3D printing of shape memory alloy based smart structures

Khoo, Zhong Xun

2019

Khoo, Z. X. (2019). 3D printing of shape memory alloy based smart structures. Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/83256>

<https://doi.org/10.32657/10220/48001>

**NANYANG
TECHNOLOGICAL
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SINGAPORE

3D PRINTING OF SHAPE MEMORY ALLOY BASED SMART STRUCTURES

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SCHOOL OF MECHANICAL AND AEROSPACE ENGINEERING

2019

3D PRINTING OF SHAPE MEMORY ALLOY BASED SMART STRUCTURES

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A thesis submitted to the Nanyang Technological University
in partial fulfilment of the requirement for the degree of
Doctor of Philosophy

2019

Statement of Originality

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

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Professor Chua Chee Kai

Authorship Attribution Statement

This thesis contains material from 7 paper(s) published in the following peer-reviewed journal(s) / from papers accepted at conferences in which I am listed as an author.

Chapter 2.4 is published as Z. X. Khoo, Y. Liu, J. An, C. K. Chua, Y. F. Shen, and C. N. Kuo, "A review of Selective Laser Melted NiTi shape memory alloy," *Materials*, vol. 11, p. 519, 2018. DOI: 10.3390/ma11040519.

The contributions of the co-authors are as follows:

- Assoc Prof Liu, Prof Chua, Dr An and I provided the formulation of research goals and development of methodology.
- I prepared the samples, conducted the experiments and verified the repeatability of the results.
- Dr An, Asst Prof Shen, Asst Prof Kuo and I analysed the data.
- Dr An and I prepared and wrote the manuscript.
- Prof Chua, Asst Prof Shen, Asst Prof Kuo and Assoc Prof Liu reviewed and revised the manuscript.

The contributions of the Chapter 3.3.4 and Chapter 4 are published as Z. X. Khoo, Y. Liu, Z. H. Low, J. An, C. K. Chua, and K. F. Leong, "Fabrication of SLM NiTi shape memory alloy via repetitive laser scanning," *Shape Memory and Superelasticity*, vol 4, pp.112-120, 2018. DOI: 10.1007/s40830-017-0139-7.

The contributions of the co-authors are as follows:

- Assoc Prof Liu, Prof Chua, Dr An and I provided the formulation of research goals and development of methodology.
- Mr Low and I prepared the samples, conducted the experiments and verified the repeatability of the results.
- Assoc Prof Liu, Dr An and I analysed the data.
- Dr An and I prepared and wrote the manuscript.

- Assoc Prof Liu, Prof Chua and Assoc Prof Leong reviewed and revised the manuscript.

Chapter 5 is published as Z. X. Khoo, J. An, C. K. Chua, Y. F. Shen, C. N. Kuo, and Y. Liu, "Effect of heat treatment on repetitively scanned SLM NiTi shape memory alloy," *Materials*, vol. 12, p. 77, 2019. DOI: 10.3390/ma12010077.

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- Prof Chua, Asst Prof Shen, Asst Prof Kuo and Assoc Prof Liu reviewed and revised the manuscript.

.....3/4/19.....
Date	Khoo Zhong Xun

List of Publications

1. Z. X. Khoo, J. E. M. Teoh, Y. Liu, C. K. Chua, S. Yang, J. An, et al., "3D printing of smart materials: A review on recent progresses in 4D printing," *Virtual and Physical Prototyping*, vol. 10, pp. 103-122, 2015.
2. Z. X. Khoo, C. Ong, Y. Liu, C. K. Chua, K. F. Leong, and S. Yang, "Selective Laser Melting of nickel titanium shape memory alloy," in *2nd International Conference on Progress in Additive Manufacturing*, Nanyang Executive Centre, NTU, Singapore, pp. 451-456, 2016.
3. Z. X. Khoo, Y. L. Lim, Y. Liu, and C. K. Chua, "Effect of hatch distance on Selective Laser Melting of nickel titanium shape memory alloy," in *2nd International Conference in Sports Science & Technology*, Nanyang Executive Centre, Nanyang Technological University, 2016.
4. Z. X. Khoo, Y. Liu, Z. H. Low, J. An, C. K. Chua, and K. F. Leong, "Fabrication of SLM NiTi shape memory alloy via repetitive laser scanning," *Shape Memory and Superelasticity*, vol 4, pp.112-120, 2018.
5. Z. X. Khoo, Y. Liu, J. An, C. K. Chua, Y. F. Shen, and C. N. Kuo, "A review of Selective Laser Melted NiTi shape memory alloy," *Materials*, vol. 11, p. 519, 2018.
6. Z. X. Khoo, Y. L. D. Lee, J. An, C. K. Chua, and Y. Liu, "Annealing of Selective Laser Melted NiTi shape memory alloy," in *3rd International Conference on Progress in Additive Manufacturing*, Nanyang Executive Centre, Nanyang Technological University, Singapore, pp. 445-450, 2018.
7. Z. X. Khoo, J. An, C. K. Chua, Y. F. Shen, C. N. Kuo, and Y. Liu, "Effect of heat treatment on repetitively scanned SLM NiTi shape memory alloy," *Materials*, vol. 12, p. 77, 2019.

Abstract

Nickel titanium (NiTi) shape memory alloy is one smart material that has the capability to directly convert thermal energy into mechanical work. This unique property gives rise to shape memory effect and superelasticity. In order to fully utilise these two behaviours, NiTi needs to be processed into the different geometries for various applications. Nonetheless, the conventional manufacturing processes have several complications. Moreover, NiTi is not an easy material to process as well due to its compositional sensitivity and poor machinability. Thus, the full potential applicability of NiTi has not been achieved. To address these issues, one proposed solution would be to adopt Selective Laser Melting (SLM) to fabricate the NiTi parts. This new method of producing NiTi components is also known as 4D printing.

The fabrication of NiTi via the SLM process not only contributes to solving the current problems encountered, it also allows complex NiTi smart structures to be produced directly for new applications. However, it is essential to first have the knowledge in fabricating functional SLM NiTi parts before manufacturing for actual applications. Furthermore, as compared to producing conventional metals through the SLM process, the fabrication of NiTi is much more challenging. Not only do the produced parts require a high density that leads to good mechanical properties, strict compositional control is needed as well for the SLM NiTi to possess suitable phase transformation characteristics. Therefore, in this thesis, the different SLM process parameters were first optimised, followed by the characterisation of the samples. Subsequently, the properties of the samples were enhanced through the implementation of repetitive scanning and post-process heat treatment.

The SLM process parameters that were studied included the laser power, laser scanning speed, hatch distance and scanning strategy. These parameters were optimised and the produced SLM NiTi parts had low internal porosity, good geometrical accuracy, minimal oxidation and similar phase transformation characteristics as the NiTi powder. The small deviations in the internal porosity and transformation temperatures of the optimised single scanned samples have indicated the high repeatability of the SLM process. However, these samples demonstrated poor mechanical properties when subjected to tensile deformation. Multiple fractures were observed before the samples failed at a highest tensile strain of about 6%. Hence, repetitive scanning was implemented to enhance the properties of SLM NiTi.

The results obtained from the repetitively scanned samples suggested that the laser absorptivity and heat conductivity of the materials before and after the first scan would significantly influence the final properties of the SLM NiTi. With carefully controlled repetitive scanning process, the fabricated samples demonstrated excellent properties. First, the samples exhibited comparable phase transformation characteristics as the raw NiTi powder used with high repeatability. Second, they displayed the capability to deform to 8% strain under the tensile mode without failure. Additionally, the samples have also demonstrated the highest magnitude of 5.11% transformation strain, with an average value of 4.61%. This scale of shape recovery was comparable to the conventionally-produced NiTi parts with a maximum transformation strain of about 6%.

Nevertheless, the gap between the transformation strains of repetitively scanned samples and conventionally-made NiTi components indicated the possibility of further enhancing the shape memory properties of SLM NiTi. Therefore, post-process heat treatment was introduced to meet this objective. The results showed that the implementation of heat treatment had both positive and negative influences. A balance between these effects was needed to obtain an improvement in the shape memory responses of the repetitively scanned samples. It was observed that the samples subjected to heat treatment at 400 °C for a period of 5 minutes had higher transformation strain and percentage of shape recovery than the non-heat treated samples. The improvement in the shape memory properties was primarily due to the formation of a high density of fine Ni_4Ti_3 metastable precipitates. Nonetheless, increasing the heat treatment temperature to above 400 °C has resulted in overaging and further enlargement of the grain size. Consequently, degradations in the shape memory responses of the SLM NiTi samples were observed.

Acknowledgement

First and foremost, the author would like to express his heartfelt gratitude to his supervisor, Professor Chua Chee Kai and former supervisor, Associate Professor Liu Yong, for providing the opportunity to work on this interesting and challenging project. Their invaluable advice and continuous support throughout the course of his research are appreciated. The author is honoured to have the chance to work and learn under the supervisions of both Professors.

The author would also like to thank Dr An Jia for his guidance on the writing of thesis and publications. His insightful suggestions have helped to refine the research from various perspectives. The author is grateful to the FYP students, Mr Kung Guangjun, Mr Liu Renchun, Ms Cindy Ong, Mr Lim Yi Long, Ms Joie Tan Mingyan, Mr Low Zhi Hong and Mr Lee Ying Le Dennis, who have worked with him during his candidature. The efforts they put in have contributed to the success of this research. The questions they raised up have inspired the author to approach the problems encountered from different angles as well.

The author would also like to show his appreciation to the help he received from the laboratory specialists from School of Mechanical and Aerospace Engineering, Nanyang Technological University, Singapore. Without their assistance, the completion of this research would not be possible.

Last but not the least, the author thanks his family and friends for their love, encouragement and understanding.

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Chapter 1: Introduction

1.1 Background

As science and technology advance, there is an increase in the understanding of the effects of processing technologies and microstructures on the materials' behaviour [1]. This progression in material science has led to the development of new alloys and composites with different material properties, including materials that meet the structural requirements and concurrently provide additional functions. This special branch of materials is known as the multifunctional materials. Within them, there is a distinctive group that can exhibit both sensing and actuation capabilities. They are otherwise known as the active materials.

Generally, active materials exhibit mechanical output when they are subjected to a non-mechanical input. The mechanical responses of active materials are usually one or more orders of magnitude larger than the mechanical responses of conventional materials, such as the thermal expansion. Moreover, active materials can be further divided into materials that exhibit direct or indirect coupling. One example of an active material that exhibits direct coupling is the shape memory alloys (SMAs).

SMAs is one category of active or smart material that has the ability to directly transform thermal energy into mechanical work [2-4]. They are generally utilised in special engineering applications due to their excellent functional properties and high actuation energy densities [1, 5-7]. One example will be nickel titanium (NiTi) SMA. Among the different types of SMA, NiTi exhibits the best shape memory behaviour such as a high percentage of shape recovery, large superelastic strain and recovery stress [1, 8-10]. As a result of these superior properties, NiTi alloy has been widely utilised in various fields of application such as aerospace [1, 11-15], biomedical implants and fixtures [1, 6, 11-22], surgical instruments [1, 15], smart composites [9, 13], actuators [12, 13, 18, 23], naval [1], micro-electromechanical systems (MEMS) [12, 13, 24], electrical safety devices [12] and sporting equipment [1], couplings and fasteners [23], etc.

NiTi has the characteristics of demonstrating both shape memory effect (SME) (thermal memory) and superelasticity (mechanical memory) [5, 7, 16, 25]. These phenomena are the result of the reversible martensitic phase transformation. This type of phase transformation is characterised by the transformation temperatures of NiTi. However, the transformation temperatures are extremely sensitive to any variation in the Ni/Ti ratio [11, 18, 25-27]. For instance, a slight decrease in the content of Ni by 1% can result in a huge increase in the transformation temperatures by 100 °C [1, 5, 6, 11, 15, 18, 25].

In order to make full use of its SME and superelasticity, NiTi SMA has to be processed into various geometries for different applications. Conventionally, net-shape cast NiTi objects are produced by the processes of self-propagating high-temperature synthesis, followed by arc or induction melting, hot working and lastly tooling [6, 17]. However, these conventional processes have their limitations [17]. For example, arc melting needs to be performed several times to ensure that the NiTi has homogenous chemical composition. However, the issue with repeated melting is that it leads to carbon and oxygen pick-up [18]. On the other hand, the crucible gets contaminated by oxygen as well when induction melting is selected over arc melting.

In addition to these problems, NiTi is also a difficult material to process [6, 10, 15, 19, 25, 28-30]. Firstly, NiTi alloys are compositional sensitive. During the processing of NiTi alloys under high temperature such as the induction melting, impurity elements tend to be picked up easily. This can lead to issues such as oxidation and microstructural defects, which will eventually cause a shift in the transformation temperatures. Second, NiTi SMA is known to have a poor machinability associated with its unconventional deformation mechanisms (detwinning and stress-induced martensitic transformation) [10, 15, 19, 25, 29]. The shape memory properties of NiTi alloy cause a significant amount of tool wear and make it difficult for precise machining [5, 6, 10, 15, 28, 30, 31]. Thus, most of the conventionally-produced NiTi parts have simple geometries such as in the form of wires, plates, bars, tubes, etc., critically limiting the full potential applicability of NiTi [6, 25, 28, 29, 32]. Additionally, conventional treatment methods such as thermomechanical treatments, annealing treatments and shape setting treatments can affect the phase transformation behaviour of NiTi significantly as well [7, 24, 28]. As a result, only about 10% of the NiTi used in the medical field is being utilised for its SME [33].

Hence, to overcome the disadvantages of conventional processes and the poor manufacturability of NiTi, one method would be to produce NiTi components from the NiTi powder by hot isostatic pressing [17]. However, this method does not allow an object with complex geometries to be manufactured. Moreover, before the components can be fabricated from the NiTi powder, the powder has to be produced first.

Powders can be produced by rapid solidification processes such as gas atomization or chemical reactions such as precipitation [6]. Gas atomization usually produces powder particles of spherical shape and these powders have to be consolidated to form the near-net shape products. The properties of the components produced from the metallic powder are generally similar or maybe even better than the parts produced by ingot metallurgy [6].

Another significant advantage of powder metallurgy is that the materials produced from the powder form can have a homogenous microstructure with higher alloy composition without any segregation [6]. This would create near-net-shape parts with consistent and enhanced isotropic physical and mechanical properties. As a result of the uniformity of the microstructure, the machinability and life cycle of the products will improve as well.

Basically, there are two types of conventional powder metallurgy techniques available to produce NiTi alloys [6]. They are raw metal powder sintering and alloy powder sintering. For the raw metal powder sintering, pure metal powders are mixed, pressed and sintered. However, this will eventually lead to inhomogeneity of the composition. As for the alloy powder sintering, the composition is more homogenous and the produced NiTi parts can exhibit a good one-way SME.

Conversely, there are some disadvantages to the powder metallurgy [6, 27]. One disadvantage is that the content of brittle oxide in the sintered parts is generally high. Moreover, it is difficult to produce a dense component as well.

Nevertheless, NiTi powder metallurgy methods are still the preferred method as it produces net-shape or near-net-shape products due to the limited machinability of NiTi. In addition, powder metallurgy reduces the wastage of material and the amount of energy needed. Moreover, it provides precise control over the chemical compositions of the NiTi.

Therefore, a better proposed solution to the problems of conventional processes and the poor manufacturability of NiTi is to utilise additive manufacturing (AM) or 3D printing techniques such as Selective Laser Melting (SLM) to fabricate NiTi components through the melting and solidification of NiTi powder [5, 7, 16, 17, 19-21, 24, 25, 28, 31, 33-40]. This new method of manufacturing NiTi SMA by 3D printing is also known as 4D printing [41-44]. The difference between 3D printing and 4D printing is that the objects fabricated in 4D printing are not static. These objects can respond to external stimuli in an intended manner due to the inherent properties of smart materials. As a result, the fabricated components will be able to change their geometries or physical properties over time.

With the use of SLM, it not only helps to solve the problem of the poor manufacturability of NiTi alloy, it also enables the direct fabrication of NiTi smart structures with complex geometries for novel applications. One possible future application is the fabrication of NiTi implants [16]. Due to the possibility of using different combinations of SLM process parameters, NiTi structures that exhibit SME and/or superelasticity can be produced from the same raw material. Furthermore, a printed component can consist of several sections with different phase transformation temperatures. For instance, an SLM fabricated NiTi implant may contain superelastic regions that assist in shock absorption and regions with reduced Young's modulus that exhibit SME.

1.2 Objectives

The objectives of this research project are to utilise SLM technology to fabricate NiTi SMA with the desired properties: low porosity, minimum impurities, optimal mechanical properties, minimal deviations in chemical composition, controllable phase transformation characteristics and comparable SME. The properties of the SLM NiTi parts are benchmarked against the properties of the NiTi ingot, NiTi powder and conventionally-produced NiTi. By achieving these objectives, NiTi components with the desired properties and controllable or predictable transformation characteristics can be fabricated. With this knowledge, it will be possible to fabricate NiTi components that demonstrate SME at predefined temperatures by SLM for various novel or existing applications.

1.3 Scope

The following work scope is essential to achieving the final stated objectives:

- Literature review on NiTi SMA, SLM and the current developments in the area of manufacturing NiTi by SLM
- Exploration of the various fabrication parameters to determine the optimal parameters to fabricate NiTi components with preferred properties
- In-depth analysis of the current limitations in SLM of NiTi SMA
- Introduction of repetitive scanning, post-processing heat treatment and characterisation of non-heat treated and heat treated NiTi samples.

1.4 Organisation of the Report

This report begins with an introduction in Chapter 1, where it contains the background information, motivations and objectives of this research project. The next chapter summarises the relevant books and research papers with regards to the basic knowledge on NiTi SMA, the research in SLM and the current developments in SLM fabrication of NiTi. It has been observed that most research groups have failed to obtain good shape recovery properties in SLM NiTi parts. Following, Chapter 3 presents the phenomena observed during the optimisation of the SLM processing parameters. Chapter 4 introduces an additional step, repetitive scanning, to the conventional SLM process and demonstrates how it improves the properties of the NiTi samples produced. Chapter 5 compares the results of SLM NiTi before and after post-processing heat treatments and what are the effects of the treatment implemented. This report ends with Chapter 6 stating the conclusion and future research of this project.

Chapter 2: Literature Review

In this chapter, publications and previous studies which are relevant to this project are reviewed. These include fundamentals of NiTi SMA, SLM and the research done on SLM fabrication of NiTi.

2.1 Nickel Titanium Shape Memory Alloy

2.1.1 Phenomenology of Phase Transformation

NiTi SMA exhibits different microstructural phases at different temperatures [1, 45]. Each of these phases will have different crystal structures and thus dissimilar properties. At a high temperature, the alloy will exhibit austenitic phase with either a body-centered cubic or a face-centered cubic structure. In the event that the alloy is cooled below a critical temperature, it will change its phase via an exothermic reaction from austenite to a low-temperature phase called martensite. The martensitic phase has a lower crystallographic symmetry than the austenitic phase. It will exhibit either a tetragonal, orthorhombic or monoclinic structure [1, 26].

The transformation from the austenitic phase to martensitic phase occurs via the shear lattice deformation rather than via the diffusion of atoms [1, 45]. This type of phase transformation is generally known as the reversible martensitic phase transformation. During this transformation process, each of the martensitic crystals formed can have a different orientation direction that is known as the variant. The collection of martensitic variants can exist in two different types. They are namely twinned martensite and detwinned or reoriented martensite. Twinned martensite is formed by a combination of self-accommodated martensitic variants while detwinned martensite is formed by a specific dominant variant. This reversible martensitic phase transformation from austenite to martensite and vice versa forms the basis for the SME and superelasticity behaviour of NiTi SMA [1, 9, 18, 20].

During the cooling process of NiTi alloy without any load applied, the crystal structure of the alloy will change from austenite to martensite upon reaching the critical transformation temperatures. The transformation process from austenite to martensite will be known as the forward transformation, in which up to twenty-four martensitic variants may be generated for the case of NiTi. Nonetheless, the variants will be arranged in such a way that the average macroscopic shape change is insignificant, resulting in twinned martensite. On the other hand, when NiTi is heated above its critical transformation temperatures, the crystal structure will revert back from martensite to austenite. This process is called the reverse transformation, during which there is no associated shape change.

The phase transformations from austenite to martensite and vice versa are characterised by four transformation temperatures [1, 45]. Figure 2.1 presents a schematic diagram of the crystal structures of twinned martensite and austenite and the transformation between these two phases, provided no loading has been applied. During the forward transformation shown in Figure 2.1a, the austenitic phase will begin to transform into the twinned martensite when the alloy temperature reaches the martensitic transformation start (M_s) temperature. Once the temperature reaches the martensitic transformation finish (M_f) temperature, the transformation from austenite to twinned martensite will be completed. At this point, the NiTi alloy will exhibit a crystal structure that only consists of twinned martensitic phase.

Likewise, when NiTi is being heated up as illustrated in Figure 2.1b, the reverse transformation from twinned martensitic phase to austenitic phase will begin when the alloy temperature reaches the austenitic transformation start (A_s) temperature. A complete austenitic phase will be obtained when the NiTi alloy temperature arrives at the austenitic transformation finish (A_f) temperature.

Figure 2.1: Schematic of the crystal structures of twinned martensite and austenite during the (a) forward and (b) reverse transformations [1].

Within a certain chemical composition region, the transformation temperatures will vary significantly with the content of NiTi [18, 26]. The relationship between the M_s temperature and the content of Ni is shown in Figure 2.2 [26]. As observed, the M_s temperature decreases with increasing Ni content when the Ni content is above 49.7%. A constant M_s temperature is maintained when the Ni content falls below 49.7%. Nevertheless, the A_f temperature will always be about 30 °C higher than the M_s temperature for all the different samples that fall within this composition region. The reason for the constant M_s temperature when the Ni content is less than 49.7% can be attributed to the formation of Ti_2Ni , which helps to maintain the content of Ni at 49.7% [18, 26].

Figure 2.2: Relationship between the M_s temperature and the content of Ni [26].

2.1.2 Shape Memory Effect

NiTi SMA will exhibit SME when a mechanical load is applied to deform the alloy while in the twinned martensitic phase, followed by unloading at a temperature that is below the A_s temperature [1-4, 45]. As shown in Figure 2.3a, during the loading process there will be a reorientation of a certain number of variants. This would then lead to the detwinning of the twinned martensitic phase and results in a macroscopic shape change. Eventually, the deformed shape will be retained when the load is released. However, the condition for the SME to occur is that the applied load must be sufficiently large enough to start up the detwinning process. This minimum amount of stress required for the initiation of the detwinning process is known as the detwinning start stress (σ_s). The higher stress level that will lead to the complete detwinning process is called the detwinning finish stress (σ_f).

Meanwhile, to get a complete shape recovery for a deformed NiTi alloy without any load applied, the alloy must be heated up to above the A_f temperature to induce a complete reverse phase transformation from the detwinned martensite to austenite. This shape recovery process is presented as a schematic diagram in Figure 2.3b. Upon cooling down to a temperature that is below the M_f temperature, the forward transformation will be initiated and twinned martensite will be produced again with no associated shape change.

Figure 2.3: Schematic of the SME of NiTi illustrating (a) the detwinning process with an applied load and (b) the unloading and heating processes to austenite without any load applied [1].

Nevertheless, the nature of the SME can be better understood by using the thermomechanical loading path in a combined stress (σ)-strain (ϵ)-temperature (T) space as shown in Figure 2.4. Starting from the austenitic phase, which corresponds to Point A in Figure 2.4, the stress-free cooling of austenite to a temperature that is below the M_s and M_f temperatures will lead to the formation of twinned martensite that is represented as Point B. However, when twinned martensite is being loaded with a stress level that exceeds σ_s , the reorientation of the variants will be initiated. As a result, there will be an increase in some preferred oriented martensitic variants at the expense of other less desired variants. The detwinning process will be completed when the applied stress reaches σ_f , which is at the end of the plateau of the σ - ϵ plane. However, one point to take note is that the required stress level for the reorientation of variants is much lower than the permanent plastic yield stress of martensitic phase.

Once the NiTi alloy has been loaded to Point C, the load will then be released and the alloy will recover elastically to Point D with the detwinned martensitic phase being retained. Upon heating the alloy without any stress applied, the reverse transformation will commence when the temperature of NiTi reaches the A_s temperature at Point E. The reverse phase transformation will only be completed when the alloy temperature reaches the A_f temperature at Point F, where the alloy solely exhibits austenitic phase. In the case where no permanent plastic strain has been induced during the detwinning process, the initial shape of

the NiTi alloy will be recovered. Moreover, the strain recovered during the phase transformation from detwinned martensite to austenite is known as the transformation strain. Subsequence cooling from the heated NiTi alloy will result in the formation of twinned martensitic variants with no associated shape change and the entire cycle of SME is repeatable. In general, this whole process described above represents a one-way SME, or simply SME. This is because the shape recovery is generated by heating alone and only the shape of the alloy at the austenitic phase is memorised [1, 6].

Figure 2.4: A stress-strain-temperature curve that represents the SME of a NiTi alloy [1].

On the other hand, NiTi SMA is also noticed to exhibit repeatable shape changes when it is subjected to a cyclic thermal load with no additional mechanical load applied [1]. This phenomenon observed is known as the two-way SME (TWSME). TWSME can be found in NiTi alloys that have experienced repeated thermomechanical cycling along a specific loading path [1, 46]. By repeating the loading path for a large number of cycles, the microstructure of the alloy will be affected and this causes permanent changes in the material behaviour that are macroscopically observable.

The entire process of generating TWSME is referred as training. Training a SMA implies that the alloy will be subjected to the repeated loadings of a cyclic thermomechanical path until the point where the hysteretic response of the material stabilises and the inelastic strain saturates. During the training process, defects are introduced into the SMA in order to generate an internal residual stress state. As a result of the residual stress, preferred

martensitic variants will be formed during the cooling process in the absence of external loads [1, 47]. In the situation where the internal residual stress state is modified by other factors such as high temperature ageing and mechanical overload, the TWSME will be affected as well.

As mentioned in the introduction, NiTi SMA has been used for actuation purposes [12]. Thus, during the application as an actuator, the alloy is often subjected to constant stress while experiencing changes in the temperatures to produce the actuation force and motion. Figure 2.5a presents the corresponding transformation temperatures of NiTi at the current constant stress level of 200 MPa while Figure 2.5b shows the effect of varying the applied stress level on the transformation temperatures of NiTi [29].

Figure 2.5: Experimental examples that present (a) the corresponding transformation temperatures of NiTi at a constant stress level of 200 MPa and (b) the effect of varying the applied stress level on the transformation temperatures of NiTi [29].

In Figure 2.5a, the almost horizontal responses of NiTi that are observed at temperatures outside the transformation regions are due to the thermal expansion. These regions correspond to temperatures below the M_f^σ temperature and above the A_f^σ temperature. Upon reaching the A_s^σ temperature during the heating process, there is a sharp decline in the strain of the deformed NiTi alloy. Once the temperature attains the A_f^σ temperature, the transformation from detwinned martensite to austenite is complete and the alloy exhibits full shape recovery as evidenced by the zero strain displayed. However, once the temperature of NiTi is cooled down, there will be a direct transformation from austenite to detwinned

martensite and the alloy will be deformed again under the constant stress applied. Nonetheless, this phenomenon is only observable when the applied stress is larger than σ_s [1].

Figure 2.5b illustrates the relationship between the transformation temperatures and the applied stress level. It can be seen that as the stress level increases, the transformation temperatures increase. Hence, this observation implies that the transformation temperatures of NiTi are strongly dependent on the magnitude of the applied stress state, with higher values of loading leading to higher transformation temperatures [1, 29]. This result will hold true irrespective of the nature of the loading, be it tension loading or compression loading.

2.1.3 Superelasticity

In addition to the SME, NiTi SMA can exhibit superelasticity behaviour as well [1, 2]. Superelasticity is associated with a stress-induced transformation whereby a sufficiently high amount of load is applied to the NiTi alloy while it exhibits austenitic microstructural phase [1, 3, 8]. As a result, strain is generated during the loading process and strain recovery is obtained when the load is removed at temperatures above the A_f temperature. A superelastic thermomechanical loading path usually begins at a higher temperature where the microstructural phase is austenitic, followed by transforming into detwinned martensite under the influence of an applied load. Upon releasing the stress to zero-state, the microstructure will transform back into the austenitic phase. As shown in Figure 2.6, there are two possible superelastic loading paths, path 1 and path 2. However, superelastic tests are generally performed at a constant high temperature that is above the A_f temperature as illustrated as path 2 in Figure 2.6. The corresponding stress-strain curve for loading path 2 is presented in Figure 2.7.

Figure 2.6: The two possible superelastic loading paths [1].

Figure 2.7: Stress-strain curve for loading path 2 in Figure 2.6 [1].

During the process of applying a load to NiTi alloy above the A_f temperature at zero stress level, the austenitic phase undergoes elastic loading from Point A to Point B as shown in Figure 2.6. This elastic loading is represented in Figure 2.7 by the almost linear response from Point A to Point B. When the stress level reaches σ^{Ms} reflected at Point B in both figures, the transformation from austenite to detwinned martensite is induced. The initiation of the transformation is characterised by the change in the gradient of the stress-strain curve in Figure 2.7, where the alloy exhibits a behaviour that is similar to plastic yielding. Moreover, a

plateau has been formed as well. The plateau region represents the amount of macroscopic deformation that the NiTi alloy generates via the microstructural movements [29]. It is an obvious consequence that spawns from the solid-to-solid phase transformation.

Upon increasing the applied stress level to σ^{Mf} at Point C, the transformation to detwinned martensite is completed. In Figure 2.7, the complete phase transformation is indicated by the end of the plateau and a change in the gradient of the stress-strain curve that is associated with the nearly linear elastic loading of the martensitic phase. Any further increase in the stress level from Point C to Point D in Figures 2.6 and 2.7 only results in the elastic deformation of the detwinned martensite.

After which, the stress is gradually released to σ^{As} as indicated by Point D to Point E in both figures, where the martensitic phase unloads elastically with an almost linear response and the conversion to the austenitic phase is initiated. The complete transformation from detwinned martensite to austenite is marked by Point F, where the stress level reaches σ^{Af} in Figure 2.6 and the stress-strain curve rejoins the elastic region of austenite in Figure 2.7. It is noticed that the plateau formed during the unloading process has the same strain length as that observed during the loading process. Further unloading from Point F to Point A shown in Figure 2.7 results in a nearly linear response with the same gradient observed during the initial loading process and a complete recovery of the strain induced. One point to note is that the stiff response at lower stress level or below the loading plateau is associated with the pure austenitic behaviour [29]. The stiff response observed at higher stress level or above the unloading plateau corresponds to the pure martensitic behaviour.

In general, for a complete superelastic cycle, the forward and reverse phase transformations lead to a hysteresis. The hysteresis represents the amount of energy loss during the phase transformations in the stress-strain space. The four transformation stress levels σ^{Ms} , σ^{Mf} , σ^{As} , σ^{Af} and the size of the hysteresis differs according to the types of SMA materials and their testing conditions. Additionally, the detwinned martensite that is produced as a result of the stress applied is a form of stress-induced martensite. This implies that it is a martensitic phase that is created from the austenitic phase under the influence of stress. Also, there are many other possible ways of producing stress-induced martensite other than the two superelastic loading paths illustrated in Figure 2.6. Furthermore, if the NiTi alloy is tested above the M_s

temperature but below the A_f temperature, the phase transformation from detwinned martensite to austenite will not be completed. Thus, only partial shape recovery will be observed in this case.

Both Figures 2.6 and 2.7 illustrate the superelasticity effect observed under a constant temperature. However, when the temperature of the superelasticity experiment varies, the stress required to initiate the phase transformation changes as well [29]. This phenomenon is demonstrated by Figure 2.8, where the four transformation stresses increase as a result of the increase in the testing temperature.

Figure 2.8: An experimental example that presents the effect of varying test temperature on the transformation stresses of NiTi [29].

2.2 Selective Laser Melting

AM, commonly known as 3D printing or rapid prototyping (RP), has undergone huge advancements since it was introduced in the late 1980s [48-51]. As opposed to the process of subtractive manufacturing, the components produced by AM are built layer-by-layer based on their 3D model data. This unique way of building parts layer-by-layer gives the advantage of producing structures with complex geometries [48, 52, 53].

AM is adopted in various applications due to the many benefits that it brings. These applications include the fabrication of physical prototypes such as mock-ups [51, 52], functional evaluation of product designs [48, 52], healthcare products and living biological structures [54-57]. Furthermore, AM has been used to manufacture customised end-use products as well such as replicated components or objects [52, 58], 3D printed electronics [49], fashion and jewellery products [42, 59] and advanced multifunctional honeycomb structures [60]. In addition to all these applications, AM also provides alternative manufacturing techniques that have the potential to overcome the various limitations of processing materials conventionally. For instance, one of the AM technologies, SLM, eliminates the problem of high tool wear and size shrinkage that are associated with the conventional methods of processing ceramics [61].

2.2.1 Introduction

SLM was first introduced into the market in 2000. It is a type of powder-based AM system that fabricates components by melting the powder material with laser energy [52, 62-64]. The structures of the components built are usually first designed on the computer-aided-design computer-aided-manufacturing (CAD-CAM) system, followed by converting the design file into the STL file format. The STL file is then sliced into different layers with each layer thickness pre-defined by the user and inputted into the system. The fabrication process can proceed anytime once the SLM equipment receives the input STL file.

In the initial step of the fabrication process, a layer of metallic powder with pre-defined thickness would first get deposited and laid uniformly across the platform by a recoater. Once that is done, the fibre laser of the SLM equipment would scan the powder bed according to the cross-section of the first layer of the input STL file. During the scanning process, the temperature of the powder bed would increase and the powder particles would start to melt when the temperature exceeds the melting temperature of the material. After the scanning is completed, the building platform would descend down by a distance that is equal to the next pre-defined powder layer thickness. This marks the end of one cycle. Next, the recoater would again deposit the powder uniformly across the platform and the process would repeat

itself till the fabrication of the components is complete. The areas that were not scanned by the laser would remain in powder form and act as support while the areas scanned by the laser will get densified. The whole fabrication process takes place in an inert environment filled with argon gas to prevent oxidation, degradation and interaction between the liquid metal with its surroundings. Finally, the left-over powder would be collected and sieved for reuse for the next fabrication process.

Generally, the main advantages of AM over subtractive manufacturing include minimal wastage of materials and the capability to produce components with complex geometries. However, different AM technologies have different strengths. The main strengths of SLM are as follow and they are the reasons why SLM has been chosen as a new manufacturing method for the fabrication of NiTi:

- SLM is able to produce high-quality homogeneous components with a density that is up to 100% [6, 52, 64].
- SLM can process almost any type of metallic materials such as stainless steel, tool steel, titanium, aluminium, gold and various non-ferrous metals [52].
- The SLM process can be fast and low cost as some fabricated components do not require post-processing such as heat treatment [6, 33, 52, 53].
- SLM is a high-resolution process. It is able to produce small parts that could not be fabricated by conventional methods and these parts will be dimensionally accurate with no distortion of the parts' geometries [16, 52, 53].
- Other than producing dense parts, SLM can produce porous components as well. An example of such component will be bone implants where these components were made porous to reduce their weight and effective stiffness so as to better match the properties of bones [6].
- SLM allows the efficient use of material due to the possibility of recycling and reusing the powder that has not been melted [63, 64].
- SLM contributes to the reduction of emissions as a result of requiring fewer raw materials and the possibility to design light-weight structure with a weight reduction [63].

In addition to these advantages, the SLM process also allows the transition of phases to occur across a wider span of the temperature range and at a more gradual rate as compared to the conventional methods [6]. This gradual change in phase transition allows the one-way SME to be more controllable by optimising the operating conditions [6].

Conversely, SLM does have its drawbacks. These drawbacks include:

- The SLM equipment has a large physical size. Thus, it requires a large area to house [52].
- The laser system of the SLM machine consumes a large amount of power [6, 52].
- Compared to high-speed machining, SLM process is a relatively slow process due to the slow scanning speed [6, 52].
- Precision and surface finishes of fabricated parts are inferior as compared to parts produced by liquid-based processes such as casting [6, 63, 64].
- Components produced by SLM have a high amount of residual stress [6].
- It is difficult to remove unbounded powder from components with porous geometries [6].
- There is a possibility that the material properties, which are related to the microstructure of the fabricated components, are not able to meet the industrial standards after processing [63].

In order to address these demerits, post-processing treatments such as polishing, painting, heat treatment and furnace-infiltration can be introduced [63]. Nonetheless, these post-processing treatments do increase the number of production cycles and the cost of production.

2.2.2 Process Parameters

One of the advantages of SLM is that it can process a wide range of materials. However, different materials would require various combinations of process parameters to produce high-quality parts due to the different material properties. At the current stage, the determination of the optimal process parameters for each material is mainly by trial-and-error method [62]. Some of these process parameters have been classified into six different

categories and they are listed in Table 2.1 [6, 53, 63, 65, 66]. Due to the huge number of process parameters that can influence the densification mechanism and microstructure of the processed materials, the SLM process becomes very complicated.

Table 2.1: Six different categories of SLM process parameters [6, 53, 63, 65, 66].

Types of Parameters	Process Parameters
Beam-Related Parameters	Laser power
	Spot size
	Pulse duration
	Pulse frequency
	Beam spatial distribution
	Laser wavelength
Scan-Related Parameters	Scanning speed
	Pitch/hatch distance
	Number of scans
	Scan track length
	Scanning strategy
Powder-Related Parameters	Particle size
	Particle shape
	Particle density
	Size distribution
	Layer thickness
	Viscosity
	Surface tension
	Absorptivity/reflectivity
	Specific heat
	Thermal conductivity
	Emissivity
	Melting temperature
	Chemical composition
Temperature-Related Parameters	Powder-bed temperature
	Powder-feeder temperature
	Temperature uniformity
Atmosphere-Related Parameters	Atmospheric control
	Gas flow
Machine-Related Parameters	Laser type
	Type of SLM machine

2.2.3 Effects of Process Parameters on the Densification Mechanism

2.2.3.1 Energy Density and the Corresponding Parameters

The linear energy density and volumetric energy density of the SLM process are related to the following parameters; laser power, laser scanning speed, hatch distance and powder layer thickness. In theory, a higher amount of energy density delivered to the powder bed during the SLM process would produce parts with higher density. However, this may not be the case in reality. Various research have shown that similar magnitude of energy density adopted does not necessarily produce samples with similar density and properties [7, 53, 67]. In other words, each individual parameter may have an influence on the densification of the samples instead of just the energy density inputted. Thus, this result illustrates the importance of optimising the processing window so as to fabricate a fully dense component. In addition, many research have also been conducted to investigate the effects of the laser power, scanning speed, hatch distance and powder layer thickness on the densification mechanisms of the various studied materials.

Based on the research done by Ghosh et al., the density of their fabricated Al_2O_3 , TiC and TiB_2 reinforced Al metal matrix composite samples depends on the hatch distance, chemical composition and layer thickness, while the porosity is influenced by the hatch distance, layer thickness and laser power used [68]. However, these results differ from the results obtained by Read et al. [67]. In their paper, they reported that the laser power, scanning speed and the interaction between the scanning speed and hatch distance have a significant effect on the porosity of their SLM fabricated AlSi10Mg samples. Meanwhile, Olakanmi et al. have stated an increase in the densification of their samples as the laser power increases and as the scanning speed, layer thickness and hatch distance decrease [69]. Their result obtained is similar to the other results reported for other materials such as iron, Ni-Sn powder blends and Cu-Solder (Pb-Sn) [70, 71].

The differences in how these process parameters affect the densification behaviour may be associated with the different mechanisms of sintering or melting that arise from the chemical composition of the materials. Again, these results emphasise the importance of optimising the processing window for each material. Moreover, the theory behind the higher

densification of samples when the process parameters are being varied can be related to the amount of liquid phase formed during the fabrication process [69, 72-74]. It was noted that when the laser power and laser scanning speed are low, the energy density supplied is inadequate to produce sufficient liquid phase to bond the particles together. Thus, the outcome will be partial melting or sintering and the result will be poor densification. However, as the laser power increases with a low scanning speed, the increasing energy density provided causes the temperature of the powder bed to rise. Hence, a sufficient amount of liquid phase will be generated and it produces a significant amount of powder's inter-particulate melting. As a consequence, there will be higher densification of the parts produced due to the instability of the molten pool, which occurs during the minimization of the surface free energy. Therefore, it can be inferred that the increase in the energy density leads to a high working temperature, which in turn causes the viscosity and surface tensions of the molten pool to decrease.

Even though the magnitude of energy density delivered to the powder bed is the most significant parameter that determines the density of the produced parts, it is not the only factor that contributes to the successful fabrication of metals by SLM [63]. Layer thickness is the other parameter that will affect the outcome of the SLM process. For instance, when the layer thickness used is high, it will be impossible to completely melt all the powder particles due to the inadequate amount of energy penetrated into the powder bed [69]. As a result, large and interconnected pores will be generated within the built component, leading to lower density. During the processing of AlSi12 by SLM, Olakanmi et al. have discovered that there exists a critical value for the layer thickness [69]. At this critical layer thickness, the majority of the gas bubbles formed during the melting process are able to travel upwards to the layer surface and collapse when the molten pool solidifies. Thus, the built part will have fewer pores and higher density. Moreover, the samples produced with the critical value of layer thickness is observed to have superior microstructural properties as the previous layer was re-melted during the processing of the top layer. Hence, the layers formed are bonded together with a lesser degree of spheroidisation.

Furthermore, it has been concluded that spheroidisation does not occur when the previous layer is re-melted and there is wetting of the solidified material by the molten pool [69, 75]. Based on the findings by Agarwala et al., the minimum layer thickness is determined by the

maximum powder size and the precision of the powder delivery system [70]. If the layer thickness is below a certain level, the roller mechanism of the equipment tends to displace the previous layer from its initial position during the deposition of the new powder layer. In addition, Olakanmi et al. found out that if the layer thickness is below the minimum allowable magnitude for a particular powder delivery system, there will be other issues encountered during the deposition of new powder layer across the previously built layer [69]. One issue faced will be the higher surface roughness of the processed layer, which will eventually hinder the inter-particulate bonding or melting.

Additionally, various researchers have reported that there is a direct relationship between the resultant fractional density of the fabricated sample and the energy density provided by the laser [71, 76]. The fractional density is an exponential function of the delivered energy density as shown in Equation (2.1).

$$\rho = C_1 - C_2 e^{-KE} \quad (2.1)$$

where ρ is the resultant fractional density of the produced component, C_1 , C_2 and K (densification coefficient) are material constants of the specific powder and E is the volumetric energy density. According to the equation, the fractional density will increase with the increase in energy density till it reaches saturation [71]. The maximum fractional density will remain constant regardless of the amount of energy density supplied. Nonetheless, an excessive amount of energy density provided at high laser power and low scanning speed will lead to issues such as balling and layer delamination [63]. These problems are caused by the increase in the lifetime of the generated liquid phase.

Overall, with a lower scanning speed, small hatch distance and high laser power, the amount of liquid phase produced is larger and the sintering or melting time is longer. Thus, it promotes higher densification. Conversely, with a high scanning speed, large hatch distance and low laser power, the liquid phase generated is insufficient or has little time to enhance wettability. Moreover, there seems to be a maximum density that the sample can achieve once the energy density provided attains a critical value. Any further increase in the energy density would have no effect on the density of the fabricated sample. This is because any increase in the energy density above the critical value would increase the lifetime of the liquid phase,

which promotes the occurrence of balling effect and inhibits densification. However, the only exception is when the wetting of the substrate occurs.

2.2.3.2 Laser Scanning Strategy

Porosity, residual stresses, cracking and poor surface finish are the common issues encountered in SLM due to the uneven thermal gradients. To control the thermal gradients so as to fabricate unwarped and uncracked layers, different studies were done to study the effect of scanning strategies on the densification of the produced samples. Dewidar et al. have tested for standard, diagonal and perimeter scanning strategies for the production of single layers shown in Figure 2.9 [77] while Su and co-investigators have tested on four types of scanning strategies shown in Figure 2.10 together with varying hatch distance [78].

Figure 2.9: (a) Standard, (b) diagonal and (c) perimeter scanning strategies [77].

	 Pattern 1	 Pattern 2	 Pattern 3	 Pattern 4
Travel time		minimum	maximum	

Figure 2.10: The four scanning strategies investigated in laser sintering of tool steel powder by using a Nd:YAG pulsed laser [78]. The numbers represent the sequence of scanning and the arrows indicate the direction of scanning.

According to Dewidar et al. work, they have found out that the perimeter scanning strategy is less successful while the standard and diagonal scanning strategies produce similar results [77]. On the other hand, Su et al. have discovered that the adoption of different scanning strategies will result in different processing time and that affects the microstructure of the fabricated parts [78]. Hauser et al. investigated the scanning lengths for small-scale SLS processing of components at room temperature [79]. They concluded that the scan length of the single layer affects warping while the height of the samples does not.

Conventionally, the traditional scanning strategy presented in Figure 2.11a involves the repetitive scanning of the tracks at the same position along the fabrication direction [80]. Due to the design of the scanning strategy, the adjacent layers will overlap along the centre line of the scanned tracks. Thus, there is a possibility that there is an over-concentration of energy at the centre line of the tracks as compared to the sides. This may eventually contribute to the generation of defects along the centre line and generation of porosity at the sides. Hence, to ensure that the energy input is uniform, Su and Yang came out with three different types of inter-layer staggering scanning strategies [80]. They are namely intra-layer overlapping strategy, inter-layer overlapping strategy and mixed overlapping strategy that comprises of the previous two types in Figure 2.11b, 2.11c and 2.11d, respectively.

Figure 2.11: The (a) conventional scanning strategy and three types of inter-layer staggering scanning strategies, namely (b) intra-layer overlapping strategy, (c) inter-layer overlapping strategy and (d) mixed overlapping strategy [80].

As reported by Su and Yang, the inter-layer overlapping strategy is achievable only when the hatch distance is less than 0.2 mm [80]. This will produce parts with high relative density with the specific processing parameters. However, only hatch distance was investigated in this study and not on other process parameters. Thus, further investigations on other factors are to be conducted to understand more about the track overlapping strategy during the SLM process.

Next, Kruth et al. discussed on how the internal stresses induced by temperature gradient are dependent on the geometry of the fabricated part and the adopted scanning strategy [81]. They stated that when the scanned area is small with a short scan length, there is insufficient time for the surface to cool down before the next track is scanned. This will result in high temperature across the scanned area. However, if the track length to be scanned is large, the laser has to travel a longer distance and hence the preceding scanned tracks have more time to cool down. This will then result in a lower temperature of the scanned area. As a consequence, the low temperature of the scanned area will lead to poor wetting conditions

and subsequently a decrease in the sample's density. This is because of the larger heat sink between the loose powder and the solidified molten pool.

2.2.3.3 Chamber Atmospheres

The presence of oxygen in the processing chamber and the presence of passive oxide layer on the powder surfaces will aggravate the balling effect due to the initiation of Marangoni convection [63]. The main results of this will be a higher amount of laser energy absorbed by the sintering or melt pool and the increase in the wetting angle between the solid phase and liquid phase [82]. The rise in the wetting angle can then impede inter-particulate bonding between the layers. Thus, it is important to control the chamber atmosphere during the SLS or SLM processes to prevent any unwanted reactions.

In one of the research on the effects of chamber atmospheres done by Wu et al., they have studied the influence of the oxygen content on the microstructural properties of a burn-resistant alloy Ti-25V-15Cr-2Al-0.2C (weight percentage) [83]. The alloy was processed in air and in a glove box with argon atmosphere that has an oxygen content less than 5 ppm. Wu et al. discovered that the atmosphere has an effect on the microstructures obtained. For instance, the alloy processed in air contains large titanium carbide dendrites. The alloy processed in argon atmosphere consists of finer and more uniformly distributed carbides. However, they were not able to provide an explanation for the results that they have observed.

Nonetheless, Das et al. researched on a wider range of atmospheres on the SLS fabrication of superalloy cermet abrasive turbine blade tip [84]. The atmospheres that they have investigated include a rough vacuum condition of the order of 30 mtorr, a rough vacuum condition purged with argon, a high vacuum condition that is less than 5×10^{-5} torr and a high vacuum condition followed by argon-2% hydrogen backfill. Their results showed that under the rough vacuum condition and rough vacuum purged with argon condition, they contain sufficient amount of oxygen for the superalloy to oxidise. As a result, balling effect, separation and tearing phenomenon can be observed in the samples due to the effects of surface tension. Das et al. concluded that by adopting a high vacuum condition, the samples produced will

exhibit relatively uniform surface features with no cracking, tearing and separation, provided that the samples are produced with parameters within the acceptable processing window.

Nevertheless, Wang et al. studied the effect of the atmosphere on the densification of Al₁₂Si alloyed powder via SLM [85]. The atmospheres that have been investigated are filled with argon, nitrogen and helium respectively. According to their results, the different types of the atmosphere have no effect on the densification of the material that they tested.

However, the results from Asgharzadeh et al. [86] and from Simchi et al. [71] showed otherwise. They reported that the laser processing of metallic powders under argon atmosphere will produce a better densification than under the nitrogen atmosphere, especially when the scanning speed is high. The differences in the effect of chamber atmosphere on the densification of metal powders via SLS or SLM might most probably be due to the different mechanisms of chemical reactions that occurred during the fabrication process of different materials. The exact nature and mechanisms of chemical reactions for the different materials need to be further studied. Additionally, the observation made by Hauser et al. agreed with the research mentioned in this section [82]. They have noticed that during the heating, melting and bonding process of the metallic powder, the amount of oxygen content present in the processing chamber has a huge negative influence on the effectiveness of laser power and laser scanning speed for a successful SLS fabrication.

2.2.3.4 Types of Laser

The type of laser used in the SLS and SLM processes is one of the key factors that has an influence on the properties of the fabricated components [70]. As presented in Table 2.2, different materials have different laser absorptivity, depending on the type of laser used or on the wavelength of the laser selected, the nature of materials, surface geometry, ambient gas, temperature, etc. [87, 88]. Generally, the laser absorptivity of the metallic materials decreases as the laser wavelength increases [70, 87].

Table 2.2: Different laser absorptivity of metallic powders for Nd:YAG and CO₂ lasers [87].

Material	Types of Laser	
	Nd:YAG ($\lambda = 1.06 \mu\text{m}$)	CO ₂ ($\lambda = 10.6 \mu\text{m}$)
Cu	0.59	0.26
Fe	0.64	0.45
Sn	0.66	0.23
Ti	0.77	0.59
Pb	0.79	-

The densification mechanism of the powder material is largely dependent on the resultant energy density absorbed by the powder bed. The initial magnitude of energy density required depends on the type of laser, the mode of laser and the laser absorptance of the material. Hence, due to the different types of laser equipped, different machines may require different combinations of processing parameters to produce a fully dense part even though the same raw material is being used.

2.3 Laser Re-Melting

Even though the SLM process is able to produce components with very high density, obtaining a completely dense part by merely optimising the SLM process parameters is still a challenging task. Hence, one possible method to improve the density of fabricated components would be to introduce laser re-melting or repetitive scanning [89].

Laser re-melting is a process where a solidified layer is re-scanned to create melting and solidification for the second or more time without the deposition of any new powder layer [89]. The re-scanning strategy can be in any form such as point scanning, contour scanning, area scanning, etc. [90]. Nevertheless, laser re-melting is not exclusive to the SLM process. It has been studied and implemented as a conventional technique for enhancing the materials' properties. However, the majority of these research focus on surface modifications rather than improving the core properties of the fabricated components. For instance, laser re-melting was utilised to improve the surface hardness and wear resistance of hyper-eutectic Al-Si cast alloy [91]. It was also used to increase the metallurgical bonding strength between magnesium alloy substrate and Al₂O₃-13 wt.%TiO₂ protective layer [92].

In recent years, laser re-melting has been improvised and introduced into the SLM fabrication process. It acts as a potential solution to the difficulties encountered in producing components with the desired properties. In the study done by Yasa et al., they reported a decrease in the porosity of their AISI 316L stainless steel samples upon the implementation of laser re-melting [89]. However, re-melting the solidified layer more than one time does not result in any significant reduction in the porosity. Moreover, using a smaller hatch distance does not increase the density of the samples substantially as well.

Another research published by Yasa et al. has also reported similar results [93]. They stated that the introduction of laser re-melting has been found to improve the density of the produced 316L stainless steel samples, regardless of the combinations of parameters used for the re-melting scan. However, these process parameters have a huge effect on the porosity of the samples. Generally, it was observed that the porosity increases with the amount of energy density inputted. Variation in the laser scanning speed and hatch distance can lead to a huge discrepancy in the porosity. Meanwhile, the effect of the number of re-melting scans is dependent on the other parameters. When the laser power used is high and/or when the hatch distance adopted is small, the increase in porosity with the number of scans tends to be more substantial. However, in contrast to the other parameters, the effect of laser power is relatively negligible. In addition, a lower magnitude of energy density would also produce a smaller degree of “edge effect”, where it relates to the occurrence of more material accumulating at the edges as compared to the central regions of every layer built.

Besides reducing porosity, laser re-melting can improve the surface quality of the SLM parts as well [93]. Samples that were subjected to laser re-melting demonstrated a reduction in the surface roughness and an increase in the microhardness for all the various combinations of re-melting scans tested. On the contrary, the better surface properties were observed only when a higher amount of energy density was supplied instead. When insufficient energy was directed to the samples, it could not produce full melting of the peaks to fill in the valleys completely. Furthermore, higher energy densities used would generate sufficient recoil pressure to push the molten pool towards the previously solidified layer. Thus, the surface produced would be flatter and smoother. Also, the higher hardness observed in the re-melted surface was found to be associated with the finer microstructure.

Meanwhile, in another work of Yasa et al., they have successfully fabricated 316L stainless steel parts with relative density as high as 99.96% via the use of laser re-melting [94]. The reduction in the porosity was achieved by eliminating the internal pores formed in between the adjacent molten pools during the re-melting stage. Additionally, the microstructure was refined as well when the solidified material undergoes melting and solidification for the second time. However, the “edge effect” was still observable and has been reported.

On the other hand, in the more recent research conducted, the simulation and experimental results by Jung et al. demonstrated that single scanning was not sufficient to produce a dense H13 steel component [95]. They have observed a significant amount of large and small internal pores, together with some cracks, for their single scanned samples. A better densification and higher hardness of the samples can be achieved with three-time scanning. However, large and irregularly shaped internal pores can be found again for samples produced by five-time scanning. Jung et al. proposed the reason for the increase in the internal porosity to be caused by the over-melting of the H13 material.

In another study on laser re-melting of H13 tool steel, Choe et al. investigated the effects of laser scanning speed [96]. It was noticed that all samples produced with scanning speed ranging from 100 to 200 mm/s in either first, second or both scans exhibited spherical pores. This occurrence was believed to be caused by over-melting, which differs from what Jung et al. proposed earlier. Nevertheless, samples fabricated by 400 to 600 mm/s during the second scan demonstrated a higher density than the other conditions. Especially, the samples had the lowest porosity when the scanning speed used in both scans were ranged between 400 to 600 mm/s. These results obtained have presented the importance of optimising the SLM process parameters for both scans in order to achieve the lowest internal porosity possible.

However, Yu et al. have reported different effects observed while introducing laser re-melting to the SLM fabrication of AlSi10Mg [97]. Their results have shown a minimal increase in the density of their samples with the addition of laser re-melting. Moreover, the direction of the second scan had no noticeable effect as well. They suggested the reason to be due to the parameters used for the first scan, which the samples have already exhibited about 98.63% relative density after the first scan. Hence, it limited the amount of density improvement that can be observed with the implementation of laser re-melting. Furthermore, the laser re-

melted samples have demonstrated a slight reduction in their tensile strength as compared to the single scanned samples. Nonetheless, the ductility has shown a great improvement by about 57%. Thus, Yu et al. concluded that laser re-melting could improve the performance of AlSi10Mg for those applications that require high ductility.

In another separate research conducted by Aboulkhair et al., they have shown that by selecting the correct scanning strategy, porosity and defects in the SLM processed AlSi10Mg parts can be minimised [65]. The scanning strategies that they have experimented on include the following:

- “X” scanning strategy, which is a unidirectional scanning with a single scan per layer.
- “2X” scanning strategy, which is a unidirectional scanning with each layer being scanned twice.
- “Alternating” scanning strategy, where each layer is scanned in a direction that is rotated 90° to the previous layer.
- “X & Y 2HS” scanning strategy, where each layer is scanned twice and each scan is perpendicular to the previous scan with different hatch distances.
- “Pre-sinter” scanning strategy, where the layer is first scanned with half the power, followed by a second scan with full power.
- “Overlap” scanning strategy, where each layer is scanned twice with the second scan directed at melting the overlap between the adjacent melt pools.

According to their results, the experimented scanning strategies that consist of scanning each layer twice (2X, X and Y 2HS, pre-sinter and overlap) can be observed to significantly reduce the number of keyhole pores at all scanning speeds tested as compared to scanning each layer once (X and alternating) [65]. This is especially so at low scanning speed. However, there is an extensive formation of metallurgical pores in the SLM fabricated components with low scanning speed due to the higher energy density supplied. In other words, this observation implies that the keyhole pores were eradicated at the expense of introducing metallurgical pores.

Nonetheless, adopting double scanning to each layer at a higher scanning speed can ensure that the metallurgical pores were less significant due to the lower energy density used for each scan. In addition, Aboulkhair et al. concluded that the “pre-sinter” scanning strategy

produces samples with the highest relative density. All their results illustrate the importance of achieving a compromise between the different process parameters and scanning strategies in order to produce a fully dense part.

2.4 Selective Laser Melting of Nickel Titanium Shape Memory Alloy

NiTi SMA has the best combination of properties among the different SMAs. However, the limitations of conventional manufacturing processes and the poor manufacturability of NiTi have critically limited its full potential applicability. Thus, due to its advantages, SLM has the potential to be a solution in fabricating complex NiTi smart structures. Recently, a number of studies on SLM of NiTi were conducted to explore the various aspects of SLM-produced NiTi [5, 7, 16, 17, 19-21, 24, 25, 28, 31, 33-41]. Compared to producing conventional metals through the SLM process, the fabrication of NiTi SMA is much more challenging. Not only do the produced parts require a high density that leads to good mechanical properties, strict composition control is needed as well for the SLM NiTi to possess suitable phase transformation characteristics. Additionally, obtaining a good SME from the SLM NiTi samples is another challenging task that requires further understanding. This section reviews some of the results of the effects of energy density and process parameters on the properties of SLM-produced NiTi, their shape memory responses and potential applications.

2.4.1 Effects of Energy Density

In general, the density of SLM-produced parts increases with increasing energy density directed to the powder bed [18]. The magnitude of energy density delivered is usually calculated using Equation (2.2) [16, 21, 31, 63, 67, 69, 71, 85, 98].

$$E = \frac{P}{vhd} \quad (2.2)$$

where E refers to the energy density (J/mm^3); P denotes the laser power (W); v indicates the laser scanning speed (mm/s); h signifies the hatch distance (mm); and d represents the powder layer thickness (mm).

Among the different research conducted, Meier et al. [28] and Haberland et al. [25] reported that the minimum energy density required to produce a highly dense SLM NiTi sample was 85 and 200 J/mm^3 , respectively. Nonetheless, three adverse effects were observed when the energy density increased beyond the optimal magnitude.

First, Bormann et al. [21] and Haberland et al. [25] noticed an increase in the porosity of their samples with increasing energy density above the critical amount, leading to a decrease in the relative density by up to about 10%. There are two possible explanations for this phenomenon. First, it could have been due to the increase in the volume of the molten pool [21]. Thus, the diffusion of the gas bubbles to the surface during the solidification process was hindered, resulting in the production of high porosity samples. Second, an excessive amount of energy density could have led to the balling effect and the formation of voids [25]. Eventually, the fabricated samples exhibited high porosity. Nevertheless, Meier et al. reported a contradicting result [28] where they observed a minimal effect on the density of the produced parts as energy density continued to increase above the minimum value needed.

Second, it has been reported that the transformation temperatures of the SLM NiTi samples increase as the energy density delivered increases [16, 25]. The increment could be as much as 75 °C [16]. The occurrence of this phenomenon is the result of Ni loss via evaporation as Ni has a lower evaporation temperature than Ti (evaporation temperature of Ni is 3186.15 K and the evaporation temperature of Ti is 3560.15 K) [16, 21, 25, 99, 100]. Furthermore, the increase in the transformation temperatures coincides with the results of other researchers who have also detected a drop in Ni content in their SLM NiTi samples [21, 28, 35].

Third, Haberland et al. observed a direct relationship between the impurity-pick up by SLM NiTi and the input energy density magnitude [25]. In their study, they adopted an inert environment for the fabrication of their SLM NiTi samples. Nevertheless, the amount of oxygen and nitrogen picked up by their samples increased significantly by up to about 0.14 wt. % as the energy density delivered continued to increase above the minimum magnitude.

This was most likely due to the material experiencing a higher temperature, larger dimension of the molten pool and a lower rate of solidification when exposed to unnecessarily high energy density. Collectively, these three reported adverse effects illustrate the importance of determining the optimal energy density required. This is to produce a SLM NiTi part that exhibits high density, desired transformation temperatures and low impurity content.

2.4.2 Effects of Process Parameters

The studies mentioned in the section 2.3.1 presented the potential for controlling the chemical composition and transformation temperatures of SLM NiTi via the alteration of energy density. On the other hand, Dadbakhsh et al. [7] and Speirs et al. [35] demonstrated the possibility of influencing the transformation characteristics by varying the different SLM process parameters.

In the research by Dadbakhsh et al., they came up with various combinations of parameters with similar magnitudes of energy density [7]. These sets of parameters were categorized as low laser parameters (LP) and high laser parameters (HP). LP was associated with low laser power (40 W), low laser scanning speed (160 mm/s) and lower heating and cooling rates. HP corresponded to high laser power (250 W), high laser scanning speed (1100 mm/s) and higher heating and cooling rates. These two combinations of parameters were capable of producing SLM NiTi samples with comparable chemical composition and approximately 99% density.

However, the samples produced by the different parameter combinations demonstrated different transformation temperatures. Samples that were fabricated using the LP combination exhibited the martensitic phase and SME while samples produced with the HP combination exhibited the austenitic phase and superelasticity at room temperature. The difference in the transformation temperatures was attributed to the different cooling rates, grain sizes and precipitations [7].

Dadbakhsh et al. proposed the formation of precipitations as a possible reason for the higher transformation temperatures of the LP samples [7]. The presence of the precipitates generated incoherency stresses and altered the local Ni content of the Ni-rich NiTi. As the

scanning speed used for the LP combination was lower, more time was available for growing the precipitates. Thus, the formation of these precipitates led to the increase in the transformation temperatures of the LP samples.

Additionally, Meier et al. also reported the presence of Ti_2Ni precipitates in their SLM NiTi samples [28]. These precipitates were formed during the solidification process. As a result of the geometric conditions, heat transfer during the SLM process was not uniform. Hence, the regions with reduced heat transfer experienced a higher temperature for a longer period. Eventually, more Ni was lost due to evaporation and ultimately led to the formation of Ti_2Ni precipitates. Meanwhile, any content variation of NiTi would cause the transformation temperatures to change significantly. In this case, the presence of Ti-rich NiTi due to the evaporation of Ni led to the increase of the transformation temperatures. As expected, this coincided with what Meier et al. observed in their SLM NiTi samples [28].

On the other hand, since the HP combination produces a higher cooling rate, it may have resulted in the presence of higher Ni content and less precipitation due to the reduction in Ni evaporation. Moreover, the smaller grain size due to the higher cooling rate could also have caused a significant decrease in the transformation temperatures. Thus, the HP combination tends to result in the lowering of the A_s and A_f temperatures of the SLM NiTi samples [7].

Based on these results, Dadbakhsh et al. continued to explore the effects of SLM parameters on the mechanical behavior and geometrical characteristics of porous scaffold components fabricated with HP and LP combinations [20]. Such porous structures can provide a suitable environment for cell seeding and vascularization and still act as a load bearing medium concurrently [19, 20]. According to their findings, the HP combination has resulted in a large geometrical mismatch between the actual produced thin struts and the computer-aided design (CAD) model. The main reason was that of the longer time required to accelerate and decelerate the Galvano scanner to achieve a higher scanning speed. Instead, a lower scanning speed was obtained during the scanning process of producing thin struts. Consequently, the energy density directed to the powder particles would be higher than desired, resulting in the formation of larger molten pools and thicker struts.

Moreover, the HP samples were observed to fracture at a higher compressive load than the LP samples. This was mainly due to the thicker struts formed as they provide a more uniform distribution of strains. In addition, the HP samples also demonstrated a better load bearing ability against directional loading. Besides the geometrical differences, the higher cooling rate experienced by the HP samples could have also led to a finer microstructure and higher overall strength. One suggestion to achieve higher scanning speed would be to adopt point scanning to avoid the acceleration and deceleration of the Galvano scanner [20].

In a separate study performed by Speirs et al., they reported that the oxygen content present during the fabrication process had a strong effect on the transformation characteristics of the SLM NiTi samples [35]. Although an identical magnitude of energy density was delivered, samples produced in a low-oxygen atmosphere (about 220 ppm oxygen) had comparable transformation temperatures. A huge difference in transformation temperatures existed for the samples fabricated under a high-oxygen environment (about 1800 ppm oxygen). Furthermore, high-oxygen content resulted in the formation of brittle oxides and led to harmful mechanical responses. These results suggested that the quality of the produced SLM NiTi parts was heavily dependent on the atmospheric condition.

Other than affecting the transformation characteristics, SLM process parameters can also have an effect on the porosity of the samples produced. Bormann et al. observed a decreasing trend in the relative density of their SLM NiTi samples with an increase in the exposure time (point distance divided by laser scanning speed) [21]. The occurrence of these two phenomena: (1) a decrease in relative density by up to about 10% as energy density increases above optimal value; and (2) a decrease in relative density by up to roughly 7% as scanning speed decreases or as exposure time increases, can be associated to the volume of the molten pool [21]. The amount of NiTi powder melted and the volume of molten pool formed is expected to increase as input energy density rises or as scanning speed decreases. Hence, the diffusion of the gas bubbles within the molten pool to the surface will be progressively hindered during the process of solidification. Subsequently, it causes a larger number of closed pores and the production of high porosity samples.

Generally, the results reported by Dadbakhsh et al., Speirs et al. and Bormann et al. implied a strong influence of SLM process parameters on the transformation characteristics and

porosity of SLM NiTi. This interesting discovery has demonstrated another possibility of obtaining the desired transformation temperatures by varying the process parameters in addition to energy density alone.

Nevertheless, the presented findings on the effects of energy density and SLM process parameters did not offer a clear answer to the complicated problems encountered in the study of SLM NiTi. This is a result of the dependency of energy density on the laser power, laser scanning speed, hatch distance and powder layer thickness as shown in Equation (2.2). Varying the parameters will alter the magnitude of the energy density inputted. Therefore, the effects of energy density and SLM parameters cannot be well differentiated as it is impossible to have only one variable. The adjustment of energy density will result in the variation of another parameter and vice versa. This may also be the reason why various researchers have reported different phenomena. For instance, Zhang et al. stated that the laser scanning speed did not have much effect on the transformation temperatures of SLM NiTi [33]. However, this contradicts the work reported by Bormann et al. [21] and Speirs et al. [35]. Bormann et al. observed that the amount of Ni lost decreased with increasing exposure time or reduction in scanning speed, indicating that Ni evaporation was time-dependent [21]. They proposed the formation of oxide on the surface of the molten pool as the reason for obstructing the amount of Ni evaporated. Speirs et al. noted a decrease in the M_s temperature as the scanning speed increased [35]. Unquestionably, more studies are required to validate these contradictory findings. Even though it is possible to have constant energy density while the scanning speed varies, the other parameters also have to be altered in order to achieve that. Therefore, the results reported on the effects of scanning speed at a given constant energy density may not be totally accurate.

To summarise, in the research of producing a high-quality NiTi SMA component by SLM, different research groups have proposed different combinations of process parameters. As a result, this leads to different magnitudes of energy density being used or recommended. Table 2.3 presents the process parameters and energy densities that were mentioned and adopted by the different researchers.

According to the information shown in Table 2.3, some of the published research papers do not provide complete information on the adopted SLM process parameters. Moreover,

Dadbakhsh et al., Yadroitsev et al. and Read et al. have stated that using a similar magnitude of energy density may not necessarily produce samples with similar or identical properties [7, 53, 67]. Various researchers have also observed different phenomena on the influence of energy density [16, 21, 25, 28] and the effect of process parameters [7, 20, 21, 33, 35] on the transformation characteristics, shape memory responses and mechanical properties of NiTi. Additionally, some of the published papers stated a larger value for the hatch distance used than the laser spot size [17, 19, 21, 25, 31, 34]. This occurrence suggests that the molten track produced has a larger width than the laser spot size. One implication from this would be overheating of the NiTi powder at the centre of the irradiation region in order to generate a molten pool that is larger than the irradiated zone [101]. This would then result in the evaporation of Ni and/or Ti at the centre of the irradiated region, causing the chemical composition of NiTi to alter and the transformation characteristics to differ from the initial material. For instance, one of the research by Bormann et al. has shown large deviations in the transformation temperatures of their fabricated samples as compared to the ingot form [21]. Thus, due to various factors such as the lack of complete information and the effect of individual process parameter, there is still no clear guideline on how to obtain SLM NiTi components with desired transformation characteristics and properties. More work is required on the optimisation process and the effect of the process parameters on the transformation characteristics of SLM NiTi. Furthermore, different SLM equipment would most probably require different sets of optimised parameters due to several reasons such as the type of laser used, powder properties and processing conditions. Therefore, this suggested why different researchers are not using the pre-determined parameters from the other research groups. It is essential that they develop their own combinations of optimised parameters before they could fabricate samples for further characterisation and research.

Table 2.3: SLM process parameters and energy densities adopted for the fabrication of SLM NiTi.

Beam-Related Parameters		Scan-Related Parameters			Powder-Related Parameters			Temperature-Related Parameter	Atmosphere-Related Parameters	Machine-Related Parameters		Energy Density (J/mm ³)	Ref
Laser Power (W)	Laser Spot Size (μm)	Laser Scanning Speed (mm/s)	Hatch Distance (μm)	Scanning Strategy	Powder Size (μm)	Layer Thickness (μm)	Chemical Composition	Powder-Bed Temperature (°C)	Atmospheric Control	Laser Type	SLM Machine		
100		100	120	Bi-directional scanning with contour	30 to 120, D ₅₀ = 65	100	49.7 at.% Ni 50.3 at.% Ti		Argon	Yb fibre laser	Realizer SLM100	85	[28]
				Bi-directional scanning with contour	25 to 75	50	50.2 at.% Ni 49.8 at.% Ti		Argon	Yb fibre laser	Realizer SLM100	85	[5]
50	70	100 and 160	100		Average 45	60	55.0 wt.% Ni 45.0 wt.% Ti	500	Argon	Yb fibre laser	Phenix Systems PM 100	83.33 and 52.08	[17, 34]
40 and 250	80	160 and 1100	75 and 60	Bi-directional scanning with 90° rotation between layers	25 to 45	30	55.2 wt.% Ni		Argon	Yb:YAG fibre laser	Custom-made	111 and 126	[7]
60 to 80		171 to 133	120		Average 60	50	56.1 wt.% Ni				Realizer SLM100	60, 70, 84 and 100	[16]
100	50	50 to 400		Alternate scanning with equal	Average 30 for Ni	50	Pure Ni and Ti powder with a ratio of 1:1	80	Argon	Nd:YAG fibre laser	MCP Realizer 250		[33]

				spacing in X and Y directions	and 35 for Ti								
80	60				20 to 100		54.4 at.% Ni		Argon, less than 0.2% O ₂		MCP Realizer		[24]
	61 and 128		120 and 400	Bi- directional and XY- alternating hatching scheme	D ₁₀ = 45 D ₉₀ = 110	75	49.7 at.% Ni 50.3 at.% Ti		Argon	Yb fibre laser	Realizer SLM100		[19]
40 and 250	80	160 and 1100	75 and 60		25 to 45	30	55.2 wt.% Ni		Argon	Yb:YAG fibre laser	Custom- made	111 and 126	[20]
56 to 100	50 to 60	107 to 297	120		35 to 180	50					Realizer SLM100	70 to 125	[21]
40 to 250	80	160 to 2333	50 to 80		25 to 45	30	55.7 wt.% Ni		Argon, with about 1800 and 220 ppm of O ₂ remain	Yb:YAG fibre laser	Custom- made	100 and 111	[35]
250	80	1100	60	Bi- directional scanning with 90° rotation between layers	25 to 45	30	50.2 at.% Ni		Argon	Yb:YAG fibre laser	Custom- made	126	[36]
77	52	200	120		25 to 75	50	49.7 at.% Ni 50.2 at.% Ni 50.5 at.% Ni 50.7 at.% Ni		Argon	Yb fibre laser	Realizer SLM100	234	[25]
250	80	1250	120		25 to 75	30	50.8 at.% Ni 49.2 at.% Ti			Yb fibre laser	Phenix/ 3D Systems PMX	55.5	[31]

2.4.3 Shape Memory Responses

Other than influencing porosity and transformation characteristics, the SLM process was also found to strongly orient the austenitic crystals towards the building direction [36]. Another work by Dadbakhsh et al. demonstrated the effects of austenitic crystals orientation on the shape memory responses of SLM NiTi [36]. It was discovered that the samples aligned vertically to the building stage exhibited the highest percentage of elastic recovery upon removal of the compressive force. However, these samples had the lowest transformation strain measured. On the other hand, samples that were produced horizontally to the building stage had the lowest elastic recovery and highest shape recovery strain upon heating. A suggested reason for the difference in shape memory responses is due to the reduction in the stability of twinned martensite formed as a result of the elongated austenite crystals.

Furthermore, the orientation of the austenite sub-grains was also observed to influence the mechanical properties of the produced samples [36]. The material had a higher resistance to the compressive load applied when the samples were produced horizontally. The resistance decreased for samples fabricated in a vertical manner. This occurrence was suggested to be associated with the more ordered arrangement of the martensite twins when the compressive force was applied horizontally.

In addition, Dadbakhsh et al. proposed that the internal stresses introduced during the SLM process may have induced the formation of large martensitic plates [36]. These plates would lead to a decrease in the elastic recovery of the samples upon unloading. Although annealing followed by furnace cooling could remove these martensitic plates, these treatments could not produce isotropic properties in the samples. Introducing furnace cooling after annealing may even have resulted in the segregation of austenite and martensite within the solidified scanned track, leading to a mixed shape memory response.

In another separate study, Haberland et al. demonstrated the potential in producing high-quality SLM NiTi samples that exhibited SME and superelasticity upon compression loading [25]. They compared their samples to the conventionally-produced NiTi with identical chemical composition. Both the near-equiatomic SLM NiTi and conventional NiTi samples exhibited the typical cyclic behaviour. For each cycle, some irreversible deformation and

shape recovery via SME were observed. The amount of irreversible deformation accumulated during the cycling testing, while showing a decreasing trend as the number of cycles increased. However, the magnitude of residual strain differed for both samples. The conventional NiTi had a higher residual strain in the first few cycles while the SLM NiTi had a higher residual strain in the later cycles. Nonetheless, the irreversible effects were less pronounced for the SLM samples. Furthermore, the decrease in the maximum strain of each cycle was more prominent for the conventional NiTi. Hence, these observations implied that the SLM-produced samples had a more stable shape recovery. Moreover, the comparison of the ratio of reversible strain (sum of strains recovered upon unloading and upon heating via the SME to the maximum strain) developed for each cycle showed that the SLM NiTi samples had a more stable and higher shape recovery in the initial cycles. No difference was observed between the SLM and conventional samples after the sixth cycles.

In the case of the superelasticity behaviour, it was evaluated from the Ni-rich conventional and SLM samples [25]. Both materials illustrated superelasticity with the typical mechanical hysteresis loop. For each testing cycle, these materials exhibited superelastic shape recovery with some irreversible deformation. Likewise, the amount of irreversible deformation accumulated as the number of cycles increased, with an additional decrease in the hysteresis width with each cycle. Additionally, the maximum and reversible strains decreased as the number of cycles increased. Nevertheless, the SLM NiTi samples still appeared to demonstrate a higher maximum strain and slightly higher amount of shape recovery than the conventional NiTi.

Moreover, the NiTi parts produced by SLM can also exhibit different extents of shape recovery per unit change in temperature. In the research done by Meier et al. [5, 28], Bormann et al. [16], Dadbakhsh et al. [7, 20, 36] and Haberland et al. [25], sharp transformation peaks were observed during the differential scanning calorimetry (DSC) tests. However, Clare et al. managed to fabricate SLM NiTi samples with a much gradual phase transformation than the conventional NiTi [24]. The potential applications related to the gradual phase change will be discussed in the next section.

2.4.4 Applications

Among the research done on the applications of SLM NiTi, its biocompatibility effect has been the most widely studied [19]. Shishkovsky et al. reported the absence of free Ni, Ti and other intermetallic phases such as Ni₃Ti and NiTi₃ during the rapid solidification of their samples [17, 34]. This indicated that the samples produced were suitable for medical procedures due to the lack of precipitated phase and highly homogeneity in composition. For example, an excessive amount of Ni released can cause toxicity, carcinogenic effects and immune responses [6].

Another research by Habijan et al. worked on the determination of the suitability of SLM NiTi for biomedical implants [19]. They also experimented on their samples to determine if SLM NiTi could be a potential carrier for the human mesenchymal stem cells. According to the obtained results, the surface topography of the samples and the morphology of the cells could be varied by adjusting the SLM parameters. Although both dense and porous samples were deemed to be suitable for carrying human mesenchymal stem cells, porous samples tend to release more Ni ions. Nonetheless, the amount of Ni released was still much lower than the cytotoxic concentration. The mean concentration of Ni ion released could also be significantly reduced by decreasing the laser spot size. Thus, SLM NiTi can be concluded to be a suitable carrier.

In contrast, the NiTi samples were observed to be susceptible to the release of loose particles. This is unacceptable for biomedical implants. However, the number of particles released depends on the orientation and focus adjustment of the laser. Horizontal surfaces should be produced using a less focused laser due to a large but plain laser intensity distribution within the laser-material interaction zone. Vertical surfaces can be produced with a focused laser and a reduced powder layer thickness to minimize the powder particles released. Nevertheless, a smaller powder size is required for decreasing the layer thickness, which may come with an increase in the content of impurities. In addition, smaller powder particles have poor flowability as a result of powder agglomeration. It is also not possible to totally prevent any particle released by the SLM NiTi parts. Hence, post-processing treatments such as an additional sintering process or subjecting the built parts to ultrasonic cleaning for a prolonged period of time may be required. More work is still needed in order to successfully produce

SLM NiTi components suited for biomedical implants. A good prospect of SLM NiTi is that the NiTi implants can be easily tailored for individuals.

Other than biomedical applications, SLM NiTi can also be utilized in other areas. For instance, Clare et al. produced SLM NiTi samples that demonstrated a much gradual phase transformation [24]. This gradual response has presented many potential benefits for the applications in MEMS. For example, the micro-thermal actuators for heat exchangers may require more discrete intervals of actuation. This can be achieved with a SMA that exhibits gradual phase transformation. Unless the temperature of the NiTi material can be controlled precisely within a certain range of phase transformation, an abrupt phase change may only result in a near 100% austenitic composition or martensitic phase. Furthermore, the gradual transformation of microstructural phases also tends to allow better control of the material properties. A complete martensitic composition is softer and more malleable while a 100% austenitic phase is relatively hard with a much higher Young's modulus [13]. With a gradual phase transformation, the amount of each phase present can be controlled more easily by regulating the temperature. Thus, the material properties will also be easier to manage. The capability to have control over both form and material properties may find many other different applications. Overall, due to the advantage of addressing the poor machinability of NiTi, the SLM process presents an endless possibility of producing complex smart structures for various engineering sectors. Hopefully, in the near future, additional fields of application of SLM NiTi will be reported.

2.4.5 Conclusion

In this chapter, various studies conducted on SLM of NiTi were reviewed. These findings were mainly classified into the effects of energy density, the influence of SLM process parameters, shape memory responses of SLM-produced NiTi and potential applications of SLM NiTi.

1. Three adverse effects were observed when energy density directed to the powder bed exceeded the optimal amount; the increase in porosity, transformation temperatures and impurities of SLM NiTi.

2. SLM process parameters have a strong influence on the transformation characteristics, mechanical properties, porosity and geometrical characteristics of SLM NiTi. Optimization of the parameters is required to obtain a SLM NiTi with controllable transformation characteristics, desired mechanical properties, minimal porosity, low impurity and optimal shape memory responses.
3. SLM NiTi can demonstrate comparable SME and superelasticity as the conventionally-produced NiTi. However, its shape memory responses differ according to the loading direction. Furthermore, it is possible to produce a SLM NiTi that exhibits a much gradual phase transformation than the conventional NiTi.
4. The potential applications of SLM NiTi include being carriers for human mesenchymal stem cells, biomedical implants and MEMS. The list could get longer as the research in this area matures.

On the other hand, there are still no standard guidelines yet on how to produce SLM NiTi parts with the desired phase transformation characteristics, shape memory responses and mechanical properties. As presented in Table 2.3, various combinations of SLM process parameters with diverse magnitudes of energy density have been developed. This is most likely the result of the differences in the raw NiTi powder, SLM equipment used and processing conditions, etc. Therefore, this suggested why different researchers are not using the pre-determined parameters from the other research groups. It is essential that they develop their own combinations of optimised parameters before they could fabricate samples for further characterisation and research

Chapter 3: Optimisation of Process

Parameters

The recent research conducted on the SLM fabrication of NiTi SMA have illustrated the importance of optimising the process parameters. Various research groups have developed different combinations of parameters with diverse magnitudes of energy density due to the differences in the NiTi powder, SLM equipment used and processing conditions, etc. These differences have eventually resulted in the samples produced with dissimilar properties. Moreover, adopting a similar value of energy density may not always produce samples with similar properties [7, 53, 67]. Various researchers have observed the different effects of energy density [16, 21, 25, 28] and process parameters [7, 20, 21, 33, 35, 36] on the transformation characteristics, shape memory responses and mechanical properties of SLM NiTi. At the current stage, there is still no clear guideline on how to fabricate SLM NiTi components with the desired phase transformation characteristics and properties. Therefore, in this chapter, the SLM process parameters are optimised to obtain SLM NiTi parts with low porosity, good dimensional accuracy, minimum oxidation and similar phase transformation characteristics as the raw NiTi powder. Furthermore, the influence of each parameter on the properties of SLM NiTi is discussed in detail.

3.1 Characterisation of Nickel Titanium Ingot

NiTi ingot (SAES Smart Materials, United States of America) is the raw state of the SMA before being processed into the powder form. Nevertheless, it is important to characterise the ingot so as to provide a comparison against the fabricated samples. The characterisation process involves cutting small samples from the ingot to test for their phase transformations characteristics. The experiment is conducted through the use of the DSC (TA Instruments, DSC 2920 Modulated DSC) [1, 29, 45, 102, 103].

During the testing, the samples were cooled to -30 °C, followed by heating up to 120 °C and then cooled down to -30 °C again at a constant ramp rate of 5 °C/min. This process constitutes one cycle. Since the ingot samples were cut off from a larger ingot piece, they might experience some internal stresses that could cause a shift in the transformation temperatures [1, 18, 29, 103]. Thus, these samples were subjected to five cycles of heating and cooling in order to relieve the stresses. The transformation temperatures of the ingot were obtained from the fifth cycle as shown in Figure 3.1. The transformation temperatures were determined by drawing tangent lines to the start and end regions of each transformation peak and to the baseline of the heating and cooling curves [1, 18, 29]. The intersection points of these tangent lines provide the readings for the transformation temperatures. A total of four different ingot samples were tested. Their average transformation temperatures were tabulated and are presented in Table 3.1.

Figure 3.1: Phase transformation characteristics of one NiTi ingot sample tested.

Table 3.1: Average transformation temperatures of four NiTi ingot sample tested.

	Transformation Temperatures			
	M_s (°C)	M_f (°C)	A_s (°C)	A_f (°C)
NiTi Ingot	54 ± 1	38 ± 1	64 ± 1	87 ± 0

3.2 Characterisation of Nickel Titanium Powder

Similar to the NiTi ingot, the pre-alloyed NiTi powder (Metal Powders and Materials LLP, Singapore) was also characterised to provide a comparison for the printed samples. However, as the powder was mass-produced by gas atomization of the ingot, some internal stresses might exist within the powder particles. Hence, during the testing for its phase transformation characteristics, the powder was subjected to five cycles of heating and cooling with identical temperature range and ramp rate as the ingot. Likewise, only the fifth cycle was selected in determining the transformation temperatures of the NiTi powder.

Figure 3.2 shows one of the fifth DSC cycles of the NiTi powder and Table 3.2 presents its average transformation temperatures. By comparing the transformation temperatures of the powder and ingot, it can be observed that there is a widening of the transformation interval (M_f temperature to A_f temperature) after processing into the powder form. Moreover, two-step phase transformations seem to have occurred for the NiTi powder as well.

Figure 3.2: Phase transformation characteristics of NiTi powder.

Table 3.2: Average transformation temperatures of NiTi powder tested.

	Transformation Temperatures			
	M _s (°C)	M _f (°C)	A _s (°C)	A _f (°C)
NiTi Powder	47 ± 0	17 ± 0	48 ± 1	79 ± 0

On the other hand, the chemical composition of the NiTi powder was also determined. The average chemical composition was obtained by two methods. The first method is by using the empirical relationship between the chemical composition of NiTi and its M_s temperature [26]. The M_s temperature was obtained from the DSC test and used to read off the Ni concentration in Figure 2.2. The atomic percentage of Ni present in the powder is estimated to be about 50.23%. This result is further confirmed by the second approach, which is through the use of Energy-Dispersive X-ray Spectroscopy (EDS) (Oxford Instruments, Inca x-stream). Different regions of the powder sample were scanned by EDS to get an average composition. Table 3.3 compounds the different weight percentages and atomic percentages of Ni and Ti at the different scanned regions of the powder sample. Based on the EDS results, the chemical composition of the powder was found to have an average atomic percentage of 50.09% Ni and 49.91% Ti. Hence, by taking an average of the readings collected from these two methods, the atomic percentage of the NiTi powder can be approximated to be about 50.16% Ni and 49.84% Ti.

Table 3.3: Chemical composition of NiTi powder based on EDS results.

Section	Weight Percentage		Atomic Percentage	
	Titanium (%)	Nickel (%)	Titanium (%)	Nickel (%)
1	43.88	56.12	48.93	51.07
2	45.93	54.07	51.01	48.99
3	43.75	56.25	48.81	51.19
4	46.62	53.38	51.70	48.30
5	45.18	54.82	50.26	49.74
6	43.71	56.29	48.76	51.24
Average	44.845	55.155	<u>49.91</u>	<u>50.09</u>

Additionally, the shape of the powder particles was determined by taking microscopic images of the particles using the SEM. The SEM micrographs can be seen in Figure 3.3. The particle size of the NiTi powder ranges mainly from 20 to 50 µm and they are generally spherical in shape. Spherical powder particles are preferred as they provide good flowability [24, 95].

Figure 3.3: SEM micrographs of NiTi powder.

3.3 Fabrication and Characterisation of Nickel Titanium Samples

In this research, a custom-made SLM machine (Precision Laser Solutions Pte. Ltd., Singapore, PLS-FLM100W) was used for the production of SLM NiTi samples. The equipped laser is a Ytterbium (Yb) fibre laser with a wavelength of 1070 nm and an estimated spot size of 26 μm . The calculation of the laser spot size is presented in Appendix A.

The step-by-step fabrication procedures of NiTi samples are listed as follows:

1. Main power switches were first switched on.
2. A custom-made SLM machine (Precision Laser Solutions Pte. Ltd., PLS-FLM100W) and dry vacuum pump (Ebara, PDV250) were then switched on. The pump was allowed to warm up for 20 minutes before the start of the fabrication process.
3. The inlet to the argon gas used to purge the air within the fabrication chamber was switched on.
4. NiTi powder was transferred from the original container into a small container to prevent contamination.
5. NiTi powder separated from the original container was deposited on top of an aluminium base plate to form a thick layer of powder.
6. The powder was spread across to make it as flat as possible.

7. The base plate and powder were then placed inside the fabrication chamber.
8. Focal length from the laser to the powder bed was adjusted to be roughly 181 mm.
9. Trial laser scanning function was used to determine if the scanning area falls within the powder bed. Adjustments to the position of the base plate were made when necessary.
10. The fabrication chamber was then closed tightly to prevent atmospheric air from entering during the operation of the vacuum pump or argon gas from escaping when it was being pumped into the chamber. This is to reduce the number of cycles needed for the purging process.
11. Oxygen setting time on the programme that monitors the oxygen sensor reading was set to 30 s. This provides some time for the sensor to react to the changes in the oxygen content inside the fabrication chamber. The targeted oxygen percentage setting on the programme was set to 0.1%; the maximum accuracy that the sensor can detect.
12. Once the programme settings were fixed, the dry pump would then be switched on to purge the air inside the chamber with argon gas.
13. The purging process will stop once the oxygen concentration level reaches 0.1% or lower. The end of the purging process is marked by a green light signal.
14. The default chamber environment will be filled with argon gas at a high pressure of about 7.5 kPa and higher.
15. While waiting for the purging process to be completed, the samples to be produced were drawn using another programme that controls the fabrication process. The samples' shapes, dimensions, positions, printing order and processing parameters to be used were inputted through that programme. For the determination of the optimal processing window, square samples of dimensions 5 mm by 5 mm were manufactured. Long strip samples of 5 mm by 78 mm were produced for the testing of shape memory properties.
16. Once the purging process has completed and the process parameters were entered, the fabrication process would be initiated.
17. Due to the thick layer of the powder bed, only the top layer would be melted and solidified when the laser scanned across the powder bed. There would still be a layer of powder beneath the solidified samples and the base plate. This method

of fabricating NiTi samples helps to prevent contamination of the samples due to the possible reaction between the aluminium base plate and NiTi alloy. Moreover, it makes the removal of the samples much easier and more convenient as well.

18. Four samples were produced for each combination of parameters.
19. Upon completion of the printing process, the pressure valve was switched on to release the high pressure built up inside the chamber.
20. Aluminium base plate together with the solidified samples can then be removed from the fabrication chamber.
21. The samples were collected and kept for further characterisation tests.

Before undergoing any other types of characterisation tests, visual inspections were first performed to reduce the huge number of fabricated samples required for testing. The three basic physical criteria that the samples need to exhibit are the visible melting of the powder particles, good dimensional or geometrical accuracy and minimal oxidation. The samples that met these criteria were subjected to the other testing, where five of its properties were determined: porosity, surface morphology, dimensional measurement, phase transformation characteristics and stress-free shape memory responses.

The fabricated samples are required to have high bulk densities or low porosity. This is because porosity is known to have a direct influence on the material's mechanical strength, fatigue strength and elongation to rupture [104]. As mentioned in Sections 2.1.2 and 2.1.3, NiTi samples have to be deformed first in order for them to exhibit SME or superelasticity [29]. However, samples with high porosities tend to fracture easily under the tension load. Thus, it is very important for the SLM NiTi samples to have minimum porosities and density measurement is an essential test to obtain that information. Nevertheless, the solid density of the samples will not be determined in this project. Since solid density refers to the density of a component without considering its porosity, the bulk density of the samples will be measured instead [105]. It is to be noted that the bulk density readings obtained in this study only account for the amount of closed pore (internal porosity) that exist within the NiTi samples [105]. Hence, the porosity of the samples can be determined by the percentage difference between their theoretical and bulk densities. The determination of the theoretical density is presented in Appendix B.

In order to obtain the density of a material, the mass and volume of the sample material must be determined first. The mass of a sample can be found out easily by using a weighing instrument. However, an accurate determination of the sample's volume is usually difficult, especially if the sample has an irregular shape. Thus, the buoyancy method that is based on the Archimedean Principle has been adopted to overcome this problem [105]. The equipment used consists of a mass balance (Sartorius, Entris Balance) fitted with a density measurement kit (Sartorius, Density Kit YDK01LP). The bulk density of the samples was calculated using the following equation [104-106]:

$$\rho_s = \rho_{fl} \left[\frac{m_a}{m_a - m_{fl}} \right] \quad (3.1)$$

where ρ_s is the bulk density of the NiTi sample, ρ_{fl} is the density of the liquid used, which is temperature dependent, m_a is the mass of the sample measured in air and m_{fl} is the mass of the sample measured while fully submerged in the liquid. The liquid chosen was boiled deionised water and its temperature was measured to obtain its density value. Each sample was weighed in the air for five times and in boiled deionised water for five times to get an average reading of m_a and m_{fl} respectively.

The buoyancy method is selected as the technique for density measurement due to its high repeatability and accuracy [104]. Moreover, this method is easy to adopt, economical and is a relatively fast process as compared to the other techniques. Nevertheless, it is still important to consider the possible sources of error that might occur. Precautions were then taken to avoid them.

One of the main sources of error is the temperature dependency of the fluid's density readings [105, 106]. The reason for choosing deionised water over other types of fluid is because of its smaller fluctuation in density values per unit change in temperature [105]. For instance, when the temperature of the liquid rises from 20 to 21 °C, the density of the deionised water decreases by 0.00021 g/cm³ while for alcohol such as the ethanol, its density decreases by 0.00085 g/cm³. In this scenario, the difference in the decrease of densities is more than four times as much. Hence, this phenomenon would imply that the temperature of the liquid has to be more strictly controlled, or else the results of the density measurement with the use of ethanol can lead to a larger error.

The second possible source of error is the effect of air buoyancy during the measurement of the sample's mass in the air [104, 106]. Nonetheless, as the density of air is about 1000 times smaller than the density of deionised water, the effect of air buoyancy can be assumed to be negligible [104].

The third source of error could come from the additional buoyancy effect due to the formation of air bubbles on the sample's surfaces [106]. To reduce the number of air bubbles formed, deionised water was boiled and cooled prior to the density measurement. Additionally, the air bubbles could also be removed by using a fine brush or by wetting the sample [106]. This is accounted for by the multiple measurements made when the sample was repeatedly submerged into the boiled deionised water. Consistent m_{fl} readings were obtained during the bulk density measurements as well.

Prior to the DSC test, selected high-density samples had their micrographs taken either by the optical microscope (Olympus SZX7 Microscope) or SEM (Jeol, JSM-5600LV). The reason for this particular order of testing is because the samples produced were too large and heavy to fit into the holding pan for the DSC machine. Thus, after observing their surface morphologies and measurement of their dimensions, the borders of the samples were then cut away and the central region was used for DSC testing. The samples went through five cycles of heating and cooling with a ramp rate of 5 °C/min from a temperature range of -30 to 120 °C. However, only the DSC curves that correspond to the fifth cycle were utilised for the determination of the stress-free transformation temperatures.

Upon deciding on a particular combination of optimised parameters, long strip samples were fabricated next for the determination of their shape memory responses. These samples were produced by scanning an area of 5 mm by 78 mm. Prior to the testing, the strip samples were wire cut to a width of about 3.5 mm, followed by polishing to remove the burrs, surface unevenness and excess powder particles. Afterwards, the cut samples were heated above their A_f temperature and cooled below their M_f temperature. The heating process helps to remove the detwinned martensite formed during the sample preparation. The cooling process ensures that the samples exhibit only twinned martensitic phase before testing.

The stress-free shape memory responses of the optimised samples were studied under the effect of tensile loading. The samples were first deformed to a maximum pre-defined strain, followed by unloading to a minimum load of 0.5 N with a strain rate of 0.01%/min at room temperature (Shimadzu, AG-X Plus). The 0.5 N tensile load was then held constant for the remaining of the testing process. Next, the deformed samples were heated up inside a thermal chamber (Shimadzu, TCE-N300-CE) at a rate of 2 °C/min and the strain recovery due to SME was recorded. The elongation and thermal expansion of the clamps during the loading and heating phases were taken into account by calibrating with an alumina plate.

In the determination of the elongation of the clamps, the alumina plate was subjected to the tensile load from 0 to 200 N at room temperature. A displacement-force curve with the best-fit line was then plotted and the elongation coefficient was determined. The test was repeated once more to get the average elongation coefficient, which was then used to correct for the elongation of the clamps. As for the thermal expansion, the alumina plate was loaded with a constant tensile load of 0.5 N, followed by heating the clamps from room temperature to 120 °C. Similarly, a displacement-temperature curve with the best-fit line was drawn and the thermal expansion coefficient was determined. The test was conducted once more and the average thermal expansion coefficient was utilised to account for the thermal expansion of the clamps. The alumina plate was assumed to demonstrate negligible deformation during both processes and the results recorded were entirely contributed by the clamps. Appendix C presents the corresponding displacement-force and displacement-temperature curves with the average elongation and thermal expansion coefficients. A better estimate of the deformation of the samples was achieved by removing these contributions from the raw data collected.

3.3.1 Optimisation of Laser Power and Laser Scanning Speed

There are many different SLM process parameters to consider during the fabrication process. These parameters can be classified into six categories as shown in Table 2.1 [6, 53, 63, 65, 66]. Nevertheless, only the beam-related parameters and scan-related parameters were optimised in this research. The beam-related parameter that has been varied was the laser

power while the four scan-related parameters that have been tested were the scanning speed, hatch distance, scanning strategy and the number of scans (Chapter 4).

During the initial stage of the optimisation process, only the laser power and laser scanning speed were selected to be the variable parameters while the rest of the process parameters were kept constant. The laser power was varied from 10 to 100 W with an interval of 10 W and the laser scanning speed was varied from 100 to 6000 mm/s with an interval of 100 mm/s. Four samples were fabricated for each combination of parameters. Table 3.4 presents the varying and fixed process parameters and their respective magnitudes for the initial optimisation process. Appendix D shows some micrographs of the samples produced during this preliminary phase.

Table 3.4: Process parameters for the optimisation of laser power and laser scanning speed.

Types of Parameters	Process Parameters	Magnitudes
Beam-Related Parameters	Laser power	10 to 100 W, with an interval of 10 W
	Spot size	About 26 μm
	Pulse duration	10 μs
	Pulse frequency	100 kHz
	Beam spatial distribution	Gaussian beam TEM00
	Laser wavelength	1070 nm
Scan-Related Parameters	Scanning speed	100 to 6000 mm/s, with an interval of 100 mm/s
	Pitch/hatch distance	5 μm
	Number of scans	1
	Scan track length	5 mm
	Scanning strategy	Bi-directional scanning with contour and perimeter scanning

As mentioned in Section 3.3, visual inspections were first employed to reduce the number of samples required for further testing. The three physical phenomena that the samples need to exhibit are the visible melting of the powder particles, high dimensional or geometrical accuracy and minimal oxidation. Figure 3.4 presents some examples of the NiTi samples with a poor melting of the powder particles (sintering), poor dimensional accuracy and the occurrence of oxidation. It also shows an example of a potentially high-quality sample for comparison.

Figure 3.4: NiTi samples that demonstrate (a) poor melting of the powder particles (20 W, 3000 mm/s), (b) poor dimensional accuracy (100 W, 3800 mm/s) and (c) occurrence of oxidation (20 W, 100 mm/s). An example of (d) a potentially high-quality sample (50 W, 4700 mm/s) is also presented.

Based on visual inspections, samples that were fabricated with a low laser power of 10 W to 30 W generally did not exhibit complete melting of the powder particles. However, when the samples were produced with low scanning speed coupled with a low laser power, high degree of melting could still be observed. Nonetheless, these samples were noticed to be oxidised. On the other hand, samples that were manufactured with a high laser power ranging from 80 to 100 W could be seen to be oxidised and deformed as well. These observations made were further verified by conducting EDS testing on three selected samples to get a rough estimate of the amount of oxygen present. The average atomic percentage (at. %) of oxygen in each region of the samples is indicated in Figure 3.5. It is to be noted that the main aim is to minimise the occurrence of oxidation. This is because the presence of the oxide film can lead to poor wetting condition and balling effect during the layer-by-layer fabrication [63, 98]. It can cause problems in the spreading and flattening of the molten pool on the previous layer.

Consequently, the densification mechanism will be affected. Moreover, the oxides are usually brittle and can result in a deterioration of mechanical properties. Hence, oxidation should be minimised at all cost. The types of the oxide layer formed on the samples' surfaces are not of concern.

Figure 3.5: The different degree of oxidation with the average atomic percentages (at. %) of oxygen present in each region.

As shown in Figure 3.5, the extent of oxidation of the sample with a low laser power of 20 W decreases as the scanning speed increases. Moreover, with the same laser scanning speed of 1000 mm/s, a higher laser power used tends to produce samples with a larger extent of oxidation and balling effect. Thus, both high laser power and low scanning speed can be associated with the occurrence of oxidation. The possible explanation for these phenomena could be related to the time required for the molten pool to cool down. When either a high laser power or a low scanning speed was used, the molten pool would be brought to a higher temperature due to the higher amount of energy density delivered. Thus, this lead to the

molten pool requiring a longer period of time to cool down and solidify. As a result of this prolonged cooling process, more time was generated for the oxidation to occur.

In addition, the presence of the less-oxidised portion at the lower part of the sample also suggested that oxidation was caused by the prolonged heating of the sample. During the fabrication process, the laser started scanning from the top region. As the laser travelled down to the next adjacent scan track, the preceding scan track was heated up due to the heat conducted away from the molten pool. This would result in the solidified scan track to be under high temperature for a longer period of time and hence allowing more time for the oxidation to occur. Once the laser has completed scanning the lower portion of the sample, the laser energy was cut off and the lower region was left to cool down rapidly. Hence, there was inadequate time for heavy oxidation to take place at the bottom part of the sample.

After the completion of the visual inspections, the remaining samples were then subjected to the measurement of their bulk densities. The bulk density readings were utilised to derive the relative density of the samples by comparing them to the theoretical density of NiTi. The difference between the relative density and the theoretical density would amount to the internal porosity within the samples. These results are presented in Figure 3.6 with their respective error bars. The error bars indicate the maximum value and the minimum value obtained from the four samples manufactured using the same combination of process parameters.

Figure 3.6: Internal porosity of SLM NiTi samples fabricated with different laser powers against the varying laser scanning speed.

Generally, according to the results obtained, the samples exhibit a lower porosity when a higher laser power is used. For the optimisation of laser power and laser scanning speed, the samples fabricated should have a low percentage of porosity and a high repeatability. The repeatability of the readings is associated with the difference between the maximum value and the minimum value obtained from the four samples, where a small difference between these readings implies a higher repeatability. The ranges of samples found to fulfil these two criteria are highlighted by the red dash boxes shown in Figure 3.6. The samples that lie in the centre of these ranges are selected for the measurement of their dimensions and DSC test. Figure 3.7 provides some micrographs of the samples tested with their dimensions indicated. The process parameters and properties that correspond to these samples are presented in Table 3.5. Their average transformation temperatures are displayed in Table 3.6.

Figure 3.7: Dimensions of samples produced with laser power and laser scanning speed of (a) 60 W and 3600 mm/s and (b) 70 W and 4700 mm/s.

Table 3.5: Process parameters for samples with optimised laser power and laser scanning speed. Their internal porosity, data variation and average dimensions were also determined.

Process Parameters	Combination A	Combination B
Laser Power (W)	60	70
Laser Scanning Speed (mm/s)	3600	4700
Hatch Distance (μm)	5	
Number of Scans	1	
Scanning Strategy	Bi-directional scanning with contour and perimeter scanning	
Internal Porosity (%)	3.10	3.14
Data Variation (%)	1.23	1.88
Average Dimensions of Length and Width (mm)	(5.11 ± 0.01) by (5.17 ± 0.02)	(5.09 ± 0.11) by (5.18 ± 0.04)

Table 3.6: Comparison of the transformation temperatures between NiTi ingot, powder and SLM NiTi samples fabricated by Combination A and B.

	Transformation Temperatures			
	M_s ($^{\circ}\text{C}$)	M_f ($^{\circ}\text{C}$)	A_s ($^{\circ}\text{C}$)	A_f ($^{\circ}\text{C}$)
NiTi Ingot	54 ± 1	38 ± 1	64 ± 1	87 ± 0
NiTi Powder	47 ± 0	17 ± 0	48 ± 1	79 ± 0
Combination A	46 ± 1	19 ± 1	47 ± 0	78 ± 1
Combination B	46 ± 1	21 ± 1	48 ± 1	79 ± 1

Following the density and dimension measurement, the next characterisation test to be conducted is the DSC testing. This is an important test as it determines the samples' ability to

exhibit phase transformation. The presence of the phase transformation would suggest the possibility of the samples demonstrating a high percentage of shape recovery. Based on the results presented in Table 3.6, samples fabricated using either combination have exhibited phase transformation. However, when being compared to the NiTi powder, samples produced with Combination B have slighter similar transformation temperatures than samples produced with Combination A. The only exception is the M_f temperature. The reason for comparing the transformation temperatures of the SLM NiTi samples to the powder is to prevent large alteration in the chemical composition during the fabrication process. The composition can vary when an excessive amount of energy density has been delivered to the powder bed [16, 21, 28]. Nonetheless, the samples manufactured by Combination A have slightly lower internal porosity and data variation. Moreover, they showed a lower deviation in their average dimensions as compared to the samples produced using Combination B. The linear energy density ($E = P/v$, where P refers to the laser power and v indicates the laser scanning speed) required for Combination A ($E = 0.0167 \text{ J/mm}$) is also higher than Combination B ($E = 0.0149 \text{ J/mm}$) [98]. Thus, the samples would be less susceptible to the balling effect [71, 98]. Furthermore, the largest difference between the transformation temperatures of the powder and samples manufactured with Combination A is 2°C . Hence, it can be concluded that both powder and samples have very similar chemical compositions. Therefore, Combination A was selected for further optimisation of the remaining process parameters.

3.3.2 Optimisation of Hatch Distance

Upon determining a suitable magnitude for the laser power and laser scanning speed, the hatch distance was varied next to determine an appropriate value to be adopted. Hatch distance is an influential process parameter [24, 38]. During the process of optimising the hatch distance, it has to be smaller than the track build width in order to have a good bonding between the melted tracks and to achieve minimal porosity. Table 3.7 presents the process parameters with their respective magnitudes and range used for the optimisation of hatch distance. Appendix E shows the micrographs of the samples produced during this stage of the optimisation process.

Table 3.7: Process parameters for the optimisation of hatch distance.

Types of Parameters	Process Parameters	Magnitudes
Beam-Related Parameters	Laser power	60 W
	Spot size	About 26 μm
	Pulse duration	10 μs
	Pulse frequency	100 kHz
	Beam spatial distribution	Gaussian beam TEM00
	Laser wavelength	1070 nm
Scan-Related Parameters	Scanning speed	3600 mm/s
	Pitch/hatch distance	1 to 9 μm , with an interval of 1 μm
	Number of scans	1
	Scan track length	5 mm
	Scanning strategy	Bi-directional scanning with contour and perimeter scanning

Similar to the procedure adopted during the optimisation of the laser power and laser scanning speed, visual inspections were first performed to reduce the number of samples required for bulk density measurement. Samples that were fabricated with a hatch distance of 8 and 9 μm were found to exhibit poor melting of the powder particles. The remaining samples were subjected to the measurement of their bulk densities and their internal porosities were derived. Figure 3.8 presents the internal porosity of the samples with their respective error bars plotted against the varying hatch distance.

Figure 3.8: Internal porosity of SLM NiTi samples fabricated with a laser power of 60 W and laser scanning speed of 3600 mm/s against the varying hatch distance.

As observed from Figure 3.8, there is an optimal range of hatch distance that is roughly between 3 to 5 μm where samples with low porosity were produced. The samples fabricated

within this range of hatch distance have a smaller variation in their readings as well. It is noticed that as the hatch distance gets further away from the optimal range, the average internal porosity and the variation in the readings recorded increase. Similar behaviour can be observed in another study conducted on different size of NiTi powder particle [38]. The bulk densities and relative densities of the samples produced by the different combinations of parameters are shown in Figure 3.9 for comparison purposes.

Figure 3.9: Bulk densities and relative densities of SLM NiTi samples produced by (a) Combination 1 (laser power of 30 W and laser scanning speed of 100 mm/s), (b) Combination 2 (laser power of 40 W and laser scanning speed of 100 mm/s) and (c) Combination 3 (laser power of 40 W and laser scanning speed of 200 mm/s) [38].

Theoretically, it is expected that by using a smaller hatch distance, there would be more overlap and re-melting between the adjacent scan tracks. Thus, the fabricated samples would exhibit a higher bulk density. However, the result presented in Figures 3.8 and 3.9 contradict this conventional rationale. In this research, lower bulk densities or higher porosity were obtained for the samples produced with a lower hatch distance. As suggested by Bormann et

al., one possible explanation for this phenomenon could be associated with the volume of the molten pool generated [21]. By using a smaller magnitude of hatch distance, the energy density deposited to the powder bed would be higher. Hence, the volume of the molten pool formed would be greater. Consequently, the large amount of molten pool would hinder the diffusion of the gas bubbles to its surface during the solidification process. Likewise, Olakanmi et al. have also mentioned that in order for the samples to have high densities, the majority of the gas bubbles formed during the melting process need to travel upwards and collapse [69]. Even though the varying parameter may not be the hatch distance, various authors have reported their observation of higher porosities SLM NiTi samples with increasing magnitude of energy density as well [21, 25]. 316L stainless steel parts were also observed to exhibit a lower density with decreasing hatch distance [107].

Nevertheless, the bulk densities of the samples showed a decreasing trend or the internal porosity of the samples showed an increasing trend as the hatch distance increases beyond the optimal range. This occurrence is expected since the larger hatch distance adopted during the fabrication process would lead to less overlap between the adjacent laser scan tracks [65]. As a result, porosity will be generated within the sample, leading to the samples produced with lower bulk densities or higher porosity.

During the optimisation of the hatch distance, the samples that exhibit the highest bulk density were found to be fabricated with a hatch distance of 3 μm . Thus, these samples were subjected to the measurement of dimensions and DSC testing. Figure 3.10 demonstrates the dimensional measurement of one sample produced. Table 3.8 shows the comparison between the average length and width of the samples prior and after the optimisation of hatch distance. The transformation temperatures were also estimated from the DSC curves and the average temperatures were then compared to the transformation temperatures of the ingot and powder. The various temperatures are presented in Table 3.9.

Figure 3.10: Dimensions of sample produced with laser power of 60 W, laser scanning speed of 3600 mm/s and hatch distance of 3 μm .

Table 3.8: Average dimensions of samples produced before (5 μm) and after (3 μm) the optimisation of hatch distance.

	Before Optimisation (5 μm)	After Optimisation (3 μm)
Average Dimensions of Length and Width (mm)	(5.11 ± 0.01) by (5.17 ± 0.02)	(5.02 ± 0.11) by (5.29 ± 0.05)

Table 3.9: Comparison of the transformation temperatures of NiTi ingot, powder and SLM NiTi samples fabricated with a laser power of 60 W, laser scanning speed of 3600 mm/s and hatch distance of 3 μm .

	Transformation Temperatures			
	M_s ($^{\circ}\text{C}$)	M_f ($^{\circ}\text{C}$)	A_s ($^{\circ}\text{C}$)	A_f ($^{\circ}\text{C}$)
NiTi Ingot	54 ± 1	38 ± 1	64 ± 1	87 ± 0
NiTi Powder	47 ± 0	17 ± 0	48 ± 1	79 ± 0
Laser Power: 60 W Laser Scanning Speed: 3600 mm/s Hatch Distance: 3 μm	43 ± 0	18 ± 1	49 ± 1	74 ± 0

Based on Table 3.8, the width of the samples tend to increase slightly with decreasing hatch distance. This is likely due to the increase in the energy density directed to the material, leading to the surge in the volume of the molten pool. However, it is still preferred for the

samples to demonstrate a high density in order to have good mechanical properties. Hence, one implication would be to take into consideration of the slight dimensional inaccuracy when adopting the optimised hatch distance of 3 μm for future research.

Additionally, the average transformation temperatures obtained after the optimisation of hatch distance also differ slightly more than the average transformation temperatures shown in Table 3.6. Nevertheless, the difference can still be considered negligible. This is due to the compositional sensitivity of NiTi as the transformation temperatures of NiTi depend heavily on its chemical composition [11, 18, 26].

3.3.3 Optimisation of Scanning Strategy

There are a total of five different scanning strategies that will be investigated in this project. These five scanning strategies are bi-directional scanning with contour and perimeter scanning, bi-directional scanning with contour, bi-directional scanning with perimeter scanning, uni-directional scanning with perimeter scanning and spiral-in scanning with perimeter scanning. The schematics of the different scanning strategies are illustrated in Figure 3.11. For the scanning strategies that include perimeter scanning, the laser would first travel according to either schematic shown in Figure 3.11a to 3.11d, followed by scanning around the perimeter of the defined area as presented in Figure 3.11e. Appendix F presents the micrographs of the samples produced via the different scanning strategies.

Figure 3.11: Schematics of (a) bi-directional scanning with contour, (b) bi-directional scanning, (c) uni-directional scanning, (d) spiral-in scanning and (e) perimeter scanning.

During the visual inspections, uni-directional scanning with perimeter scanning and spiral-in scanning with perimeter scanning did not produce samples that met the criteria of high

degree of melting and good dimension accuracy, respectively. Thus, only samples that were fabricated by the remaining three scanning strategies were subjected to density measurement. It was observed that there was no significant difference in the porosity formed within the samples. The only difference between them lies in the data variation, where bi-directional scanning with contour and perimeter scanning produced samples with the lowest deviation. Hence, this result coincides with the scanning strategy adopted during the earlier stage of the optimisation process. There is no need for the samples to undergo another round of DSC testing.

Nevertheless, interesting physical morphology can be observed for the samples manufactured by the spiral-in scanning strategy. The first observation made is that higher degree of melting can be noticed at the four diagonals of the samples as shown in Figure 3.12a. This phenomenon can be attributed to two different factors. The first factor is due to the increase in the overlap of the laser scanning tracks at the diagonals. As illustrated in Figure 3.12b, even though the hatch distance remains constant, the distance between the two perpendicular laser tracks decreases as the laser approaches the corner. Once the laser gets sufficiently close to the corners, the laser tracks would overlap with each other as seen from Figure 3.12c. This would result in more energy being delivered at the diagonals, leading to the better melting of the powder particles.

Figure 3.12: An example of (a) a sample with a higher degree of melting at its diagonals, (b) decreasing distance between two perpendicular laser tracks and (c) an overlapping of laser tracks near the corner.

The second possible factor could be due to the time the equipment took to change the direction of the scan track at the corners. In order to change the direction, the devices or

mirrors within the equipment have to change position as well. This would require some time as it is impossible for the devices to change from one position to another position instantaneously. Thus, it would be safe to assume that more time is taken for the laser to make corners than if it were to travel the same distance in a straight line. Hence, this slight increase in the laser scanning time at the corners could possibly cause more energy to be deposited to the powder at the diagonals and result in better melting.

The next visual observation that can be seen is that the samples contain more and larger open pores on the outer region than the central region as presented in Figure 3.13. One reason for the occurrence of this phenomenon could be due to the fact that the spiral-in scanning strategy comprises of shorter scanning tracks towards the centre of the scan pattern as illustrated in Figure 3.11d. As a result, the laser tracks overlap more and more towards the centre and gives rise to the central region having longer exposure time to the laser. Hence, more energy will be supplied to the central region and the melted powder will stay liquefied for a longer period of time, allowing the liquid NiTi to smoothen out before it solidifies.

Figure 3.13: An example of a sample containing large open pores on its outer region.

Another physical attribute that can be seen from Figure 3.12a and 3.13 is that all the samples fabricated by adopting the spiral-in scanning strategy exhibit a through cavity at the centre of the samples. One possible reason for this occurrence could be related to the above-mentioned explanation, where the scanning tracks in the centre are very close to each other. Hence, the laser would be scanning roughly the same region extensively. This results in

excessive energy to be provided to the central region and causes the NiTi powder to evaporate. Another possible explanation could be associated with the shrinkage of the samples during the SLM process. Due to the pre-defined laser tracks in the spiral-in scanning strategy, the laser would first start scanning from the outermost region. Thus, powder in the outer region would melt, solidify and then contract. As the laser travels to the next inner scanning path and scans the powder, the powder would once again be melted, then solidify and contract. However, as the outermost region already has a ring of solidified NiTi, the inner region will contract outwards and towards the outer region of the solidified NiTi. Thus, the contraction of each inner region accumulates to form a cavity in the middle of the samples.

Finally, the last visual observation is that the samples exhibit a concave shape or inverted cone shape from the side views shown in Figure 3.14. The thickness in the centre of the samples is found to be the highest while the outermost region is the thinnest. Again, this physical phenomenon observed suggested that there is extensive overlapping of the scan tracks towards the central region, resulting in more energy supplied and more powder being melted and solidified underneath.

Figure 3.14: An example of a sample's side view exhibiting concave shape or inverted cone shape.

3.3.4 Limitations

At the current stage, the magnitudes of the optimised SLM process parameters (laser power, laser scanning speed, hatch distance and scanning strategy) are listed in Table 3.10. To validate the shape memory properties of the SLM NiTi samples produced by these parameters, four long strip samples were produced. These samples were studied under the effect of tension load. Compression test is not conducted as it ignores the effect of porosity. High porosity samples tend to fracture easily under tension load than under compressive load. The presence of the pores can contribute to stress concentrations when under tension and cause failure. There have been much research carried out that illustrated the importance of obtaining a low porosity component [63, 108, 109]. Furthermore, a sample that demonstrates a high magnitude of shape recovery after compression does not always translate into a high shape recovery upon tensile load. The sample must be of a sufficient quality in order to withstand the tensile stress without failure. Thus, the determination of shape recovery property under tension load is an essential experiment for the SLM NiTi SMA. It evaluates the combined quality of the sample including porosities, ductility, transformation characteristics and most importantly SME. Nonetheless, the majority of the shape memory results reported on SLM NiTi were still conducted under a compression load, which have neglected the influences of porosity [5, 7, 20, 25, 31, 36].

Table 3.10: Process parameters used for producing SLM NiTi samples after the optimisation of laser power, laser scanning speed, hatch distance and scanning strategy.

Types of Parameters	Process Parameters	Magnitudes
Beam-Related Parameters	Laser power	60 W
	Spot size	About 26 μm
	Pulse duration	10 μs
	Pulse frequency	100 kHz
	Beam spatial distribution	Gaussian beam TEM00
	Laser wavelength	1070 nm
Scan-Related Parameters	Scanning speed	3600 mm/s
	Pitch/hatch distance	3 μm
	Number of scans	1
	Scan track length	5 mm
	Scanning strategy	Bi-directional scanning with contour and perimeter scanning

Figure 3.15 presents the force-strain curves of all the samples tested. Figures 3.15b and 3.15c show the result and micrograph of the best sample. However, even the best sample could not

deform beyond 6% strain. These results have suggested that the sample experienced fractures at multiple points before failing ultimately at 6% strain. Therefore, more work needs to be done to determine the causes of failure and how to overcome these limitations.

Figure 3.15: Force-strain curves and micrograph of SLM NiTi produced after optimisation of laser power, laser scanning speed, hatch distance and scanning strategy: (a) force-strain curves of samples with poorer mechanical properties, (b) force-strain curve and (c) micrograph of the best sample tested.

3.4 Conclusion

In this chapter, various SLM process parameters have been optimised with the aim of producing SLM NiTi samples with high density, good dimensional accuracy, minimal oxidation and similar phase transformation characteristics as the NiTi powder. These beam-related and scan-related parameters included laser power, laser scanning speed, hatch distance and scanning strategy. The deviation of the readings recorded for the internal porosity and

transformation temperatures of the optimised samples were observed to be small. This indicated the high repeatability of the fabrication process. Nevertheless, the samples did not demonstrate good mechanical properties. During the determination of the stress-free shape memory responses under tensile mode, the samples exhibited multiple fractures before failure. Hence, it is concluded that the conventional optimisation strategy did not work desirably for NiTi SMA. This may be the reason why the other research groups have not reported any tensile test results. Therefore, a new approach is needed to produce SLM NiTi with satisfactory properties.

Chapter 4: Enhancements Through

Repetitive Scanning

SLM NiTi parts produced via the conventional strategy of optimising the laser power, laser scanning speed, hatch distance and scanning strategy have shown poor mechanical properties. These samples were not able to withstand a high tensile strain and they demonstrated multiple fractures before failure. Thus, more studies are required to determine the roots of failure and the possible solutions to overcome them.

4.1 Motivation

In the search for the causes of poor quality, optical micrographs of the samples were taken as shown in Figure 4.1. Though not obvious from the micrographs, through cavities (circled in red) can be observed in all the samples. The existence of the through cavities can be detrimental to the properties of the NiTi samples produced. Firstly, through cavities can result in stress concentrations when the samples are subjected to monotonic loading. This will lead to failure of the samples at a much lower stress level and a lower degree of shape recovery. Secondly, the existence of the through cavities will transform into internal pores when multiple layers are being produced. This would result in a reduction in the density of the 3D structures built since the through cavities were not taken into account during the density measurement. Hence, the next criterion to introduce during the visual inspection would be to observe minimum or no through cavities on the samples' surfaces.

Figure 4.1: SLM NiTi sample exhibiting through cavities (circled in red).

According to the research by Khairallah et al., through cavities can be produced via two different mechanisms [110]. The first type of through cavities are formed near or under the laser beam. During the SLM process, the surface temperature of the material beneath the laser spot can easily reach the boiling point [110]. Thus, the vapour produced would generate a recoil pressure and create an extra force acting on the surface of the molten pool. As a result, the liquid material was pushed away from the centre, leading to a depression with or without a thin liquid boundary layer at the bottom. At the same time, the liquid along the sidewalls would travel upwards and escape vertically at a high speed. This phenomenon results in spattering or balling effect commonly observed in the SLM process. Moreover, the formation of the depression zone is closely related to the keyhole cavity. King et al. have reported the occurrence of keyhole mode melting in laser powder bed fusion [111]. They proposed the reason to be the surface temperature reaching close to the boiling point, where the recoil force would be the main trigger for the keyhole mode melting.

Another possible mechanism for the formation of through cavities is due to the breakup of the molten track after the passing of laser beam [71, 110, 112]. This is a natural phenomenon which occurs as a way of minimising surface energy via surface tension when overheating occurs. The molten track would attain a lower surface energy by transforming from the segmented cylindrical shape to the segmented hemispherical-like region. The breakup of the molten track can be reduced by providing less heat energy [110]. Hence, the liquid material would be able to solidify quickly before it breaks up completely. Nonetheless, during the

conventional way of optimising the SLM parameters, a high amount of energy was absorbed by the NiTi powder particles due to their high laser absorptivity and low thermal conductivity [87, 112]. Thus, this explains why through cavities and spattering can be observed on the conventional SLM NiTi samples.

Meanwhile, tensile testing is an important experiment to be conducted on the SLM NiTi. However, most of their shape memory properties were determined under the compression load. This occurrence might suggest that the other research groups have failed to subject their SLM NiTi samples to tensile deformation as well. The samples they produced might have a high porosity. Therefore, a breakthrough in the SLM fabrication of NiTi is needed to bring the research in this field to a new height.

According to the general results of the various authors, double scanning or laser re-melting of the previously solidified layer tends to be more beneficial to the SLM process. However, not a lot of studies have been conducted to investigate the effects of laser re-melting. For instance, the reason behind the better densification of the laser re-melted parts has not been explicitly explained. Besides, the research on the densification of NiTi SMA through the use of laser re-melting has yet been reported. Therefore, laser re-melting will be adopted in the production of SLM NiTi and their effects will be investigated. Additionally, laser re-melting was first utilised in other non-additive manufacturing processes such as surface modifications. Hence, in this thesis, the term “repetitive scanning” will be used instead to differentiate it from the conventional laser re-melting process.

4.2 Optimisation of Repetitive Scanning

As suggested by Aboulkhair et al., through cavities can be eliminated by introducing double scanning [65]. Based on their results, double scanning was observed to significantly reduce the number of keyhole pores at all scanning speeds tested as compared to scanning each layer once. Moreover, subsequent scanning will result in re-melting of the material and generates segmental cylindrical molten pool [112]. This shape of the molten pool formed is more stable than the free cylindrical shape. Thus, re-melting of the previously solidified layer will minimise the initiation of the balling effect during the SLM process [69, 75, 112]. Therefore, repetitive

scanning was implemented next to further enhance the properties of the fabricated NiTi samples.

During repetitive scanning, the process parameters used for the first scan and subsequent scan may not be identical. Different combinations of parameters used may bring about different properties observed. Identical combination of parameters obtained from the optimisation of laser power, laser scanning speed, hatch distance and scanning strategy was first adopted for repetitive scanning as shown in Table 4.1. Figure 4.2 presents the micrographs of the samples that were fabricated with one to four-time scanning.

Table 4.1: Process parameters for the optimisation of repetitive scanning.

Types of Parameters	Process Parameters	Magnitudes
Beam-Related Parameters	Laser power	60 W
	Spot size	About 26 μm
	Pulse duration	10 μs
	Pulse frequency	100 kHz
	Beam spatial distribution	Gaussian beam TEM00
	Laser wavelength	1070 nm
Scan-Related Parameters	Scanning speed	3600 mm/s
	Pitch/hatch distance	3 μm
	Number of scans	1 to 4 times
	Scan track length	5 mm
	Scanning strategy	Bi-directional scanning with contour and perimeter scanning

Figure 4.2: SLM NiTi samples fabricated with (a) 1-time scanning, (b) 2-time scanning, (c) 3-time scanning and (d) 4-time scanning. The red dashed circles indicate the through cavities.

With the introduction of repetitive scanning, it is hoped that the amount of through cavities and open pores can be eliminated by increasing the lifetime of the liquid phase. However, none of the samples presented in Figure 4.2 exhibit zero or minimum through cavities. Hence, it may be essential to adjust the parameters between successive scans in order to achieve this objective. One method would be to first sinter the powder particles using a lower amount of energy density, followed by melting the sintered particles during the subsequent scan. The expected advantage of this fabrication method is the reduction in the balling effect due to the sintering and re-melting processes [69, 75, 112]. Table 4.2 presents the dissimilar process parameters with their respective magnitudes and ranges tested during the optimisation of repetitive scanning. The laser power was first varied for the sintering process while maintaining the hatch distance at 3 μm , followed by varying the hatch distance. Appendix G

presents the micrographs of the samples fabricated during the optimisation of repetitive scanning.

Table 4.2: Dissimilar process parameters for the optimisation of repetitive scanning.

Types of Parameters	Process Parameters	Magnitudes	
		Sintering	Melting
Beam-Related Parameters	Laser power	15 to 55 W, with an interval of 5 W	60 W
	Spot size	About 26 μm	
	Pulse duration	10 μs	
	Pulse frequency	100 kHz	
	Beam spatial distribution	Gaussian beam TEM00	
	Laser wavelength	1070 nm	
Scan-Related Parameters	Scanning speed	3600 mm/s	3600 mm/s
	Pitch/hatch distance	1 to 5 μm , with an interval of 1 μm	3 μm
	Number of scans	1	
	Scan track length	5 mm	
	Scanning strategy	Bi-directional scanning with contour and perimeter scanning	

Visual inspections were first employed after the fabrication process to reduce the number of samples required for bulk density measurement. For the samples sintered with 15 and 20 W followed by melting, they were found to warp upwards. However, the warping effect ends when the samples were sintered with 25 W before the second scan. Furthermore, these samples displayed good dimensional accuracy, minimum oxidation and most importantly no through cavities. Nonetheless, samples that were sintered with 30 W and more were found to exhibit through cavities. Thus, only the bulk densities of the samples sintered with 25 W were measured. Their average bulk density was found to be 6.23 g/cm³, accounting to about 3.60% of internal porosity with 0.702% variation in the readings. Even though the percentage of internal pores of these samples was higher as compared to the samples produced without sintering (2.98%, obtained with laser power of 60 W, scanning speed of 3600 mm/s, hatch distance of 3 μm and scanning strategy of bi-directional scanning with contour and perimeter scanning), the smaller discrepancy in the collected readings and the non-existence of through cavities outweighed the higher amount of internal pores formed. This outcome tallies with the result obtained by Aboulkhair et al., where they observed the elimination of keyhole pores at the expense of introducing metallurgical pores [65].

Once the laser power used for the sintering process was optimised, the hatch distance was varied next to determine an appropriate magnitude to be adopted. The hatch distance was varied from 1 to 5 μm , with an interval of 1 μm as shown in Table 4.2.

Likewise, visual inspections were conducted and all five sets of samples were deemed to have good quality. Hence, these samples were subjected to the measurement of their bulk densities and their corresponding internal porosity was plotted against the varying hatch distance as shown in Figure 4.3.

Figure 4.3: Internal porosity of SLM NiTi samples fabricated by sintering (laser power of 25 W) with varying hatch distance, followed by the melting process (laser power of 60 W and hatch distance of 3 μm). Throughout the repetitive scanning approach, the laser scanning speed and scanning strategy adopted were 3600 mm/s and bi-directional scanning with contour and perimeter scanning, respectively.

Based on the results presented, an optimal magnitude of hatch distance of 3 μm could be observed. The produced samples exhibited a lower percentage of internal porosity with a smaller variation in their readings. It was noticed that as the hatch distance diverged away from the optimal value, the average internal porosity and data variation increased. Similar behaviour was also observed in another study conducted on different NiTi powder size [38] and during the process of optimising the hatch distance in Section 3.3.2, further confirming the phenomenon demonstrated by the samples with various hatch distances. The selected samples were then subjected to the dimensional measurement. Figure 4.4 presents the

dimensions of one optimised repetitively scanned sample measured. Table 4.3 compares the average length and width of the optimised single scanned samples and repetitively scanned samples.

Figure 4.4: Dimensions of sample produced by repetitive scanning (sintering with a laser power of 25 W, followed by the melting process with a laser power of 60 W). Throughout the two-step scanning approach, the laser scanning speed, hatch distance and scanning strategy adopted were 3600 mm/s, 3 μ m and bi-directional scanning with contour and perimeter scanning, respectively.

Table 4.3: Average dimensions of samples produced via single scanning and repetitive scanning (sintering with a laser power of 25 W, followed by the melting process with a laser power of 60 W). Throughout the two-step scanning approach, the laser scanning speed, hatch distance and scanning strategy adopted were 3600 mm/s, 3 μ m and bi-directional scanning with contour and perimeter scanning, respectively.

	Single Scanning	Repetitive Scanning
Average Dimensions of Length and Width (mm)	(5.02 $\pm$ 0.11) by (5.29 $\pm$ 0.05)	(4.98 $\pm$ 0.04) by (5.62 $\pm$ 0.01)

According to Table 4.3, the average length of the single scanned and repetitively scanned samples was similar. However, the average width of the repetitively scanned samples differed by quite a large extent as compared to the designed dimension of 5 mm. Nevertheless,

repetitively scanned samples do exhibit a higher repeatability as seen from the small deviation in the average dimensions measured. Most importantly, they do not demonstrate any presence of through cavities. This quality is desirable as the previously optimised single scanned samples failed during the tensile test due to the existence of through cavities. Thus, repetitive scanning with the parameters indicated in Table 4.4 is considered optimised and will be used in subsequent work. For the future research and applications, the increase in the width dimension need to be taken into account during the designing phase.

Table 4.4: Optimised process parameters for repetitive scanning.

Types of Parameters	Process Parameters	Magnitudes	
		Sintering	Melting
Beam-Related Parameters	Laser power	25 W	60 W
	Spot size	About 26 μm	
	Pulse duration	10 μs	
	Pulse frequency	100 kHz	
	Beam spatial distribution	Gaussian beam TEM00	
	Laser wavelength	1070 nm	
Scan-Related Parameters	Scanning speed	3600 mm/s	
	Pitch/hatch distance	3 μm	
	Number of scans	1	
	Scan track length	5 mm	
	Scanning strategy	Bi-directional scanning with contour and perimeter scanning	

Following, the optimised repetitively scanned samples were subjected to the DSC testing. The transformation temperatures were approximated from their respective DSC curves and their average magnitudes were tabulated. The DSC curves and average transformation temperatures were compared and presented in Figure 4.5 and Table 4.5, respectively.

Figure 4.5: Comparison of the DSC curves of (a) NiTi powder and (b) sample fabricated by repetitive scanning (sintering with a laser power of 25 W, followed by the melting process with a laser power of 60 W) [39]. Throughout the two-step scanning approach, the laser scanning speed, hatch distance and scanning strategy adopted were 3600 mm/s, 3 μ m and bi-directional scanning with contour and perimeter scanning, respectively.

Table 4.5: Comparison of the transformation temperatures of NiTi ingot, powder and samples fabricated by repetitive scanning (sintering with a laser power of 25 W, followed by the melting process with a laser power of 60 W) [39]. Throughout the two-step scanning approach, the laser scanning speed, hatch distance and scanning strategy adopted were 3600 mm/s, 3 μ m and bi-directional scanning with contour and perimeter scanning, respectively.

	Transformation Temperatures			
	M_s ($^{\circ}$ C)	M_f ($^{\circ}$ C)	A_s ($^{\circ}$ C)	A_f ($^{\circ}$ C)
NiTi Ingot	54 ± 1	38 ± 1	64 ± 1	87 ± 0
NiTi Powder	47 ± 0	17 ± 0	48 ± 1	79 ± 0
Repetitively Scanned Samples	45 ± 0	15 ± 1	40 ± 1	76 ± 0

Upon comparison with the transformation temperatures of the NiTi powder, the average transformation temperatures of repetitively scanned samples are similar to that of NiTi powder, except for the A_s temperature. However, this difference can be considered negligible. This is because of the compositional sensitivity of NiTi as its transformation temperatures depends heavily on its chemical composition [11, 18, 26]. Moreover, the optimised samples

have exhibited high repeatability as shown by the small deviations in their transformation temperatures. Furthermore, they demonstrated similar phase transformation characteristics as the NiTi powder, where double peaks were observed in their DSC curves presented in Figure 4.5. In addition, previous works have also reported the same phenomenon shown by the NiTi powder [27, 113]. One possible explanation was proposed by Mentz et al. [27]. They stated that “the NiTi powders considered here were formed in a rapid process and thus the resulting material states are far from being in thermodynamic equilibrium. Decomposition processes or shrinkage related stresses may well affect the transformation behaviour.” However, more studies are needed to understand such occurrence. Additionally, the ability of the produced samples to retain that second peak suggests the potential to conserve the properties of the provided raw materials even after the SLM fabrication. Therefore, repetitive scanning approach would be utilised for further research. The associated parameters were shown in Table 4.4.

4.3 Effects of Repetitive Scanning

In order to investigate the effects of repetitive scanning on the properties of the samples produced, the surface morphology of selected samples fabricated after the first scan (S1) was captured by SEM and shown in Figure 4.6. These samples were produced using laser power of 15, 25, 40 and 60 W and they are denoted as P15, P25, P40 and P60, respectively. The other parameters were kept constant and the corresponding magnitudes of linear energy density E adopted were 4.17, 6.94, 11.11 and 16.67 J/m. During the second scan (S2), the laser power was fixed at 60 W with a constant E of 16.67 J/m. The SEM images of the samples subjected to two-step scanning are presented in Figure 4.7. These samples are referred to as P15-60, P25-60, P40-60 and P60-60.

(a)

(b)

(c)

(d)

Figure 4.6: SEM images of (a) P15, (b) P25, (c) P40 and (d) P60 samples produced after S1 [39]. The magnitudes of E used correspond to 4.17, 6.94, 11.11 and 16.67 J/m, respectively.

Figure 4.7: SEM images of (a) P15-60, (b) P25-60, (c) P40-60 and (d) P60-60 samples produced after S2 [39]. A constant E magnitude of 16.67 J/m was used throughout S2.

After the SLM process, the P15-60 samples experienced warpage while P25-60 samples demonstrated smoother and flatter surfaces with minimum defects. Significant formations of porosity (open pores and through cavities) and balling effect were observed on P40-60 and P60-60 samples. These occurrences could be attributed to the differences in the laser absorptivity and heat conductivity of materials before and after S1 (NiTi powder and P15 to P60 samples) [53, 87]. Figure 4.8 illustrates the differences between the various states of the material during laser scanning.

Figure 4.8: Schematic of the differences in the laser absorptivity and heat conductivity of NiTi materials before and after S1: (a) powder bed or poorly melted sample, (b) P25 or optimised sample, (c) P40 and P60 or excessively-melted samples [40].

According to the research by Tolochko et al. and Yadroitsev et al., the materials in the powder form tended to have a much higher laser absorptivity than in the dense form [87, 112]. This was because the laser radiation was able to penetrate through the inter-particle pores and caused interaction with the underlying powder particles. The absorption of the radiation by the pores might sometimes approach the absorption of a blackbody. Since E values of 11.11 and 16.67 J/m have larger magnitudes, the high laser absorptivity and low heat conductivity of the powder particles shown in Figure 4.8a contributed to a greater degree of melting during S1. Thus, the presence of the pores would decrease significantly during the melting phase and the P40 and P60 samples would have a high density. Consequently, as presented in Figure 4.8c, their low laser absorptivity reduced the amount of energy absorbed during S2. Moreover, their high heat conductivity assisted in transferring most of the absorbed energy away. Hence, P40 and P60 samples would experience a lower temperature during S2, resulting in a poor wetting condition and the formations of porosity and balling effect [63, 65, 81, 107]. This clarifies why repetitive scanning with identical combination of SLM process parameters did not result in the elimination of keyhole pores as presented in Figure 4.2. It also explains why Yu et al. have failed to observe any significant effect on their study of repetitive scanning on SLM-produced AlSi10Mg [97].

On the other hand, the P25 samples produced would be less dense when E decreased to an optimal magnitude of 6.94 J/m. Subsequently, these samples experienced a higher temperature than P40 and P60 samples during S2. This decreased the viscosity of the molten

pool, lowered the wetting angle and reduced the surface tension [53, 63, 71]. These phenomena then contributed to the efficient densification of the samples without the occurrence of the balling effect. Moreover, the lower surface tension restricted the Marangoni flow and capillary instability effect. Thus, it brought about another positive effect of reducing the tendency for the formation of first line scan balling phenomenon [114]. Nonetheless, further reduction of E to an insufficient amount of 4.17 J/m produced a minimum amount of melting as presented in Figure 4.6a. Thus, the P15 samples would retain a high laser absorptivity and a low heat conductivity. As a result, they experienced a higher temperature at a localised point during S2. This generated a more pronounced temperature gradient, leading to high thermal stresses and eventually caused the warping effect [115].

In general, samples with seemingly excellent properties were produced by introducing repetitive scanning and optimising the laser power and hatch distance. The different E magnitudes used have a huge influence on the laser absorptivity and heat conductivity of the samples fabricated after S1. These two characteristics will then affect the final properties of the SLM NiTi parts produced after S2. The apparent superior quality of the P25-60 samples will be characterised and verified in the next section.

4.4 Shape Memory Responses

So far, the phase transformation characteristics and surface morphology of P25-60 samples have been characterised. However, NiTi is a smart material with functional properties and thus its shape memory responses are of primary interest. Therefore, the next characterisation test will be to determine the shape memory properties of P25-60 samples. This objective is met by subjecting four P25-60 long strip samples to tensile load. Figure 4.9a illustrates the testing procedure via the stress-strain-temperature curve of the best sample tested. Figure 4.9b, c, d presents the corresponding stress-strain curve, strain-temperature and its derivative curve, respectively. The derivative curve was plotted to determine the temperatures at which the shape recovery begins and finishes. Table 4.6 presents the average strain readings. The maximum strain refers to the strain that the sample is deformed to before unloading. The residual strain indicates the strain exhibited by the sample after unloading.

The transformation strain is the strain of shape recovery while the permanent strain denotes the remaining strain after shape recovery completed. The percentage of shape recovery can be found by the ratio between the transformation strain and residual strain.

Figure 4.9: (a) Stress-strain-temperature curve of the best P25-60 sample tested. The corresponding (b) stress-strain curve, (c) strain-temperature curve and (d) strain-temperature derivative curve are presented as well [40].

Table 4.6: Average strains from the four P25-60 samples tested [39].

Maximum Strain (%)	7.94 ± 0.01
Residual Strain (%)	6.50 ± 0.09
Transformation Strain (%)	4.61 ± 0.36
Permanent Strain (%)	1.49 ± 0.21
Shape Recovery = $\frac{\text{Transformation Strain}}{\text{Residual Strain}}$ (%)	0.71 ± 0.05

According to Table 4.6, the average transformation strain is 4.61%. It was calculated based on the results of four samples (4.78, 4.18, 4.37 and 5.11%). This result is comparable to the transformation strain of 6% exhibited by the conventionally produced NiTi [29]. Furthermore, the result also presented a great improvement in the transformation strain as compared to the prior work of 0.5% transformation strain [41]. It also demonstrated the significance of introducing repetitive scanning to enhance the properties of the SLM NiTi samples produced as compared to conventional SLM fabrication process.

Nonetheless, the presence of the permanent strains presented in Table 4.6 indicates incomplete shape recovery. It is well known that the SME will not be perfect [25, 116-119]. The generation of the permanent strain is a consequence of the formation of dislocations and specific martensite variants during tensile loading [116, 118-120]. An interesting observation reported by Ortega et al. [117] was the effect of alloy composition on the shape recovery magnitude in cast NiTi alloys. They attributed the better shape recovery properties in cast NiTi alloy to the formation of nanometer scale precipitates formed after mild ageing. This is worthy of further investigation in the present SLM NiTi since SLM also involves a melting and solidification process.

The importance of the formation of nanoscale grains on the stress-induced phase transformation has also been reported in NiTi through Joule heating which limited the atomic diffusion due to very short heating time [32]. Both strengthening mechanisms of precipitation hardening [117, 118] and grain refinement aim to reduce irreversible plastic deformation and improve the functionality of NiTi. Another method would be the deformation of NiTi at an intermediate temperature, for instance, 500 °C, to enhance its transformation strain and mechanical properties [121]. Besides, the incomplete detwinning of the presently optimised samples may also be related to the rapid solidification nature of the SLM process. Internal

stress field might exist within the samples, leading to an adverse effect on the detwinning process [122]. Hence, the future research could include various post-processing treatments to improve the transformation strain. All the above mechanisms can be considered and explored in the future for improving the mechanical and thermomechanical properties of SLM NiTi alloys.

4.5 Conclusion

In this chapter, high-quality SLM NiTi samples were fabricated by implementing repetitive scanning. The laser powers adopted during the first scan and second scan corresponded to 25 and 60 W while the laser scanning speed and hatch distance were kept constant at 3600 mm/s and 3 μ m, respectively. The scanning strategy used for both scans was bi-directional scanning with contour and perimeter scanning.

The final properties of the produced SLM NiTi parts were found to be heavily influenced by the differences in the laser absorptivity and heat conductivity of materials before and after the first scan. The introduction of a first scan aided in controlling the amount of energy absorbed by the NiTi material during the second scan, in turn minimising the formation of through cavities due to recoil pressure and surface tension. The advantages of adopting repetitive scanning and the excellent properties of the samples were confirmed by two results:

1. The fabricated samples have demonstrated similar phase transformation characteristics as the given NiTi powder with high repeatability.
2. The produced samples were able to withstand tensile load and exhibited transformation strain as high as 5.11% with an average value of 4.61%, comparable to the conventionally made NiTi components.

These results suggested the potential of fabricating SLM NiTi with complex geometries and similar properties to the NiTi parts produced by conventional technologies.

Chapter 5: Effects of Post-Process Heat Treatment

SLM NiTi parts fabricated via the implementation of repetitive scanning have shown the capability to withstand tensile loading and demonstrated an average of 4.61% transformation strain. However, there is still room for improvement as the conventionally produced NiTi components can exhibit a transformation strain of about 6%. Therefore, post-process heat treatment was introduced to enhance the shape recovery of SLM NiTi samples.

5.1 Rationale and Procedures of Heat Treatment

The SME and superelasticity demonstrated by NiTi SMA is the result of the reversibility of its phase transformation from martensite to austenite and vice versa. However, the introduction of plastic deformation such as slip and dislocation are irreversible and the strains generated could not be restored even upon heating [123, 124]. Additionally, it has been reported that the formation of dislocations in the NiTi material could be initiated at a low stress level of about 100 MPa [125]. Thus, it is essential to increase the critical stress level that the plastic deformation occurs in order for NiTi to exhibit good shape memory properties.

In physical metallurgy, there are four main methods to increase the critical stress level, work-hardening, precipitation hardening, alloy-hardening and grain refinement [31, 121, 123, 124]. However, alloy-hardening is not preferred as it would alter the transformation temperatures. Moreover, unlike the conventional way of producing NiTi parts, the SLM process has provided the freedom of fabricating structures with complex geometries. Hence, it is not necessary to deform or cold-work the finished components into the desired shapes. In addition, annealing is required for the work-hardened components to restore back to the defect-free lattice, which could further increase the production time. Therefore, heat treatment is introduced to possibly generate the other two types of strengthening mechanism: precipitation hardening and grain refinement.

Prior to the heat treatment, repetitively scanned samples with dimensions of 5 mm by 10 mm and 5 mm by 78 mm were fabricated. The longer strip samples (5 mm by 78 mm) were then wire cut to a width of about 3.5 mm to remove the uneven sides due to powder adhesion. Subsequently, polishing was performed on the cut samples to remove the burrs, surface unevenness and excess powder particles. Afterwards, the prepared samples were subjected to post-process heat treatment. The step-by-step procedures of the heat treatment are listed as follows:

1. The furnace (Elite Thermal Systems Limited, BRF14/5-2416) to be used for the heat treatment was first heated up to a temperature that was 10 °C higher than the desired heat treatment temperature.
2. The furnace door was opened up and the temperature was allowed to drop by 10 °C to the designated temperature.
3. Upon reaching the preferred temperature, samples that were placed on a ceramic holder were sent together into the furnace.
4. The furnace door would then be closed and the furnace temperature was monitored.
5. A timer of 5 minutes would be activated once the furnace temperature has reached the desired temperature.
6. Successively, the samples were removed and air-cooled under atmospheric condition.
7. The heat treatment was performed at four different temperatures, ranging from 400 to 700 °C, with an interval of 100 °C.
8. After the heat treatment process, the samples were then further cooled down to a temperature that was below their M_f temperature. This ensured that the samples only exhibited twinned martensitic phase before any testing.

5.2 Characterisation of Heat Treated Samples

5.2.1 Shape Memory Responses

The main objective of introducing post-process heat treatment is to improve the transformation strain of repetitively scanned SLM NiTi samples. The stress-free shape

memory behaviour of the long strip samples was determined under the tensile mode. The samples were first loaded up to a 6% strain, followed by unloading to a load of 0.5 N (Shimadzu, AG–X Plus). A strain rate of 0.01%/min and room temperature condition were used for both loading and unloading processes. The 0.5 N load was then maintained constant throughout the remaining test to simulate a stress-free condition. Afterwards, the samples were heated up with the use of a thermal chamber (Shimadzu, TCE-N300-CE) at a rate of about 2 °C/min. The magnitude of strain recovery due to SME was recorded. Elongation and thermal expansion of the clamps during the loading and heating processes were accounted for to ensure that the data collected was accurate. Details of the accounting process can be found in Section 3.3 and Appendix C.

Table 5.1 presents the average strain readings, detwinning start stress (σ_s) and Young's modulus of the martensitic phase (E_m) measured during the tensile test. The determination of the σ_s gives an indication of the stress needed to proceed into the detwinning phase for SME to occur. The E_m provides an indication of the ductility of the repetitively scanned samples. Meanwhile, the specimens tested were non-heat treated samples (NT), samples heat treated at 400 °C (H400), 500 °C (H500), 600 °C (H600) and 700 °C (H700). Four samples were tested for each set of condition. According to Table 5.1, H400 samples demonstrated an improvement in the transformation strain and shape recovery percentage as compared to the NT samples. However, a further increase in the heat treatment temperature resulted in a decreasing trend for both shape recovery and transformation strain. Figure 5.1 presents the stress-strain and strain-temperature curves of the best samples tested for NT and H400 conditions.

Additionally, the implementation of heat treatment has also been observed to cause an increase in the σ_s and decrease in the E_m . Nevertheless, both σ_s and E_m showed a decreasing trend with rising heat treatment temperature.

Table 5.1: Average strain readings, detwinning start stress (σ_s) and Young's modulus of martensite (E_m) for NT and heat treated repetitively scanned SLM NiTi samples that were tested under the tensile mode [126].

	NT	H400	H500	H600	H700
Maximum Strain (%)	5.99 ± 0.01	5.98 ± 0.00	5.98 ± 0.00	5.98 ± 0.01	5.98 ± 0.00
Residual Strain (%)	5.14 ± 0.11	4.99 ± 0.01	4.96 ± 0.09	5.01 ± 0.07	4.96 ± 0.02
Transformation Strain (%)	3.37 ± 0.19	3.59 ± 0.17	3.36 ± 0.28	3.18 ± 0.21	3.08 ± 0.30
Permanent Strain (%)	1.20 ± 0.20	0.98 ± 0.26	1.05 ± 0.28	1.32 ± 0.21	1.37 ± 0.09
Shape Recovery = $\frac{\text{Transformation Strain}}{\text{Residual Strain}}$ (%)	0.66 ± 0.04	0.72 ± 0.04	0.68 ± 0.05	0.63 ± 0.04	0.62 ± 0.06
σ_s (MPa)	29 ± 2	50 ± 6	51 ± 5	37 ± 9	37 ± 9
E_m (MPa)	108 ± 44	96 ± 14	93 ± 13	82 ± 30	78 ± 11

Figure 5.1: Stress-strain and strain-temperature curves for the best (a, b) NT and (c, d) H400 samples tested [126].

5.2.2 Transformation Characteristics

The transformation characteristics of NT and heat treated samples were determined by using the DSC equipment. The samples were subjected to five thermal cycles with a ramp rate of 5 °C/min from a range of -30 to 120 °C. Only the fifth cycle was used and presented in determining their phase transformation temperatures. Figure 5.2 shows the fifth DSC cycles of both NT and heat treated samples. Table 5.2 reports the average transformation temperatures of the NiTi ingot, NiTi powder, NT and heat treated samples. The average transformation temperatures of the SLM NiTi materials before and after the heat treatment were found to be similar to each other. However, the M_f temperature was observed to show

a decreasing trend, accompanied by an increase in the standard deviation, as the temperature of the heat treatment decreases. This could indicate some changes in the chemical composition of the samples as the heat treatment condition varies. This is due to the high dependency of the transformation temperatures on the chemical composition of NiTi [11, 18, 26].

Figure 5.2: Fifth DSC cycle of (a) NT, (b) H400, (c) H500, (d) H600 and (e) H700 samples.

Table 5.2: Average transformation temperatures of the NiTi ingot, NiTi powder, NT and heat treated samples tested.

	Transformation Temperatures			
	M _s (°C)	M _f (°C)	A _s (°C)	A _f (°C)
NiTi Ingot	54 ± 1	38 ± 1	64 ± 1	87 ± 0
NiTi Powder	47 ± 0	17 ± 0	48 ± 1	79 ± 0
NT Samples	45 ± 0	15 ± 1	40 ± 1	76 ± 0
H400 Samples	47 ± 1	12 ± 3	40 ± 1	78 ± 1
H500 Samples	47 ± 1	11 ± 2	41 ± 1	79 ± 1
H600 Samples	47 ± 0	14 ± 1	40 ± 1	79 ± 0
H700 Samples	48 ± 1	15 ± 1	41 ± 1	79 ± 0

5.2.3 Phase Analysis

Due to the rapid solidification nature of the SLM process, there is a possibility of generating an internal stress field within the samples fabricated [6]. The stress field produced could have an adverse influence on the detwinning process [122]. Thus, heat treatment was introduced to eliminate the possible presence of the stress field. Nonetheless, heat treatment could also lead to the formation of precipitates, which might contribute to the better shape recovery observed in Section 5.2.1 [117]. Hence, in order to investigate the phases present in the repetitively scanned samples before and after the heat treatment, X-ray diffraction (XRD) (Malvern Panalytical Ltd, Empyrean) was performed on 5 mm by 10 mm samples with Cu-K α radiation (wavelength = 1.5406 Å). The NiTi powder was tested for comparison as well. The XRD patterns of the powder, NT and heat treated samples are presented in Figure 5.3.

Figure 5.3: XRD patterns of NiTi powder, NT, H400, H500, H600 and H700 samples.

In general, the XRD patterns of the powder and samples were similar. However, both NT and heat treated samples have demonstrated a Ni_4Ti_3 peak that was absent from the NiTi powder. Moreover, an additional austenitic peak has also been observed in the XRD pattern of the H400 sample. The H700 sample has exhibited a Ni_3Ti peak that was not seen in the XRD patterns of the other samples as well.

5.2.4 Grain Size Measurement

The size of the grains is known to play a part in affecting the shape recovery and functionality of NiTi SMA [32]. During the heat treatment process, the grain size of the heat treated samples could have been altered. Thus, the average grain size of these samples needs to be determined. This could be done according to the methods mentioned in ASTM E112-13 [127].

Prior to the measurement of the grain size, 5 mm by 10 mm samples were first prepared. Both NT and heat treated samples were hot mounted (Metkon Instruments Inc, Ecopress 100) into a polymer resin. These mounted samples were then subjected to polishing with diamond lapping films of different grades, starting from the coarsest of 18 μm and ending with the finest of 0.1 μm . After which, the polished samples were etched with Kroll's Reagent (Best Chemical Co (S) Pte Ltd, 2 – 6% HNO_3 , 1 – 3% HF and 91 – 97% H_2O) for a period of 2 minutes. Lastly, the microstructures of the polished and etched samples were viewed using an optical microscope (Carl Zeiss, Axioskop 2 Mat) with a magnification of 50 times.

According to the ASTM standards, there are a total of three methods to determine the average grain size; comparison procedure, planimetric procedure and intercept procedure [127]. Comparison procedure consists of comparing the grain structure to graded images such as wall chart, clear plastic overlays and eyepiece reticle. The planimetric method involves the counting of the number of grains within a specific region. The intercept procedure estimates the average grain size by counting the number of grains or grain boundary intercepted by a test line. Among the three methods, comparison method is the least accurate while the other two methods have the same level of precision. However, intercept procedure will be less time consuming than the planimetric method. Additionally, the intercept method is also more suitable for materials with elongated grains. Hence, the average grain size of both NT and heat treated samples would be determined using the intercept procedure, specifically the Abrams three-circle procedure [127]. The reason for selecting the circular interception method is because it compensates any deviations from the equiaxed grain shapes. It eliminates the problem of biases due to distorted grain shapes as well.

The test pattern for Abrams three-circle procedure consists of three concentric and equally spaced circles with a total circumference of 500 mm as shown in Figure 5.4. The

circumferences of the largest to the smallest circle are 250.0 mm, 166.7 mm and 83.3 mm while their diameters are 79.58 mm, 53.05 mm and 26.53 mm, respectively. The pattern was applied blindly to five different fields of dimensions 203.2 mm by 254 mm (8 inch by 10 inch) and the number of intersections were recorded. Figure 5.5 presents the micrographs of the NT and heat treated samples. Afterwards, the mean linear intercept with its standard deviation for each heat treatment condition was determined according to Equations 5.1 and 5.2 [127].

Figure 5.4: Schematic of the test pattern for Abrams three-circle procedure [128]. The circumferences of the smallest to the largest circle are 83.3 mm, 166.7 mm and 250.0 mm. Their corresponding diameters are 26.53 mm, 53.05 mm and 79.58 mm.

(a)

(b)

(c)

(d)

(e)

Figure 5.5: Micrographs of (a) NT, (b) H400, (c) H500, (d) H600 and (e) H700 samples under 50 times magnification.

$$N_L = \frac{N_i}{L/M} \quad (5.1)$$

$$\bar{\ell} = \frac{1}{N_L} \quad (5.2)$$

where N_L is the number of intercepts per unit length of the test line, N_i refers to the number of intercepts counted on the field, L denotes the total length of the test line, which is 500 mm and M represents the magnification used, which is 50 times. $\bar{\ell}$ indicates the mean linear intercept. Table 5.3 shows the average N_i , N_L , $\bar{\ell}$ and ASTM grain size number (G) for each heat treatment condition, where G is calculated based on an empirical Equation (5.3) [127]. It is to be noted that a larger G magnitude implies a higher amount of grains per unit area.

$$G = (-6.643856 \log_{10} \bar{\ell}) - 3.288 \quad (5.3)$$

Table 5.3: Average N_i , N_L , $\bar{\ell}$ and G for both NT and heat treated samples.

Parameters	NT	H400	H500	H600	H700
N_i	99.8 ± 2.56	87.4 ± 2.15	71.2 ± 3.54	63.8 ± 3.97	57.2 ± 2.48
N_L	9.98 ± 0.26	8.74 ± 0.22	7.12 ± 0.35	6.38 ± 0.40	5.72 ± 0.25
$\bar{\ell}$	0.100 ± 0.003	0.114 ± 0.003	0.141 ± 0.007	0.157 ± 0.010	0.175 ± 0.008
G	3.35 ± 0.07	2.97 ± 0.07	2.37 ± 0.14	2.05 ± 0.18	1.74 ± 0.12

From Table 5.3, G is observed to decrease after heat treatment and with increasing heat treatment temperature. This phenomenon indicates that the average grain size increases after subjecting the samples to heat treatment and as the temperature of the heat treatment rises. This result also tallies with the micrographs shown in Figure 5.5, where the grains appear to experience grain growth and elongate upon the heat treatment with increasing temperature.

5.3 Mechanism for the Effects of Heat Treatment

5.3.1 Analysis of Phase Transformation Characteristics

During the characterisation of NiTi powder, heat treated and NT samples, double peaks have been observed from their DSC curves. Conventionally, the existence of the double peaks indicates the presence of the rhombohedral phase (R-phase) transformation [13, 24-26, 31, 129]. This type of R-phase transformation is a result of the formation of fine and coherent Ni_4Ti_3 precipitates [14, 24, 31, 130]. The Ni_4Ti_3 precipitates would suppress the martensitic phase transformation by acting as an obstacle to high transformation strains. Thus, the formation of the R-phase is favoured as it can accommodate the coherency stresses and reduce the overall strain energy to the minimum. As a result, the R-phase transformation would occur prior to the martensitic phase transformation.

Initially, the double peaks found in the DSC curves of the NiTi powder (from Figure 3.2), NT, H400 and H500 samples (from Figures 5.2a, 5.2b and 5.2c) were thought to be caused by the R-phase. This impression was supported by the XRD patterns of the powder and samples tested, where the presence of the Ni_4Ti_3 precipitates has been detected. Nevertheless, studies have shown that heat treatment conducted at 600 °C and above would lead to the disappearance of the R-phase [129, 131]. However, as seen in Figures 5.2d and 5.2e, double peaks are still observable in the DSC curves of the H600 and H700 samples. Moreover, the transformation temperatures of the R-phase and martensitic phase tends to be separable [123]. Hence, the additional peak caused by the R-phase would be divided and distinct from the martensitic peak. Conversely, in this research, the double peaks demonstrated by the samples and powder appeared close and overlapped each other. Thus, it can be concluded that the cause of the double peaks demonstrated by the NiTi powder and repetitively scanned samples is not due to the formation of Ni_4Ti_3 precipitates.

It is hypothesized that the proximity of the two peaks is caused by the inhomogeneity of the NiTi powder and repetitively scanned samples. In Chapter 3, the average atomic percentage of the NiTi powder used was determined to be 50.16% Ni and 49.84% Ti. According to the phase diagram of the NiTi shown in Figure 5.6, the boundary of the Ni-rich region decreases significantly with decreasing temperature. Furthermore, the solubility of NiTi becomes

negligible when its temperature drops to below 600 °C. Therefore, based on the chemical composition of the NiTi powder, the material should be in a metastable equilibrium state where both NiTi and Ni_4Ti_3 precipitates would coexist together in equilibrium.

Figure 5.6: Phase diagram of NiTi [14, 123].

However, one of the objectives mentioned in introducing repetitive scanning is to control the amount of energy absorbed by the NiTi material during the second scan. The formation of the through cavities is eliminated when less energy was absorbed by the partial melted NiTi material during the second scan, as compared to energy absorbed by the NiTi powder during the conventional single scan process. Hence, with the implementation of repetitive scanning, the temperature of the molten NiTi would be relatively lower. Thus, this resulted in a shorter time to complete the solidification process.

Similarly, during the gas atomization of the NiTi ingot, the material experienced a high solidification rate and a short solidification time. As a result, the atoms would have little time to diffuse. Therefore, the formation of the Ni_4Ti_3 precipitates was suppressed [18, 123].

Consequently, it could lead to two peaks observed in the DSC curves, where the main peak corresponds to the NiTi matrix, while the other peak corresponds to the transition region that is slightly Ni-rich. This slight compositional segregation is caused by the diffusion of the atoms to form Ni_4Ti_3 precipitates but has yet to diffuse adequately before solidifying. However, for the case of slow cooling, the atoms would have sufficient time to diffuse and two different phases would be produced if the alloy composition deviates from atomic percentage of 50% Ni. These two phases are pure NiTi (austenitic or martensitic phase) and precipitates (either Ni-rich or Ti-rich precipitates). The type of precipitates formed depends on the chemical composition of NiTi.

This hypothesis is also supported by the characteristics of the phase transformation exhibited by the single scanned samples. The DSC curves of the NiTi powder from Figure 3.2, conventionally optimised single scanned sample and H400 sample from Figure 5.2b are presented together in Figure 5.7 for comparison.

Figure 5.7: Fifth DSC cycle of (a) NiTi powder (from Figure 3.2), (b) conventionally optimised single scanned NiTi sample and (c) H400 sample (from Figure 5.2b). The single scanned sample demonstrates a single peak while the NiTi powder and H400 sample exhibit double peaks during the heating and cooling processes.

In order to achieve full melting of the powder particles in a single scan, the amount of linear energy density directed to the powder bed would be relatively high. However, the high laser absorptivity and low heat conductivity of the powder particles as illustrated in Figure 4.7a contributed to the huge amount of energy absorbed by the material. Thus, the temperature of the molten pool would reach a higher magnitude, resulting in more time required to dissipate the heat and solidify. Subsequently, the atoms would have sufficient time to diffuse and rearrange to obtain a more homogenous chemical composition of the main NiTi matrix, with or without the formation of precipitates. Hence, only a single peak can be observed for

each of the heating and cooling processes for the conventionally optimised single scanned NiTi sample.

Nevertheless, the presence of the double peaks after repetitive scanning may not be a drawback. Instead, it encourages the implementation of repetitive scanning as double peaks can be found in the DSC curves of the NiTi powder as well. The conservation of the double peaks suggested the ability of the repetitive scanning approach to retain the properties of the raw material used, especially since the SLM process involves both melting and solidification processes. One of the common problems encountered in the studies conducted by the other researchers includes the alteration of the material's properties after the SLM fabrication. For instance, the issue of Ni evaporation during the melting phase of the SLM process was reported, where huge deviations in the transformation temperatures could be observed [16, 21, 25, 28, 35]. Therefore, for the future research, homogenous NiTi powder and repetitive scanning approach can be utilised together. It is expected that the repetitively scanned SLM NiTi parts will exhibit a single peak.

5.3.2 Analysis of Shape Memory Responses

Repetitively scanned SLM NiTi samples have demonstrated an increase in their transformation strain and shape recovery percentage after subjecting to a heat treatment process of 400 °C for a period of 5 minutes. The improvement in their shape memory properties is mainly due to the formation of Ni_4Ti_3 precipitates, which increases the critical stress level for the plastic deformation to occur.

5.3.2.1 Formation and Effects of Ni_4Ti_3 Precipitates

In Section 5.3.1, the double peaks found in the DSC curves of the NiTi powder, NT and heat treated samples are hypothesized to be caused by the diffusional transformation of the atoms to form precipitations. In order to determine what precipitates are present within the NiTi materials, an XRD test was conducted.

According to the XRD patterns shown in Figure 5.3, no traces of Ni_4Ti_3 precipitate can be found on the NiTi powder. However, the presence of the intermediate Ni_4Ti_3 phase has been identified on the SLM-produced NiTi samples. One possible explanation would be that during the fabrication procedure, the melting phase of the SLM process provided an additional opportunity for the atoms to complete diffusion. Thus, it resulted in the formation of Ni_4Ti_3 precipitates. No precipitation has been detected in the NiTi powder as the rapid solidification rate of the gas atomization process did not provide sufficient time for the diffusion to complete. Hence, only the transition region was observable in the DSC curve of the NiTi powder. Both the transition region and Ni_4Ti_3 precipitates found in the DSC curve and XRD pattern of the NT samples were due to the partial completion of the diffusion process.

Nevertheless, during the process of heat treatment and quenching under atmospheric air condition, the occurrence of oxidation was inevitable. The manifestation of oxidation would lead to the depletion of Ti as Ti was more reactive to oxygen than Ni [132]. Thus, the content of Ni in the NiTi matrix would increase, resulting in two phenomena; 1) the decrease of the transformation temperatures and the transformation of martensitic phase into austenitic phase and 2) the promotion of the precipitate formation.

Precipitation will occur when the condition of supersaturation is met. The NiTi material would be in a supersaturated state when the content of Ni has exceeded its solubility limit but had yet to form precipitation due to the quenching process. Hence, the supersaturation of NiTi would provide a driving force for the initiation of precipitation during the heat treatment process. The relationship between the driving force and nucleation barrier ΔG_c is shown in Equation (5.1) [123].

$$\Delta G_c = \frac{16\pi\sigma^3}{3(\Delta G_v + \varepsilon)^2} \quad (5.1)$$

Here, ε indicates the strain energy per unit volume related to the formation of a nucleus and σ refers to the interfacial energy related to the formation of a new interface. ΔG_v denotes the chemical free energy of the precipitation reaction. It can be seen as the driving force for the initiation of precipitation and ΔG_v must be negative for the precipitation to happen. According to Equation (5.1), a small driving force or a less supersaturated state would produce a larger magnitude of nucleation barrier. Consequently, the rate of precipitation formation would be

lower. However, with a higher degree of supersaturation or a larger driving force, the nucleation barrier would experience an exponential decrease. Thus, the nucleation rate would increase tremendously as well.

When the temperature of the heat treatment process conducted was in the lower range, for instance at 400 °C, the depletion of Ti would not be as much. This was because the main oxidation process did not start immediately at a lower temperature [132]. Moreover, the oxidation rate tended to slow down and saturate after some time. Hence, the slight increase in the Ni content could be within the overlapped region between the metastable equilibrium phase (NiTi and Ni₄Ti₃) and the solubility limit of NiTi as presented in Figures 5.6 and 2.2, respectively. In this region, the increase in the Ni content would lead to the decrease in the transformation temperatures. The decrease in the transformation temperatures was reflected in the M_f temperature of the H400 samples while the identification of austenitic phase among the main martensitic matrix was shown in their XRD pattern. Likewise, Firstov et al. have also reported the detection of austenitic phase when their NiTi material with an atomic percentage of 50% Ni and 50% Ti was processed between a heat treatment temperature of 300 to 500 °C [132]. Additionally, the small increase in the content of Ni would also result in a slighter degree of nucleation rate of the Ni₄Ti₃ precipitates.

However, when the heat treatment temperature started to increase to 500 and 600 °C, more Ti would be depleted. This is the result of oxidation proceeding earlier when at a higher temperature than at a lower temperature [132]. Thus, the increase in the content of Ni could exceed the solubility limit of NiTi and extend into the metastable equilibrium state of NiTi and Ni₄Ti₃ precipitates. Subsequently, the austenitic phase disappeared as presented in the XRD patterns of the H500 and H600 samples. Instead, the rate of precipitation increased and the existing Ni₄Ti₃ precipitates started to grow larger at the expense of the smaller particles [133]. The results obtained were also supported by the similar observation of Ni₄Ti₃ precipitates found in samples which were heat treated at a temperature of 500 to 600 °C for a period of 6 minutes [123, 134].

Nonetheless, when the heat treatment temperature increased to 700 °C, the depletion in Ti was so strong that the Ni₄Ti₃ precipitates began to decompose into the equilibrium Ni₃Ti phase [14, 123, 132, 135, 136]. Hence, both Ni₄Ti₃ and Ni₃Ti precipitates could be found in the

XRD pattern of the H700 sample. The results obtained were confirmed by the works of the Firstov et al. as well [132]. They have reported the observation of Ni_3Ti precipitates at a higher heat treatment temperature of above 600°C [132].

Conversely, a higher nucleation rate and the decomposition of Ni_4Ti_3 precipitates into Ni_3Ti phase may not be beneficial to the shape memory properties of repetitively scanned SLM NiTi samples. Based on Table 5.1, only H400 samples have demonstrated improvements in the transformation strain and shape recovery percentage as compared to the NT samples. The percentage of shape recovery and transformation strain were found to show a decreasing trend with increasing heat treatment temperature. The occurrence of these phenomena could be understood from the physical metallurgy principle. Figure 5.8 presents the schematic of the effects of heat treatment temperature on the shape memory properties of repetitively scanned NiTi samples with respect to the formation of Ni_4Ti_3 precipitates.

Figure 5.8: Schematic of effects of heat treatment temperature on the shape memory responses of repetitively scanned NiTi samples with respect to the formation of Ni_4Ti_3 metastable precipitates.

Based on the physical metallurgy principle, the formation of a high density of fine precipitates is widely known to be the most effective method in preventing the movement of dislocations [14, 123, 137]. Concurrently, it increases the critical stress magnitude for the slip to occur as well [125]. Both dislocations and slips are plastic deformations and they are irreversible processes. It is not possible to restore the strains produced by these two defects via the

mechanism of the reversible martensitic phase transformation. Therefore, heat treating the repetitively scanned NiTi samples at a temperature of 400 °C for a period of 5 minutes would initiate the precipitations of fine Ni₄Ti₃ particles as shown in Figure 5.8 to deter the generation of plastic deformation. This result has also coincided with several past research where the conventionally-produced NiTi parts demonstrated the best SME and superelastic properties when subjected to heat treatment at a temperature of 400 °C [125, 129, 136]. Other studies have also attributed the improvement in the shape memory properties to the presence of fine Ni₄Ti₃ precipitates [31, 136, 138, 139].

Nevertheless, as the temperature of the heat treatment increases, particle agglomeration of the Ni₄Ti₃ precipitates occurs [31, 135, 138, 140]. The relationship between the volume ratio $\alpha(\tau)$ of Ni₄Ti₃ phase and heat treatment temperature T (in Kelvin) can be expressed by Equations (5.2) and (5.3) [139].

$$\alpha(\tau) = 1 - e^{-(k\tau)^n} \quad (5.2)$$

$$k = k_0 e^{-\frac{Q}{RT}} \quad (5.3)$$

where k refers to the reaction rate constant and τ indicates the reaction time. For all different heat treatment conditions, the exponent n would have the magnitude of 3 while the value of k would differ according to Equation (5.3) [139]. Q represents the activation energy needed for the occurrence of precipitation and R signifies the universal gas constant. Based on Equations (5.2) and (5.3), the volume of the Ni₄Ti₃ precipitates would increase with rising heat treatment temperature. Experimental observation of Ni₄Ti₃ enlargement by 30 times as the heat treatment temperature varied from 400 to 500 °C has been reported by Yan et al. as well [136]. Thus, with the increment of the heat treatment temperature, the density distribution of the precipitates would decrease. Eventually, it would lead to a reduction of their effects on the shape memory properties of the heat treated NiTi samples. In addition, it has been reported that Ni₄Ti₃ with a coarse grain size would lose its coherency with the NiTi matrix [135, 136, 140]. Hence, dislocations would be introduced to relieve the stress fields generated around the precipitates [14, 131, 135, 136]. Consequently, it would then lead to an overall decrease in the fatigue strength of the NiTi samples. Therefore, based on the results obtained, the heat treatments of repetitively scanned NiTi samples at a temperature of above 400 °C

have resulted in overaging of the material [137]. Eventually, the samples demonstrated poorer shape memory responses than the NT samples.

5.3.2.2 Formation and Effects of Grain Boundary Migration

Other than introducing the formation of Ni_4Ti_3 metastable precipitates, the implementation of heat treatment was also found to alter the microstructures of the repetitively scanned NiTi samples. According to Figure 5.5 and Table 5.3, the average grain size of the NT and heat treated samples increases with the application of heat treatment and with rising heat treatment temperature. Specifically, the grains were observed to elongate with increasing temperature.

At the first glance, it might appear that the heat treated samples have undergone through the recovery and recrystallisation processes. The migration of the grain boundary was the result of ordinary grain growth after recrystallisation as the grains grew larger at the expense of the other grains. However, on closer inspection, it is inferred that the heat treated samples did not experience recrystallisation. This deduction came about based on the following factors.

For the recrystallisation process to occur, there are a few requirements that need to be fulfilled. Firstly, the samples have to be subjected to a certain magnitude of deformation [141]. It has been reported that the recrystallisation phenomenon did not happen for samples deformed below the strain of 20% [142]. Moreover, the recrystallisation temperature is a function of the degree of deformation [141]. A less deformed sample would have a higher recrystallisation temperature than a severely deformed sample. As reported in the past research, NiTi has a recrystallisation temperature of between 550 to 600 °C when they experienced cold-working by about 30% [129, 140]. During the sample preparation, precautions were taken to ensure that the repetitively scanned NiTi samples did not suffer any unnecessary deformation prior to the heat treatment and the determination of grain size. Thus, it is expected that the heat treated samples would not experience recrystallisation within the temperature range of the heat treatment implemented.

The second factor that suggests the absence of recrystallised grains in the heat treated samples is the lack of time for the formation and growth of the recrystallised nuclei to microscopic size [143, 144]. Figure 5.9 presents a typical recrystallisation curve [141]. It shows the percentage of the material recrystallised against the period of heat treatment at a constant temperature, chemical composition and degree of deformation. The initial incubation period indicates the time required to develop sufficient energy in order for the first strain-free nucleus to grow to a visible microscopic size. In addition, the recrystallisation temperature for a particular material denotes the approximated temperature at which its highly cold-worked form would completely recrystallise in 1 hour [141, 144]. Since the recrystallisation temperature of NiTi is roughly about 550 to 600 °C, it is highly unlikely that the heat treated samples could accumulate an adequate amount of energy to form defect-free nuclei with appreciable size during the heat treatment of 5 minutes.

Figure 5.9: Recrystallisation curve [141].

The third condition that needs to be met is the additional energy required to initiate the formation of the strain-free lattice. The schematic energy representation of the recrystallisation process is shown in Figure 5.10 [141]. During the process of cold-working, plastic deformation was introduced into the samples. The internal energy evolved from the deformation would increase the energy state of the atoms to a level of E_1 . However, it is not possible for the atoms or dislocations to revert back to a defect-free lattice from the distorted lattice at room temperature due to the nature of strain hardening. Hence, additional energy is required to bring the atoms to the next level of energy state E_2 in order to overcome the

rigidity of the distorted lattice. The additional amount of energy, which corresponds to the difference between E_2 and E_1 , would be supplied in terms of heat energy. Nonetheless, as the repetitively scanned samples were not severely deformed prior to the heat treatment, the internal energy state of the samples would be much lower. Thus, a larger amount of additional energy needs to be provided to the samples to initiate recrystallisation. Since the highest heat treatment temperature tested is only about 100 °C higher than the recrystallisation temperature of a heavily deformed NiTi material, the energy supplied in this case may not be sufficient to start up the recrystallisation process.

Figure 5.10: Schematic energy representation of the recrystallisation process [141].

Besides needing to fulfil the three requirements for the recrystallisation process to occur, another phenomenon that provided the evidence of the non-existence of recrystallised grains lies in the shape of the grains observed. In Figure 5.5, the grains were noticed to elongate upon heat treatment and with increasing heat treatment temperature. Moreover, despite the short heat treatment period of 5 minutes, the elongation seems to start promptly at the start of the heat treatment. However, in a typical recrystallisation process, no observable differences can be seen in the microstructures of the material during the recovery phase [141]. Even when the recrystallisation temperature has been reached, it requires a certain period of incubation for the formation of new nuclei and for them to grow to microscopic sizes.

Furthermore, the recrystallised grains were observed to be equiaxed [141], which contradicted what were captured on the microscopic images. Thus, it is concluded that the heat treated samples did not experience recrystallisation. The elongation of the grains is postulated to be a result of strain-induced boundary migration [143].

The difference between strain-induced boundary migration and the recrystallisation process is that in the former, the annealed material left behind due to the movement of the grain boundary has the same orientation as the strain hardened parent grain [143]. However, in the recrystallisation process, nuclei with different orientations are produced. The movement of the grain boundaries in the strain-induced boundary migration is towards the distorted regions due to the strain gradients generated [145]. Correspondingly, this would result in the increase of the size of one grain and the disappearance of the other grain. One characteristic of the strain-induced boundary migration is shown in Figure 5.11a. The annealed material (smoother region) produced is constricted by the ordinary grain boundary 2 on one side, while bounded by the parent grain A on the other side without the intervention of grain boundary [143]. Nevertheless, in a typical recrystallisation process seen in Figure 5.11b, the produced recrystallised grains A and B would be located in between the strain hardened grains C and D. These grains were separated by grain boundaries. As stated by some researchers, the strain-induced boundary migration may, in fact, be considered as a type of recrystallisation process without the formation of new nuclei [143, 145].

Figure 5.11: Micrographs illustrating differences between (a) strain-induced boundary migration and (b) recrystallisation [143].

However, the reason for the occurrence of the strain-induced boundary migration is not known yet at this moment. Nonetheless, the grains were observed to elongate together in one direction. The direction of the grain elongation was aligned perpendicularly to the direction of the laser scanning path as illustrated in Figure 5.12. One possible explanation for both phenomena would be due to the directional solidification nature of the SLM process. During the fabrication of a single layer, the laser would begin scanning in a line-by-line manner, starting from the top region. As the laser proceeds down to the adjacent line, the previous scanned section could have solidified and cooled down. Hence, a temperature gradient is generated between the molten and solidified regions, resulting in the grains to grow towards the direction of the temperature gradient. In addition, the non-uniform thermal conductivity and thermal expansion coefficient of the liquid and solid phase of NiTi could also lead to the development of residual stress and/or strain. Thus, during the heat treatment process, the grains further elongate according to the produced strain gradients. Nevertheless, more studies need to be done to confirm this hypothesis.

Figure 5.12: Micrograph of the H400 sample with the schematic of laser scanning strategy (in orange).

In general, the occurrence of the strain-induced boundary migration did not contribute to the improvement in the shape memory properties of repetitively scanned NiTi samples. As presented in Figure 5.5, Tables 5.1 and 5.3, the transformation strain and shape recovery percentage of the heat treated samples decreased with increasing average grain size. The only exception is the H400 samples, where they demonstrated an improvement in their shape memory responses as compared to the NT samples. However, this enhancement could be attributed to the formation of fine Ni_4Ti_3 precipitates as discussed in Section 5.3.2.1, where it outweighs the negative impact of the strain-induced boundary migration.

As reported by various authors, the increase in grain size could be detrimental to the mechanical properties of repetitively scanned NiTi samples [32, 124, 140]. Based on the results obtained by Delville et al., they observed that samples with a larger grain size tend to be more significantly prone to the formation and build-up of dislocations [32]. The increase in the dislocation density has led to the rapid accumulation of permanent strain build-up during the cyclic test performed. Moreover, they determined that their NiTi samples had the highest resistance to slip deformation when the samples just entered into the recrystallisation phase. In this phase, the new defect-free recrystallised grains would be coexisting with the polygonised microstructure. Furthermore, the exhibition of small grain size contributed to its high strength and stability for the cyclic test as well. However, when the heat treatment

process proceeded into the phase of grain growth where the recrystallised grains continued to grow, the yield stress for plasticity and strength dropped significantly.

The improvement in the mechanical properties of NiTi SMA after a decrease in the grain size have also been reported by the other researchers [124, 140, 146]. It was found that a reduction in grain size could slow down the propagation of cracks formed during the cyclic test of NiTi material. Hence, samples with smaller grains would have a higher fatigue life than samples with coarser grains. The reason why grain size reduction could improve the shape memory properties of NiTi is due to the increase in the volume fraction of the grain boundary [124]. The grain boundary acts as a non-transformable barrier that separates the crystallites with different orientations. When the grain size decreases, the mechanical constraint of the grain boundary on the deformation of the crystallites becomes more significant as compared to samples with coarse grains. Thus, the movement of the dislocation was impeded, resulting in a decrease in the accumulation of permanent strain. Sequentially, samples with finer grain size would have a higher transformation strain and shape recovery percentage. Therefore, combining the effects of grain size and Ni_4Ti_3 precipitates, H400 samples have the best shape memory properties among the other heat treated samples.

5.3.3 Analysis of Mechanical Properties

In addition to influencing the shape memory properties, the implementation of heat treatment was also found to increase the σ_s and decrease the E_m of the repetitively scanned SLM NiTi samples. With further increment of the heat treatment temperature, both σ_s and E_m were observed to reduce. However, there is no definite answer as to whether the implementation of heat treatment and which heat treatment temperature would be more beneficial to the mechanical properties of the samples. Which decision to select could vary according to the type of application. For example, biomedical implants made of NiTi usually have a higher Young's modulus than the human bones [6]. Thus, heat treatment could be introduced to lower the Young's modulus in order to better match the properties of the bones. In another instance where NiTi was made into an actuator, it could be more useful to have a higher Young's modulus. However, it is also desirable to have a higher σ_s . A larger σ_s

magnitude would indicate that for a given total strain, a larger portion will be the elastic strain while the remaining will be contributed by the detwinning process. Moreover, it has been reported that both detwinning process and the generation of dislocations occurs simultaneously [147]. Hence, a higher σ_s would indirectly lead to lesser degree of dislocations, which is the cause for the permanent strain observed during testing. Therefore, a heat treatment condition at 400 °C could be adopted to produce a high σ_s while minimising the reduction in E_m .

Furthermore, the decrease in the σ_s and E_m with increasing heat treatment temperature have also been reported by the other researchers [124, 129, 146, 148]. It was proposed to be a result of the increase in the grain size [124, 148]. Firstly, the decrease in E_m was suggested to be caused by the decrease in the volume fraction of the grain boundary phase [124]. This is because the Young's modulus of the grain boundary could be higher than that of the grain interior or crystallite. Secondly, the drop in the σ_s as grain size increase was due to the weakening of the constraint by the grain boundary [124, 148]. Sequentially, the detwinning process could occur at a lower stress magnitude.

5.4 Conclusion

Repetitively scanned NiTi samples have demonstrated the ability to be tensile loaded and shown an average of 4.61% transformation strain. Nonetheless, its shape memory responses can be further improved as compared to the 6% transformation strain exhibited by the conventionally produced NiTi parts. Thus, post-process heat treatment was implemented to enhance the shape memory properties of repetitively scanned NiTi samples. The overall effects of the heat treatment process on the samples are summarised in Table 5.4 and Figure 5.13.

Table 5.4: Overall effects of heat treatment on repetitively scanned NiTi samples.

Positive Impacts	Negative Impacts
<ul style="list-style-type: none"> Precipitation of a high density of fine Ni_4Ti_3 precipitates at lower heat treatment temperature Improvement in the shape memory responses of repetitively scanned NiTi samples Increase of the detwinning start stress with the introduction of heat treatment and with decreasing heat treatment temperature 	<ul style="list-style-type: none"> Initiation of particle agglomeration and formation of dislocations with increasing heat treatment temperature Occurrence of strain-induced boundary migration with implementation of heat treatment and with rising heat treatment temperature Decrease in the Young's modulus of martensitic phase with the adoption of heat treatment and with increasing heat treatment temperature

Figure 5.13: Schematic of the overall effects of heat treatment on the shape memory responses of repetitively scanned NiTi samples.

As the heat treatment implemented could have both positive and negative influences, it is necessary to achieve a balance between them. The results obtained showed that heat treating the repetitively scanned samples at a temperature of 400 °C for a period of 5 minutes has led to an improvement in their transformation strain and shape recovery percentage. With the use of this heat treatment condition, a high density of fine Ni_4Ti_3 metastable phase was produced. Concurrently, the strain-induced grain boundary migration was observed as well.

Even though the increase in the grain size has detrimental effects on the mechanical properties of NiTi SMA, the positive impacts of Ni_4Ti_3 precipitates formation outweigh the negative influences as illustrated in Figure 5.12. A high density of these fine precipitates has effectively increased the critical stress level for plastic deformation to occur and successfully impede the movement of dislocations during tensile testing. Nevertheless, heat treating the repetitively scanned samples above this temperature has resulted in overaging and further increment of grain size. As a consequence, degradations in the shape memory properties were inevitable.

Chapter 6: Conclusion and Future Work

In the final chapter of this thesis, the conclusion of the current work will be presented. Additionally, the recommendations for future work of this project will be discussed as well.

6.1 Conclusion

NiTi SMA is a type of smart material that has the ability to transform thermal energy into mechanical work directly [2-4]. This unique characteristic of NiTi gives rise to two types of shape memory response, specifically SME and superelasticity [5, 7, 16, 25]. In order to make full use of these two behaviours, NiTi has to be processed into the different geometries to suit the various applications. Nevertheless, several problems were encountered during the conventional manufacturing of NiTi [17]. One such example is the oxygen contamination of the crucible during the induction melting [18]. Moreover, NiTi is not an easy alloy to process due to its inherent compositional sensitivity and poor machinability [6, 10, 15, 19, 25, 28, 29]. Thus, the majority of the conventionally-produced NiTi parts would only consist of simple geometries such as in the form of wires, plates, bars, tubes, etc. The restriction in geometries has critically limited the full potential applicability of NiTi [6, 25, 28, 29, 32]. Hence, one recommended solution to these issues faced would be to utilise the SLM process to produce the NiTi structures [5, 7, 16, 17, 19-21, 24, 25, 28, 31, 33-40]. This new method of fabricating NiTi components is sometimes referred to as 4D printing [41-44].

Other than providing a solution to the current challenges encountered, the implementation of the SLM process also contributes to the production of complex NiTi smart structures for novel applications. However, before fabricating any complex structures directly, it is necessary to ensure that the produced SLM NiTi parts exhibit functional properties. Therefore, in this research, the SLM NiTi samples produced were characterised to evaluate their properties for comparison with the properties of the NiTi ingot and NiTi powder.

6.1.1 Optimisation of Process Parameters

In Chapter 3, different SLM process parameters were optimised with the objectives of obtaining SLM NiTi parts with the following properties: low percentage of internal porosity, excellent dimensional accuracy, minimal oxidation and similar phase transformation characteristics as the NiTi powder. The beam-related and scan-related parameters that were investigated included laser power, laser scanning speed, hatch distance and scanning strategy. Upon optimisation, small deviations in the internal porosity and transformation temperatures of the optimised samples were observed. This has indicated the high repeatability of the SLM fabrication process. Nonetheless, these samples did not exhibit good mechanical properties. In the determination of their stress-free shape memory responses under the effect of tensile load, the samples demonstrated multiple fractures before failure. Thus, the conventional single scan optimisation strategy was concluded to be unsuitable for the NiTi material. This may also be the contributing factor as to why no tensile test results have been reported in the study of SLM NiTi.

6.1.2 Enhancements Through Repetitive Scanning

In the subsequent chapter, a new approach, repetitive scanning, was implemented to achieve a breakthrough in the SLM fabrication of NiTi. The properties of the repetitively scanned samples were observed to be dependent on the laser absorptivity and heat conductivity of the materials before and after the first scan. The introduction of the first scan aided in controlling the magnitude of energy absorbed by the NiTi material during the second scan, leading to the minimisation of through cavity formation due to the recoil pressure and surface tension. With the implementation of repetitive scanning, excellent properties of the repetitively scanned samples were confirmed. Firstly, the produced samples exhibited similar phase transformation characteristics as the NiTi powder used with high repeatability. Secondly, the fabricated samples displayed the ability to withstand tensile loading and demonstrated an average of 4.61% transformation strain, with the highest magnitude of 5.11%. This amount of shape recovery was comparable to the conventionally-produced NiTi parts with a maximum of about 6% transformation strain [29].

6.1.3 Effects of Post-Process Heat Treatment

Despite the improvement in the shape memory responses by adopting repetitive scanning, there is still a gap between the transformation strains of repetitively scanned samples and conventionally-made NiTi components. Hence, post-process heat treatment was introduced to further enhance the shape memory properties of the repetitively scanned samples. However, the implementation of heat treatment had both positive and negative effects. It was required to obtain a balance between these effects in order to observe an improvement in the properties of the samples. The results have shown that a heat treatment process with a temperature of 400 °C for a period of 5 minutes would lead to the increase in their transformation strain and shape recovery percentage. At this specific heat treatment condition, a high amount of fine Ni₄Ti₃ metastable phase was produced. At the same time, strain-induced grain boundary migration was observed as well. Although the enlargement of the grain size would have a detrimental impact on the mechanical properties of NiTi, the positive influence of the presence of Ni₄Ti₃ outweighed the negative effect. A high density of these fine precipitates has effectively hampered the dislocation movement during the tensile test and increased the critical stress magnitude that the plastic deformation occurred. Nevertheless, the increment of the heat treatment temperature above 400 °C has led to overaging and further enlargement of the grain size. Consequently, degradations in the shape memory properties of the repetitively scanned samples were observed. To illustrate the benefits of implementing repetitive scanning and post-process heat treatment, Table 6.1 presents the differences in the shape memory quality of conventionally-produced NiTi parts, single scanned NiTi samples, NT and H400 repetitively scanned samples.

Table 6.1: Comparison of the shape memory quality of conventionally-produced NiTi components, single scanned NiTi samples, NT and H400 repetitively scanned NiTi parts. The SLM-produced specimens were subjected to a tensile deformation of 6% strain.

	Conventionally-Produced NiTi	Single Scanned NiTi	NT NiTi	H400 NiTi
Shape Memory Quality	Maximum transformation strain of about 6%	Demonstrated multiple fractures before failing at a highest tensile strain of 6%	Average transformation strain 3.37 ± 0.19 Average shape recovery percentage 0.66 ± 0.04	Average transformation strain 3.59 ± 0.17 Average shape recovery percentage 0.72 ± 0.04

6.2 Future Work

For the future work of this research project, one possible research direction would be to investigate the effect of low heat treatment temperature. According to the results presented in Chapter 5, a 5-minute heat treatment at a temperature of 400 °C has led to the improvement in the shape memory responses of repetitively scanned samples. However, this result falls into the lowest end of the temperature range tested. Thus, it is not known if lowering the heat treatment temperature could bring about the formation of even finer Ni_4Ti_3 precipitates and a lesser degree of strain-induced boundary migration. Furthermore, a lower heat treatment temperature could also minimise the depletion of Ti due to oxidation, ensuring minimal alteration in the chemical composition of the repetitively scanned samples. The period of the heat treatment could be varied as well since its effect on the shape memory properties of SLM NiTi has not been studied.

Another research direction would be to focus on the application of SLM NiTi. For instance, the transformation strain and shape recovery percentage of the optimised samples under different loading and cyclic conditions could be determined. The experimental procedure would consist of deforming the samples to a pre-defined stress, followed by holding the load constant while the samples undergo thermal cycling [29]. The results collected would be

useful in the design and fabrication of complex NiTi components via the SLM process for actuation applications.

Additionally, NiTi honeycomb structures could be fabricated by using the SLM process as well. The advantages of honeycomb structures include higher stiffness and strength under compression or shear, higher bending resistance, energy absorption and shock resistance [149]. Moreover, its high surface area density also enables a higher rate of heat transfer. Hence, in the case of a honeycomb structure made with NiTi, the superior heat transfer rate would enable the part to react in a shorter amount of time. One possible application would be a hot water safety valve, where the water could pass through the honeycomb structure. The valve could change its shape to shut off the hot water supply once the water temperature reaches a dangerous magnitude.

Other than the above-mentioned research directions, another potential future work would be to develop an equation that contributes to the transfer of knowledge obtained. It can be observed from Table 2.3 that different researchers have adopted different SLM process parameters and magnitudes of energy densities. Even though some of the published papers have indicated the major parameters such as the laser power, laser scanning speed, hatch distance and layer thickness used, these results were not utilised by the other researchers. The most likely reason could be due to the different degrees of heat transfer that occurred during the fabrication process. As a result, different amount of energy densities or process parameters are required to melt and produce samples with similar properties. Therefore, the next proposed future work would be to develop an empirical equation that relates the different energy densities proposed for the different SLM machine used. This can be done by considering the conservation of energy [101].

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Appendix A

This section presents the calculation of the laser spot size used in the custom-made SLM equipment.

The laser spot size can be estimated from the following equation [88].

$$d = \frac{4\lambda f M^2}{\pi D}$$

where

d = laser spot size

λ = laser wavelength = 1070 nm as provided by the manufacturer

f = focal length = 181.1 mm as provided by the manufacturer

M^2 = quality factor = 1.05 as provided by the manufacturer

D = beam diameter = 2×5 mm = 10 mm as provided by the manufacturer

Laser spot size d

$$= \frac{4 \times 1070 \times 10^{-9} \times 181.1 \times 10^{-3} \times 1.05}{\pi \times 10 \times 10^{-3}}$$

$$= 0.000025906 \text{ m}$$

$$= 25.906 \text{ } \mu\text{m}$$

$$\approx 26 \text{ } \mu\text{m}$$

Appendix B

This section presents the determination of the theoretical density of NiTi SMA material used in this project.

According to the DSC result shown in Section 3.3, the average M_s temperature of the NiTi powder is 47 °C. With the use of Figure 2.2, the atomic percentage of Ni present in the powder is estimated to be 50.23% while EDS gives an estimation of about 50.09% [26]. Thus, an average is obtained between these two readings and the Ni content of the powder is approximated to be 50.16%. The amount of Ti present in the powder will make up the rest of the alloy composition, amounting to 49.84%.

When NiTi SMA is exhibiting austenitic phase, it will either have a body-centered cubic or a face-centered cubic structure. The corresponding lattice constant for the austenitic phase is 3.015 Å, which equates to 3.015×10^{-8} cm [150].

The molecular weight of Ni is 58.693 g/mol [99] while the molecular weight of Ti is 47.867 g/mol [100]. The Avogadro's number is 6.0221415×10^{23} mol⁻¹ [151].

Assuming one unit cell contains 50.16% of Ni and 49.84% of Ti instead of 50% Ni and 50% Ti.

Mass of unit cell

$$\begin{aligned} &= \frac{\frac{50.16}{50} \times 58.693}{6.0221415 \times 10^{23}} + \frac{\frac{49.84}{50} \times 47.867}{6.0221415 \times 10^{23}} \\ &= 1.770045476 \times 10^{-22} \text{ g} \end{aligned}$$

Volume of unit cell

$$\begin{aligned} &= (3.015 \times 10^{-8})^3 \\ &= 2.740702838 \times 10^{-23} \text{ cm}^3 \end{aligned}$$

Theoretical density of NiTi used

$$= \frac{\text{mass of unit cell}}{\text{volume of unit cell}}$$

$$= \frac{1.769997331 \times 10^{-22}}{2.740702838 \times 10^{-23}}$$

$$= 6.45836335 \text{ g/cm}^3$$

$$\approx 6.46 \text{ g/cm}^3$$

Appendix C

This section presents the calculation of the average elongation and thermal expansion coefficients of the clamps used in determining the stress-free shape memory responses of the optimised samples.

Elongation of the Clamps

Two sets of displacement-force curves with best-fit lines were plotted below.

Equations of best-fit lines:

$$y = 2.96722 + 0.12687x$$

$$y = 4.00092 + 0.1103x$$

Average elongation coefficient

$$= \frac{0.12687 + 0.1103}{2}$$

$$= 0.118585 \mu\text{m}/N$$

$$\approx 0.000119 \text{ mm}/N$$

Thermal Expansion of the Clamps

Two sets of displacement-temperature curves with best-fit lines were drawn below.

Equations of best-fit lines:

$$y = -0.26011 + 0.00911x$$

$$y = -0.19956 + 0.00933x$$

Average thermal expansion coefficient

$$= \frac{0.00911 + 0.00933}{2}$$

$$= 0.00922 \text{ mm}/^{\circ}\text{C}$$

Appendix D

This section presents some of the micrographs of the samples produced during the optimisation of laser power and laser scanning speed.

Laser Power / Laser Scanning Speed	100 mm/s	1100 mm/s	2100 mm/s	3100 mm/s	4100 mm/s	5100 mm/s	6000 mm/s
10 W
20 W
30 W
40 W

50 W
60 W
70 W
80 W
90 W
100 W

Appendix E

This section presents the micrographs of the samples produced during the optimisation of hatch distance. The optimised laser power and laser scanning speed used were 60 W and 3600 mm/s, respectively.

Hatch Distance: 1 μm

Hatch Distance: 2 μm

Hatch Distance: 3 μm

Hatch Distance: 4 μm

Hatch Distance: 5 μm

Hatch Distance: 6 μm

Hatch Distance: 7 μm

Hatch Distance: 8 μm

Hatch Distance: 9 μm

Appendix F

This section presents the micrographs of the samples produced during the optimisation of scanning strategy. The optimised laser power, laser scanning speed and hatch distance were 60 W, 3600 mm/s and 3 μm respectively.

Bi-Directional Scanning with Contour and Perimeter Scanning

Bi-Directional Scanning with Contour

Bi-Directional Scanning with Perimeter Scanning

Uni-Directional Scanning with Perimeter Scanning

Spiral-In Scanning with Perimeter Scanning

Appendix G

This section presents the micrographs of the samples produced during the optimisation of repetitive scanning. The laser power for the first scan was first optimised while the laser power for second scan was maintained at 60 W. The laser scanning speed, hatch distance and scanning strategy were kept constant at 3600 mm/s, 3 μ m and bi-directional scanning with contour and perimeter scanning, respectively.

Laser Power for the First Scan: 15 W

Laser Power for the First Scan: 20 W

Laser Power for the First Scan: 25 W

Laser Power for the First Scan: 30 W

Laser Power for the First Scan: 35 W

Laser Power for the First Scan: 40 W

Laser Power for the First Scan: 45 W

Laser Power for the First Scan: 50 W

Laser Power for the First Scan: 55 W

Following the optimisation of laser power, the hatch distance for the first scan was optimised as well. The laser powers for the first and second scan were 25 and 60 W. The laser scanning speed and scanning strategy were kept constant at 3600 mm/s and bi-directional scanning with contour and perimeter scanning, respectively.

Hatch Distance: 1 μm

Hatch Distance: 2 μm

Hatch Distance: 3 μm

Hatch Distance: 4 μm

Hatch Distance: 5 μm