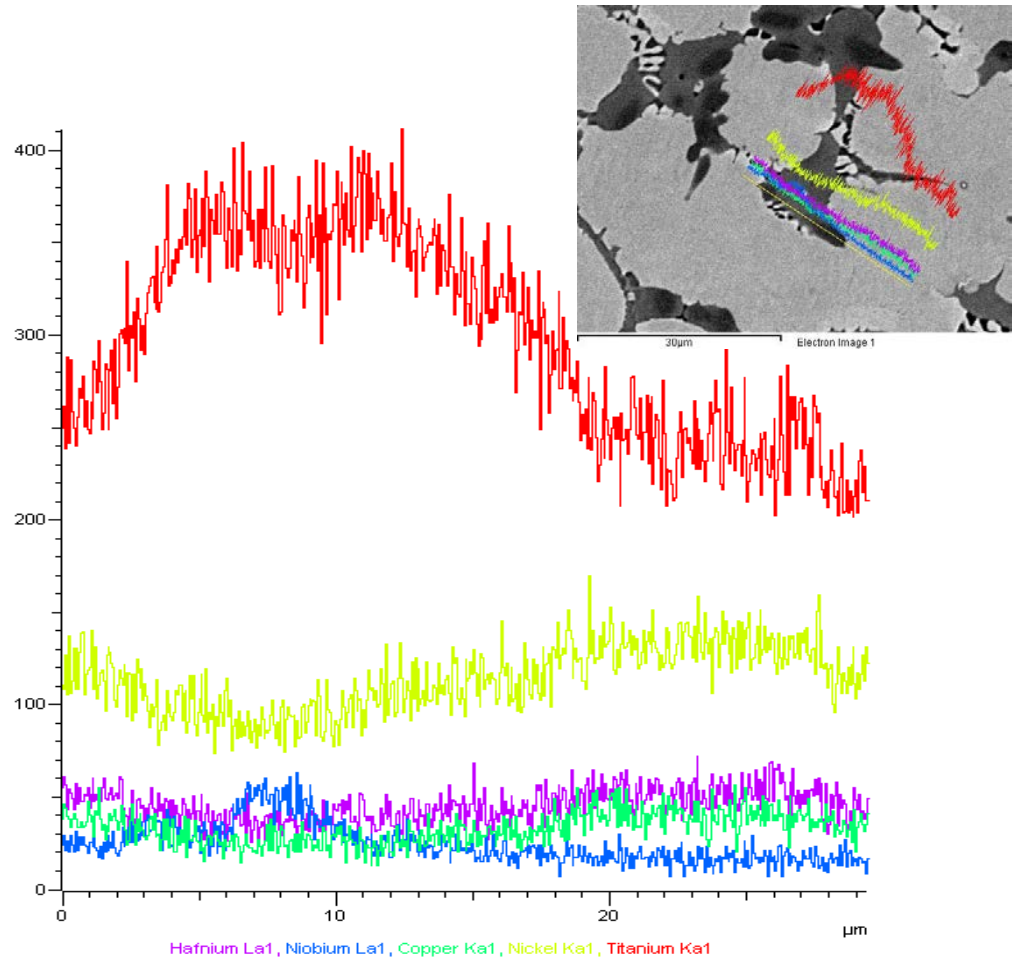


Figure 7.21. EDS line analysis cross precipitates in $\text{Ti}_{44}\text{Ni}_{33}\text{Hf}_{10}\text{Cu}_{10}\text{Nb}_2$ high Ms sample shows high Ti content in precipitate but the Ti content decreases in the flower shape precipitates while the Nb content increases.

7.4.3 X-ray diffraction analysis of TiNiHfCuNb alloys

The XRD result of high Ms alloy (labelled as TiNiHfCuNb_2 in Figure 7.22) at room temperature (RT) shows martensite due to the Ms was higher than RT, while the low Ms sample (labelled as $\text{TiNiHfCuNb}_{2.5}$) showed austenite with some small martensite peak at RT. Since the DSC result of low Ms sample showed the Af was 303 K which was slightly higher than RT, it was possible having some martensite phase under RT. The XRD result of low Ms sample also showed some small peaks, intensity lower than 100, which may refer to the precipitates but these peaks can not be observed in high Ms

sample. Since the microstructure in show four different composition precipitates in high Ms sample, the small peaks in XRD may results from these precipitates.

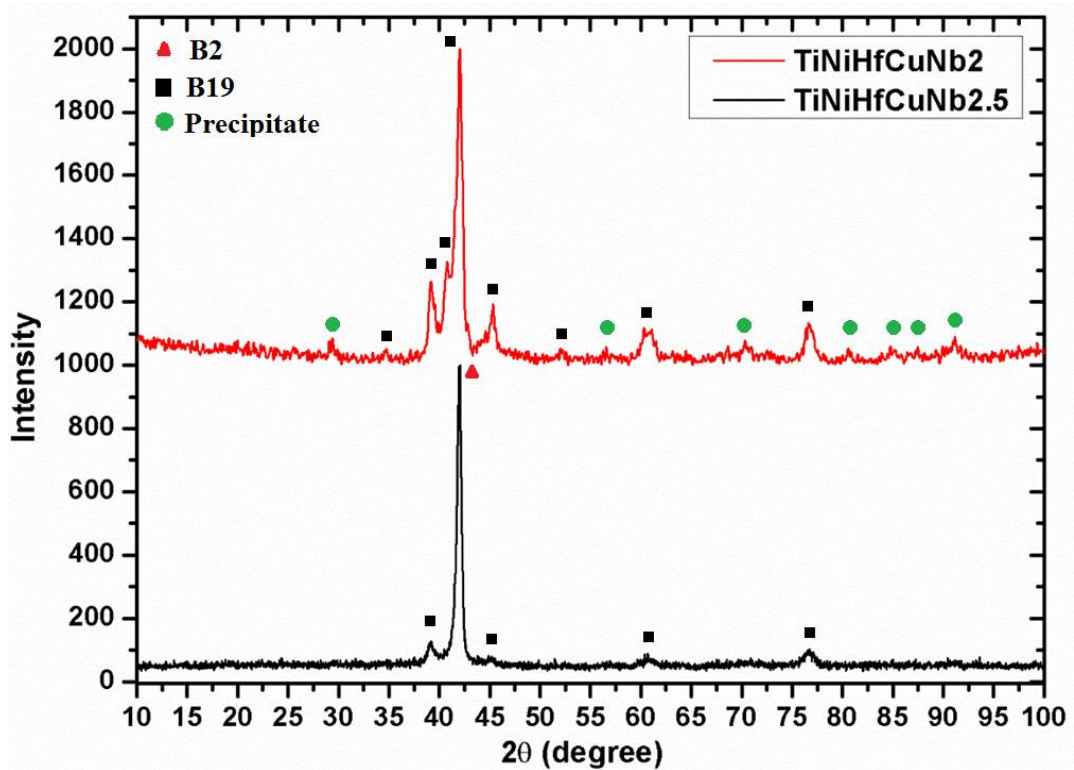


Figure 7.22. XRD result of high Ms (marked as TiNiHfCuNb2) alloy at room temperature shows martensite due to the Ms is higher than room temperature, while the low Ms (TiNiHfCuNb2.5) shows austenite with some small martensite peak at room temperature.

7.4.4 Heat treatment on TiNiHfCuNb samples

In order to homogenise the materials and alter the shape memory properties, homogenise and solution treatment has to be applied on TiNiHfCuNb samples. A DSC testing was performed on the high Ms as-built sample for heat treatment temperature determination. The testing temperature range was from room temperature (RT, 298 K) to 1773 K (limited by DSC testing machine) at 10 K/min and then the sample was

cooled down from 1773 K to 373 K (limited by argon cooling) at 10 K/min. There was an isothermal period held on 1773 K for 15 min before cooling. The testing process was protected by 99.995 % purity argon atmosphere. As shown in Figure 7.23, apart from the austenite transformation peak at 300K, there were four endothermic peaks occurred during heating. The first peak temperature was 1174 K which was slightly lower than the melting temperature of Ti_2Cu (1233 K) and Ti_2Ni (1239 K). This could be referred to the melting of $(\text{Ti, Hf, Nb})_2(\text{Ni, Cu})$ phase with low Nb content which is region 3 in Figure 7.18. EDS mapping around the precipitates in $\text{Ti}_{43}\text{Ni}_{33}\text{Hf}_{10.5}\text{Cu}_{11}\text{Nb}_{2.5}$ low Ms as-built sample shows high Nb content in the precipitates with the darkest contrast. The precipitates generally have higher Ti and Nb content. The second and third endothermic peaks were occurred at 1448 K and 1563 K which could be referred to the melting of matrix (including higher Cu content matrix around precipitates) for the energy (area under the peaks) were larger and the chemical heterogeneity were observed by EDS mapping. The last endothermic peak at 1755 K could be referred to the melting of high Nb content precipitates as the melting point of Nb-Ni phase can go higher than 1720K when the Nb content is greater than 60 at.%.

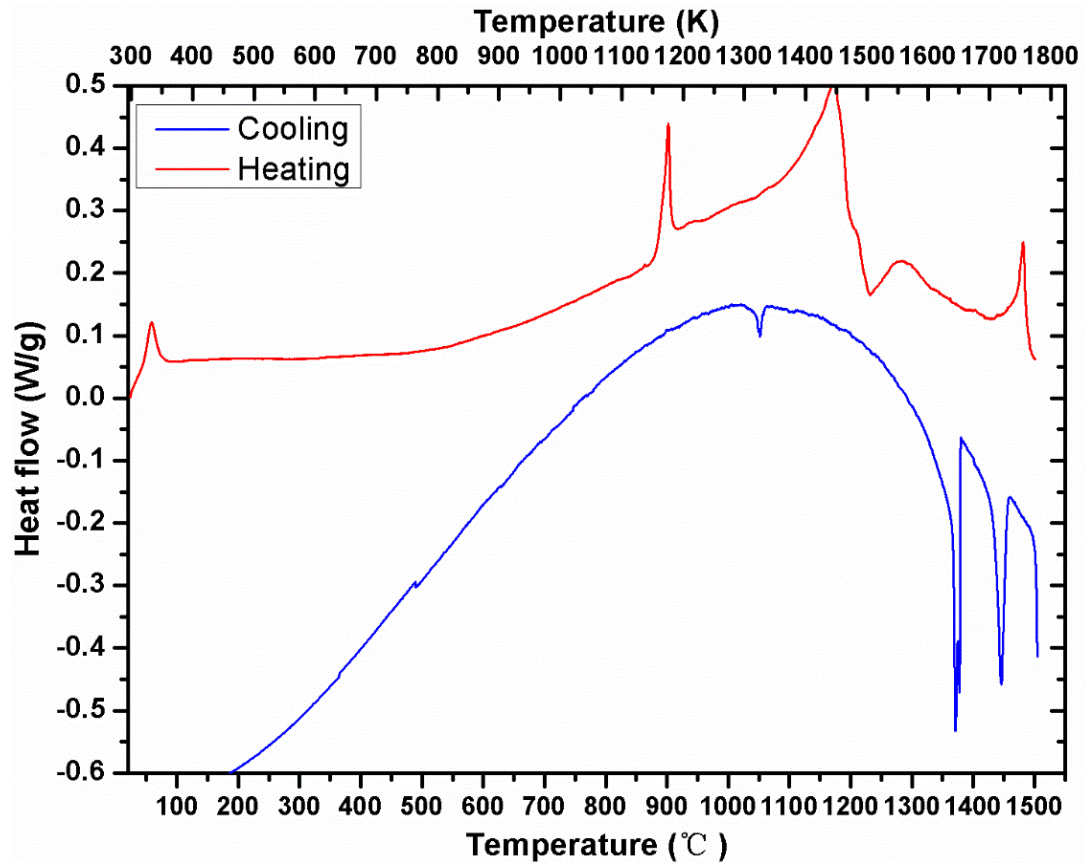


Figure 7.23. High temperature DSC testing result of as-built $\text{Ti}_{44}\text{Ni}_{33}\text{Hf}_{10}\text{Cu}_{10}\text{Nb}_2$ high Ms sample indicates multi-phases and changed of local composition in some phases.

There were 3 exothermic peaks occurred during cooling and the first exothermic was 1719K, which was 36K lower than the last peak during heating and the amount of heat of these peaks were similar. So these peaks were the melting and solidification of high Nb content precipitates. The second exothermic peak was the largest peak and the peak temperature was 1643 K. The magnified curve in Figure 7.24 shows another peak (1650 K) during solidification, but the temperature was much higher (87 K) than the peaks during heating. This might due to the chemical composition varied during isothermal

period in high temperature (1773 K), which was the high melting point elements diffused from precipitates to matrix. Since the peak width during cooling was much smaller than the heating peaks, the matrix was homogenised after high temperature isothermal period. The third peak was much smaller than the others and the peak temperature was 1324 K, which means the amount of this phase was much smaller than the other phases. Again it was more than 100K higher than the first endothermic peak during heating, which indicates change of composition. According the DSC result above, the low temperature precipitates melts below 1273 K while the matrix melt above this temperature. Therefore, 1273 K three hours heat treatment was chosen for homogenise treatment.

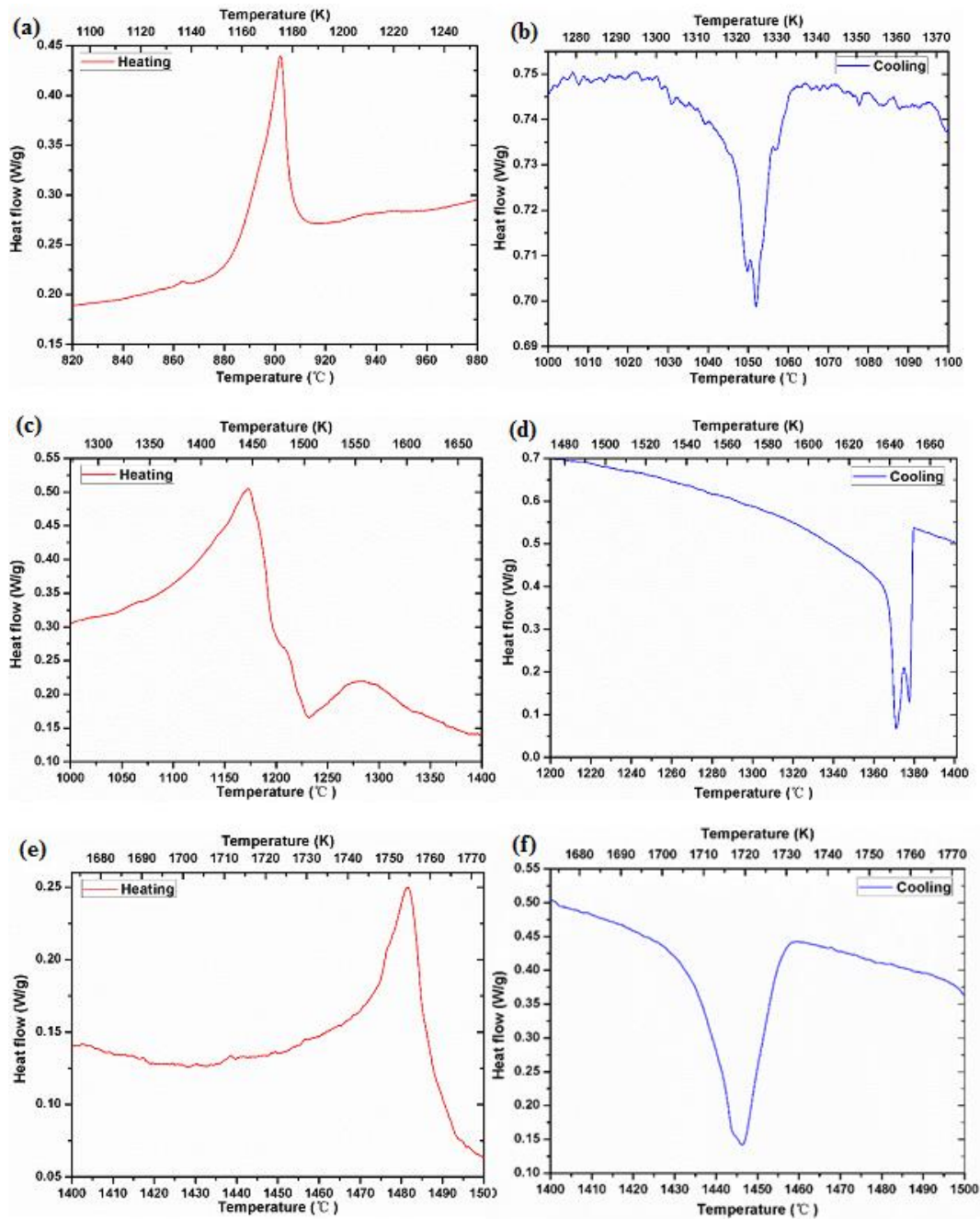


Figure 7.24. Magnified peak areas of high Ms $\text{Ti}_{44}\text{Ni}_{33}\text{Hf}_{10}\text{Cu}_{10}\text{Nb}_2$ DSC curves (a) the endothermic/melting peak of the lowest melting phase during heating, (b) the exothermic/solidification peak of the lowest melting phase during cooling, (c) the endothermic/melting peak with the highest transformation energy phase during heating, (d) the exothermic/solidification peak with the highest transformation energy phase during cooling, (e) the endothermic/melting peak of the highest melting point phase during heating, (f) the exothermic/solidification peak with the highest melting point phase during cooling.

The backscatter image (Figure 7.25) of heat treated TiNiHfCuNb low Ms sample showed significant change after heat treatment comparing with as-built sample (Figure 7.26). The size of precipitates changed from less than 10 μ m to more than 50 μ m with a few different types. The EDS mapping indicated that the precipitates at the edge of matrix with fine patterns (marked as 1) content slightly higher Ti content than matrix but less than the other precipitates area, the content of Ni, Hf, Cu elements in region 1 was lower than the matrix area but the Nb content was higher. Considering the microstructure of this precipitates this could be the mixture of (Ti,Hf,Nb)₂(Ni,Cu) with high Nb content and (Ti,Hf)(Ni,Cu) phases. The region 2 marked in shows higher Ti content, lower Ni, Hf, Cu content but similar Nb comparing to matrix. Therefore this phase could be (Ti,Hf,Nb)₂(Ni,Cu) with lower Nb content. The 2 to 3 μ m precipitates with dark contrast marked as 3 had high Ti and Nb content but the lowest Ni, Cu, Hf content comparing to the other phases. This indicated this phase was Ti-Nb-rich which was different from Ti₂Ni type phases in Ti-Ni alloys. The phases marked as 4 and 5 in the center had the same Ti content (higher than matrix), Nb content (similar to matrix) and Hf content (slightly lower than matrix). But the Ni content was higher in region 4 while the Cu content was higher in region 5. This might indicate different Ni and Cu content in (Ti,Hf,Nb)₂(Ni,Cu) precipitates.

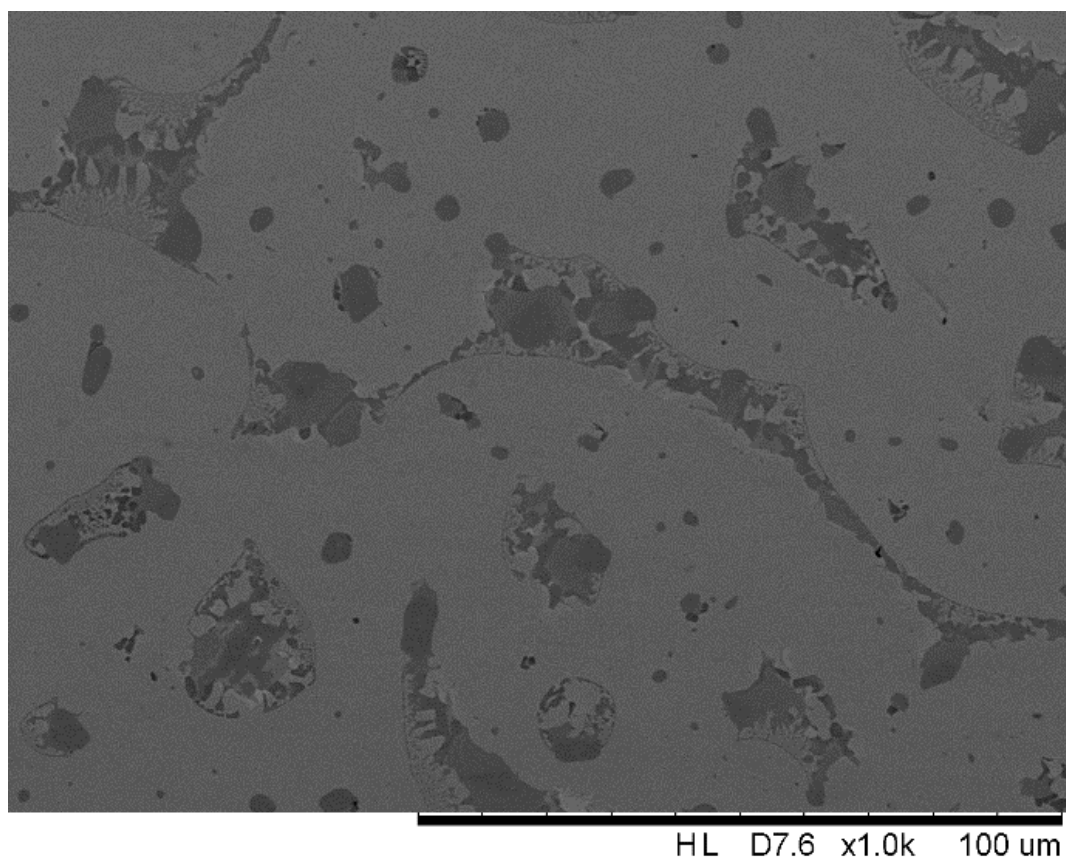


Figure 7.25. Backscatter image of heat treated TiNiHfCuNb low Ms sample shows the change of precipitates.

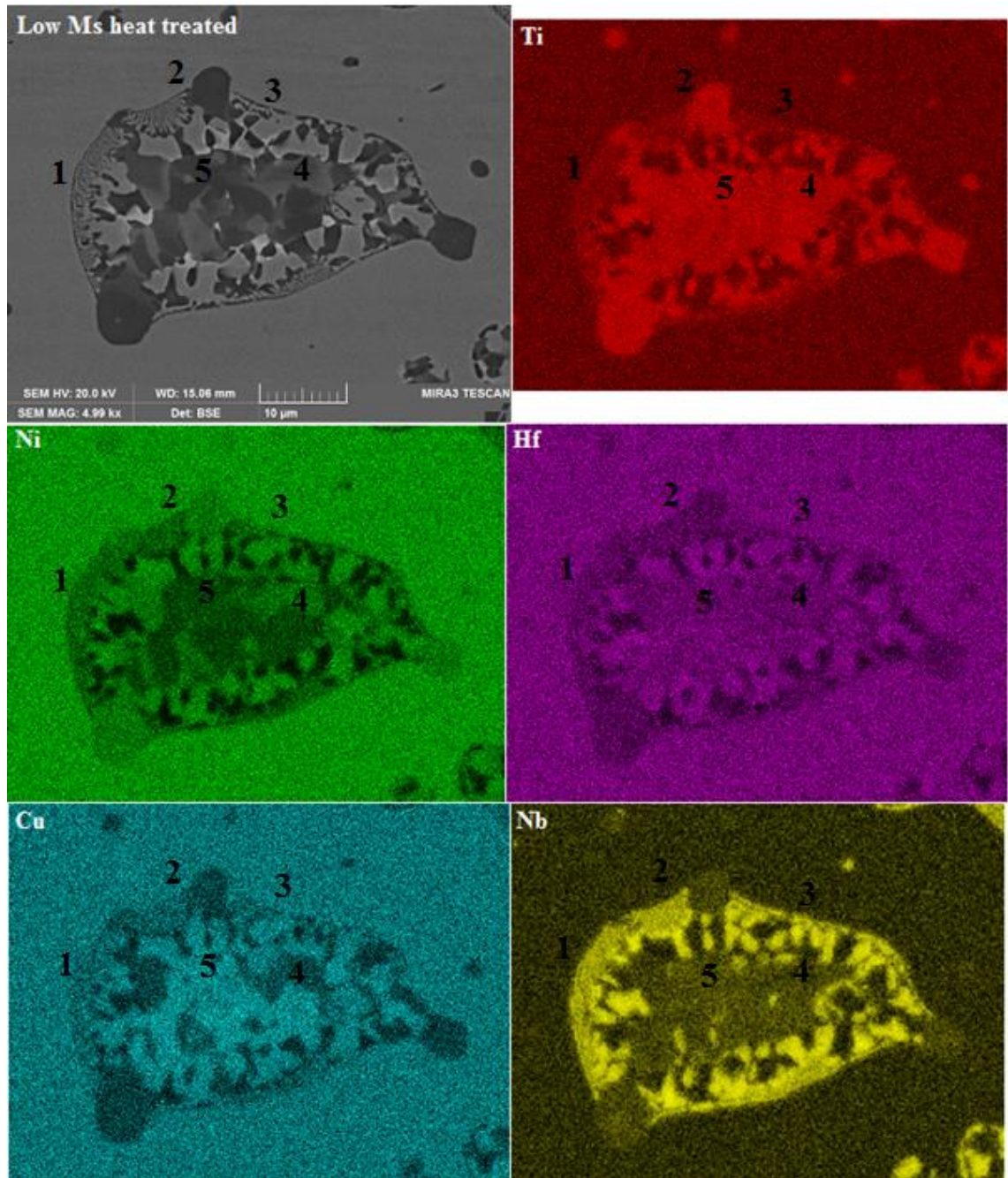


Figure 7.26. High magnification backscatter image and EDS mapping of precipitates in heat treated TiNiHfCuNb low Ms sample

In addition, there was no segregation found in matrix which means the homogenisation treatment eliminated most segregation in this alloy. The DSC testing in Figure 7.27

showed that the transformation peak of heat treated sample narrowed down to 20K with the same thermal stability as as-built sample. This indicated that the heat treatment can improve shape memory stability by eliminating the segregation in matrix. Although the high Ms sample was heat treated by the same heat treatment process, the DSC result of heat treated high Ms sample shows not significant difference to as-built sample. Regarding different precipitates between as-built and heat treated sample, the good thermal cycle stability in low Ms alloy must because of the difference of matrix composition.

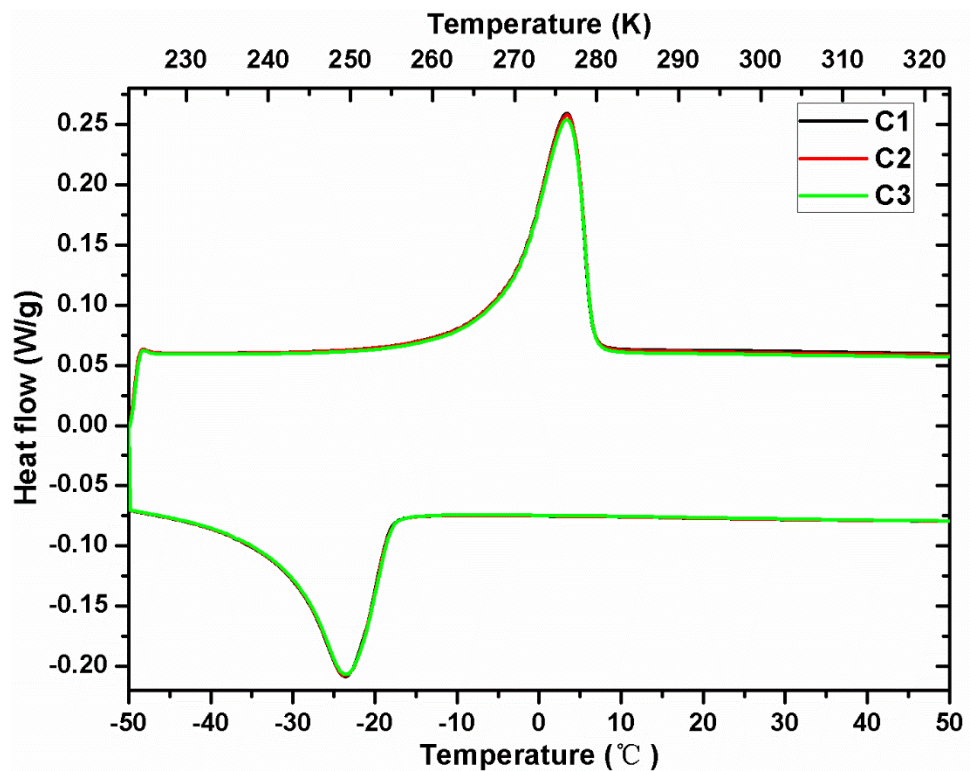


Figure 7.27. DSC testing result of heat treated $\text{Ti}_{43}\text{Ni}_{33}\text{Hf}_{10.5}\text{Cu}_{11}\text{Nb}_{2.5}$ low Ms alloys show narrow transformation peaks and stable transformation behavior with similar transformation temperature to as-built sample.

In order to investigate the segregation in low Nb TiNiHfCuNb sample, the DSC sample of as-built condition and heat treated DSC sample (HT3) are used for EDS investigation. Three EDS mapping were applied on each sample at different position, which were top, middle and bottom area of the samples. Each EDS mapping has 1024×800 index point and each point has 0.5s index live time. The average composition of matrix in each mapping area was calculated from the manually selected data points, which were within the matrix and at least 5 μm away from the precipitates. The average results of these mapping were listed in Table 7.3. The results indicated that the compositional variation in matrix of as-built sample was larger than the matrix of heat treated sample. As discussed in previous sections, the decreasing of Ti + Hf composition or the increasing of Nb content in matrix leads to lower transformation temperature in DSC result. According the equations in section 7.2 and the EDS result, the lowest M_s temperature of as-built matrix was 25.3K lower than the heat treated sample due to variation of Nb and Cu content, which was close to the experimental result (30K). Therefore, the main reason for wide transformation peak in as-built low M_s sample was due to the segregation in matrix, especially heterogeneous of Nb and Cu content.

Table 7.3 Table of average matrix composition calculated from EDS mapping of As-built and heat treated low Ms Ti₄₃Ni₃₃Hf_{10.5}Cu₁₁Nb_{2.5} DSC samples (all composition in at.%).

Sample	Area	Ti	Ni	Cu	Nb	Hf	Ti+Hf	Ni+Cu
As-built	Top	39.5	36.9	11.9	1.4	10.2	49.7	48.8
	Middle	40.0	36.3	12.5	1.0	10.3	50.3	48.7
	Bottom	40.1	36.1	12.6	0.8	10.4	50.5	48.7
	Min	39.3	34.8	11.4	0.6	10.1	49.5	47.9
	Max	40.4	37.7	13.7	2.2	10.5	50.8	49.3
HT3	Top	39.8	36.5	12.3	1.1	10.4	50.1	48.8
	Middle	39.7	36.6	12.3	1.0	10.3	50.0	49.0
	Bottom	40.0	36.6	12.3	1.0	10.2	50.2	48.8
	Min	39.5	36.3	11.6	0.8	10.0	49.7	48.0
	Max	40.2	37.0	12.8	1.4	10.6	50.3	49.2

7.5 Conclusions and further work

A series of new shape memory alloys with acceptable transformation temperature and thermal mechanical stability has been developed. The influence of Cu, Nb and Hf on transformation temperature of TiNi, TiNiCu, TiNiCuHf alloys has been investigated.

1. The addition of Cu in TiNi shape memory alloys slightly decreased the martensite transformation temperature by -0.67 K/at.%.

2. The Cu and Hf have negative influence to each other on martensite transformation temperature of TiNiHfCu shape memory alloys. The decreasing of Cu on 10 at.% and 15 at.% Hf alloys was -5.1 K/at.% and -5.7 K/at.% respectively.
3. Nb had stronger influence on martensite transformation temperature of $\text{Ti}_{51-x}\text{Ni}_{39-x}\text{Cu}_{10}\text{Nb}_{2x}$ shape memory alloys (-19 K/at.%) than $\text{Ti}_{51-0.5x}\text{Ni}_{49-0.5x}\text{Nb}_x$ alloys (-6.3K/at.%). But the Nb content did not affect the thermal cycle stability of $\text{Ti}_{51-x}\text{Ni}_{39-x}\text{Cu}_{10}\text{Nb}_{2x}$ alloys when the Nb content is lower than 3 at.%.
4. Nb content had less influence on martensite transformation temperature of $\text{Ti}_{41-x}\text{Ni}_{46-x}\text{Hf}_{10}\text{Cu}_5\text{Nb}_{2x}$ shape memory alloys (-1.5 K/at.%) than $\text{Ti}_{41-x}\text{Ni}_{39-x}\text{Hf}_{10}\text{Cu}_{10}\text{Nb}_{2x}$ alloys (-12.5 K/at.%). But the relation between Nb content and martensite transformation temperature of $\text{Ti}_{41-x}\text{Ni}_{39-x}\text{Hf}_{10}\text{Cu}_{10}\text{Nb}_{2x}$ alloys was not linear.
5. The $\text{Ti}_{41-x}\text{Ni}_{39-x}\text{Hf}_{10}\text{Cu}_{10}\text{Nb}_{2x}$ alloys with 1 at.% Nb had the highest transformation temperature but the alloys with 2 at.% Nb has the best thermal cycle stability. The decreasing of transformation heat and the transformation heat difference between austenite transformation and martensite transformation increased as Nb content increase.

6. $\text{Ti}_{43}\text{Ni}_{33}\text{Hf}_{10.5}\text{Cu}_{11}\text{Nb}_{2.5}$ and $\text{Ti}_{44}\text{Ni}_{34}\text{Hf}_{10}\text{Cu}_{10}\text{Nb}_2$ show completely different transformation behaviour which were stable low transformation temperature and unstable high transformation temperature respectively.
7. Two types of different precipitates were found in $\text{Ti}_{44}\text{Ni}_{34}\text{Hf}_{10}\text{Cu}_{10}\text{Nb}_2$ high transformation temperature alloys which may be the reason for unstable transformation and high transformation temperature. The matrix of $\text{Ti}_{43}\text{Ni}_{33}\text{Hf}_{10.5}\text{Cu}_{11}\text{Nb}_{2.5}$ and $\text{Ti}_{44}\text{Ni}_{34}\text{Hf}_{10}\text{Cu}_{10}\text{Nb}_2$ alloys were found with slightly different composition which may also affect the transformation behaviour.
8. TEM needs to be applied for further study on the different precipitates and matrix composition of these alloys. In-situ EDSB could also be applied to investigate the relation between precipitates and matrix during transformation.

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8 Chapter 8. Conclusions and Future Work

In this study, a new alloy development process, SDA, was developed for Ti-Ni-based SMA. The characteristics of SDA built binary, ternary and quaternary samples in terms of microstructural development, chemical homogeneity, and shape memory properties were investigated and compared with the literature. SLM was also utilised, as processing method, to manufacture NPR Ti-Ni structure and the process parameters for SLM Ti-Ni SMA was also optimised, and the characteristics of the structures were assessed. Thermo-mechanical testing was applied on hot-rolled reference samples, SDA built Ti-Ni and TiNiCu samples for comparison. Finally, new TiNiCuNb and TiNiHfCuNb SMAs were developed using SDA process and investigated.

8.1 The SDA process for alloy development

The SDA process has been assessed for SMA building, the homogeneity of SDA built samples were as good as the samples built by traditional process (vacuum arc melting). The cooling rate of SDA built Ti-Ni SMAs was measured and calculated.

1. Some local variations were observed in terms of the grain size and Ti_2Ni fraction due to the different cooling rates in the process. Nonetheless, the chemical composition generally approaches the target composition, despite the local variations (especially on the external surface of the SDA builds). Small-scale segregation due to the differences in melting point and density was observed in

SDA samples. Still, the wire-based approach produced samples, which achieves better chemical accuracy compared to the powder-based approach reported in the literature.

2. The texture and grain size of SDA sample are similar to arc-melting process, with a generally random texture, although the grain size variations seemed to be random across the build.
3. The temperature field in the SDA sample is linear and the sample cools down at a rate of 0.77 K/s for low deposition power and 1 K/s for high deposition power during sample building. The fastest cooling rate of SDA process is less than 5 K/s, making it comparable to other alloy development methods. A more accurate experimental result could be obtained by using more thermo couples during building or infrared camera for temperature measurement in the future work.
4. Post-processing heat treatment was generally not essential to obtain an assessment of the utility of the alloy combination (e.g. the phase transformations), but it can be used to improve the microstructural homogeneity and eliminate the small scale segregation, which are likely to affect the local mechanical properties (e.g. in structural materials). The heat treatment time at 1273 K for SDA built SMA does not affect the homogeneity and shape memory properties. A 3 hours heat treatment was chosen to homogenise the microstructure.

8.2 Thermo-Mechanical fatigue testing on SDA built Ti-Ni-based alloys

The SDA built SMA sample had similar stress-strain curve and TMF respond to the hot-rolled reference sample. The strain and Young's modulus results in this study were not comparable to the other research due to extensometer was not available for the machine.

1. Although the TMF testing results of SMA sample reported in literature varied a lot due to the sample size and test parameters (stress and temperature cycles), the result of the reference sample performed in this research was within the range reported in the literature.
2. Comparing the reference sample with SDA built sample, the permanent strain and transformation stress in SDA sample was slightly higher. The $\text{Ti}_{54}\text{Ni}_{34}\text{Cu}_{12}$ SDA sample showed different behaviour to the Ti-Ni sample due to higher precipitate fraction, which indicated the mechanism of Ti_2Cu improving TMF performance in thin film does not work in bulk materials.
3. The other way to alter the size and morphology of precipitates like adding other elements is necessary for new SMA developing.

8.3 Ti-Ni shape memory alloy negative Poisson's ratio structure built by selective laser melting

SLM process parameters was optimised for SMA, NPR SMA structure was built and tested, the performance of SMA was found strong related to the process parameters.

1. Selective laser melting of Ti-Ni shape memory alloys has been successfully optimised to reduce the porosity and crack density in the builds. Fully dense (99.9%) solid and NPR structures from Ti-Ni were built.
2. A post-process heat treatment can improve microstructural homogeneity, shape memory effect and ductility of Ti-Ni shape memory alloys by improving the morphology of Ti_2Ni precipitates and chemical homogeneity.
3. High energy input parameter in selective laser melting process could induce chemical inhomogeneities in Ti-Ni shape memory alloys by Ni-evaporation and re-condensation, which affects the SME. Unfortunately, this could not be proven experimentally, but it echoes similar findings in the literature.
4. The heat treated Ti-Ni auxetic structure has comparable Poisson's ratio to Ti-6Al-4V auxetic structure.
5. The reason of the peak width changing in the DSC trace is related to the presence of residual stress and stored energy. The impact of the energy input on this needs to be further studied.

8.4 The development of TiNiCuNb and TiNiHfCuNb shape memory alloys

The influence of Cu, Hf and Nb on Ms of Ti-Ni-based SMA was researched but the results were not related to lattice structure or electron concentration due to lack of accurate experimental method. It was found that the addition of Nb can alter the size and morphology of precipitates, which have strong influence on shape memory properties.

1. The addition of Cu in Ti-Ni shape memory alloys slightly decreases the martensite transformation temperature by -0.67 K/at.%. The Cu and Hf have negative influences to each other on the martensite transformation temperature of TiNiHfCu SMAs. The influence of Cu on Ms of TiNiHfCu alloys with 10 at.% and 15 at.% Hf are -5.1 K/at.% and -5.7 K/at.% respectively.
2. Nb has a stronger influence on the martensite transformation temperature in $\text{Ti}_{51-x}\text{Ni}_{39-x}\text{Cu}_{10}\text{Nb}_{2x}$ SMA (-19 K/at.%) than $\text{Ti}_{51-x}\text{Ni}_{49-x}\text{Nb}_{2x}$ alloys (-6.3 K/at.%). The Nb content does not affect the thermal cycle stability of TiNiCuNb alloys when the Nb content is lower than 3 at. %.
3. Nb content has less influence on the martensite transformation temperature of $\text{Ti}_{51-x}\text{Ni}_{44-x}\text{Hf}_{10}\text{Cu}_5\text{Nb}_{2x}$ shape memory alloys (-1.5 K/at.%) than $\text{Ti}_{51-x}\text{Ni}_{39-x}\text{Hf}_{10}\text{Cu}_{10}\text{Nb}_{2x}$ alloys (-12.5 K/at.%). However, the relation between the

Nb-content and martensite transformation temperature of $\text{Ti}_{51-x}\text{Ni}_{39-x}\text{Hf}_{10}\text{Cu}_{10}\text{Nb}_{2x}$ alloys is not linear.

4. The $\text{Ti}_{51-x}\text{Ni}_{39-x}\text{Hf}_{10}\text{Cu}_{10}\text{Nb}_{2x}$ alloys with 1 at.% Nb has the highest transformation temperature but the alloys with 2 at.% Nb has the best thermal cycle stability. The decreasing of heat of transformation and the transformation heat difference between austenite transformation and martensite transformation increase as Nb content increase.
5. $\text{Ti}_{43}\text{Ni}_{33.5}\text{Hf}_{10}\text{Cu}_{11}\text{Nb}_{2.5}$ and $\text{Ti}_{44}\text{Ni}_{34}\text{Hf}_{10}\text{Cu}_{10}\text{Nb}_2$ show complete different transformation behavior, which are stable low transformation temperature and unstable high transformation temperature respectively. Two types of different precipitates were found in $\text{Ti}_{44}\text{Ni}_{34}\text{Hf}_{10}\text{Cu}_{10}\text{Nb}_2$ high transformation temperature alloys which may be the reason for unstable transformation and high transformation temperature. The matrix of $\text{Ti}_{43}\text{Ni}_{33.5}\text{Hf}_{10}\text{Cu}_{11}\text{Nb}_{2.5}$ and $\text{Ti}_{44}\text{Ni}_{34}\text{Hf}_{10}\text{Cu}_{10}\text{Nb}_2$ alloys were found with slightly different composition than the target composition. Segregation of Cu might have affected the transformation behaviour.
6. TEM need to be applied for further study on the different precipitates and matrix composition of these alloys. In-situ EDSB could also be applied to investigate the relation between the precipitates and matrix during transformation.
7. Further TMF testing on TiNiCuNb and TiNiHfCuNb are needed to investigate the shape memory properties of newly developed alloys.

8. Modelling such as the first principle and electron concentration combining with high accuracy experimental method (e.g. XRD) are necessary for systematic research on SMA.