A LITERATURE REVIEW OF LASER POWDER BED FUSION OF 55NI-TI SHAPE MEMORY ALLOY FOR BIOMEDICAL APPLICATIONS

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ABSTRACT

The binary near equiatomic nickel-titanium alloy is a shape memory alloy, an intermetallic compound material which found applications in automotive, aerospace, robotics and biomedical industry due to its shape memory effect and superelasticity. The reversible martensitic transformation property and the biocompatibility of the material have drawn significant attention. However, the manufacturing and processing complications encountered when using the conventional methods to manufacture the NiTi alloy has brought shortcomings to homogeneity in the microstructure, which affects the material shape memory and superelastic behaviour. The current review will focus on the emerging additive manufacturing methods such as laser powder bed fusion that will be used to unearth the full potential of the alloy for biomedical applications. The laser powder bed fusion method could be used to manufacture NiTi objects with tailored geometrics which would enhance the biomechanical and biofunctional properties of the material and translate into quality life for implant patients.

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1. INTRODUCTION

Titanium was discovered by William Gregor in 1791 [1], and it has been widely used in many engineering application due to its outstanding mechanical properties, which are resistance to corrosion and a high strength to weight ratio. The use of titanium and its alloys was found to be applicable in constructing aircraft, jet engines, and biomedical objects since the 1950s [2]. Despite the celebrated mechanical properties of Ti alloys, especially for biomedical applications, there were obvious limitations due to its high elastic modulus. The shortcomings of Ti alloys have prompted material scientists to search for a material with thermomechanical behaviour [3].

A shape memory alloy (SMA) are alloys with large plastic deformation and when heated they "remember" their original shape [2]. It is an unusual thermomechanical behavior due to their reversible crystal structure characteristics induced by stress or temperature. The material's ability to remember its original shape is termed as shape memory effect. Superelasticity which is also known as pseudoelasticity is another thermomechanical characteristic of SMAs, and is the ability of the material to sustain elongation or strain (3-8%) after being deformed [4]. The discovery of the shape-memory effect was reported in the 1930s, according to Otsuka and Wayman, Arne Ölander discovered the superelasticity behavior of the Au-Cd alloy in 1932. Greninger and Mooradian (1938) observed the allotropic behaviour of Cu-Zn alloy when temperature is applied in the material [5]. Then basic phenomenon of the memory effect governed by the thermoelastic behavior of the martensite phase was widely reported a decade later by Chang and Read (1951), [4,5].

There are many known shape memory alloys; namely, NiTi, Cu-Al-Ni, Cu-Zn-Al, Cu-Sn, Nb-Ti, Cu-Al-Be and Ti-Nb [2,3,5]. All have found application in actuators such as hydraulic, pneumatic, and motor-based systems. They are also used in the robotics, automotive, aerospace and biomedical industries. Nickel-titanium alloys (Ni-Ti) has taken the center stage among the SMAs for many engineering applications due to it being able to exhibit temperature dependent acoustic damping properties, surface relief, unusual micro-hardness indentation behaviour, substantial ductility combined with good strength, good corrosion resistance and low density [6]. It is also reported to have superior biocompatibility as compared to other SMAs. Its biocompatibility and superelasticity make NiTi a suitable material for biomedical applications while the shape memory (SM) and the damping characteristics are used for other engineering applications such as innovative actuating systems [7, 8].

Nickel-titanium alloys (Ni-Ti) was first developed in 1962–1963 by the United States Naval Ordnance Laboratory and commercialized under the trade name Nitinol (an acronym for Nickel Titanium Naval Ordnance Laboratories). Their remarkable properties were discovered accidentally. A sample that was bent out of shape many times was presented at a laboratory management meeting. One of the associate technical directors, Beuhler, decided to see what would happen if the sample was subjected to heat and held his pipe lighter underneath it. To everyone's amazement, the sample went to its original shape [9]. Further research revealed that the TiNi alloy has unique properties of shape memory and superelasticity as a result of phase transformation within its crystal structure as a response to change in temperature and stress [6, 7, 10, 11, 12, 13]. At lower temperatures, or when deformed the NiTi structure is in the martensite phase, meaning a weaker form of the structure and at a higher temperature is in the austenite phase, which is the stronger crystal structure [14]. In Nitinol, the change is from an ordered cubic crystal structure (austenite) to a monoclinic crystal phase (martensite) [15]. This behaviour is known as the martensitic transformation. The temperatures at which the formation of martensite starts and ends are called martensitic start temperature (M_s) and martensitic finish temperature (M_f). Austenite formation starts and ends at austenite start (A_s) temperature and austenite finish (A_f) temperature [16, 17]. There are 24 habit plane martensite variants for stress-induced martensitic transformation (Fig.1). This temperature or stress-induced phase transformation (as opposed to conventional diffusion induced transformations) is the basis for the unique properties in these alloys, namely shape memory effect, superelasticity (pseudoelasticity) and damping.

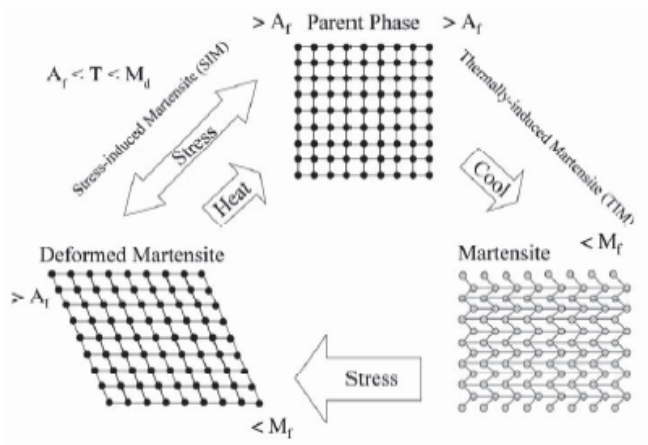


Fig.1: When NiTi cools below austenite start (As) temperature the material deforms until the Martensitic finish (Mf) temperature is reached. Then material would only retain its parent shape when heated above the austenite finish temperature (Af). [6].

Nitinol has three crystallographic phases, i.e. austenite, R phase and martensite when induced by temperature or stress [6]. Martensite is only stable at low temperatures. The atoms within the material moves through a process called diffusionless transformations from the austenite in the super ß lattice B2 structure, to the martensite which is in the monoclinic B19' weaker lattice structure (Fig. 1), while the phase during transition is known as the rhombohedral structure, or the R phase [19]. The reverse thermo-mechancial process, martensite to austenite the process happens through a diffusionless process [20]. The strains that nitinol (3-8%) can recover is based on the post-processing of the material. While the hysteresis (transformation temperature) is associated with the change of nickel or titanium content, where it was found a change of 1% in alloy content will shift the transformation temperature of this material with 100°C [18, 20]. This will then affect the superelasticity strain which will then affect the biocompatibility of NiTi used in biomedical application [20].

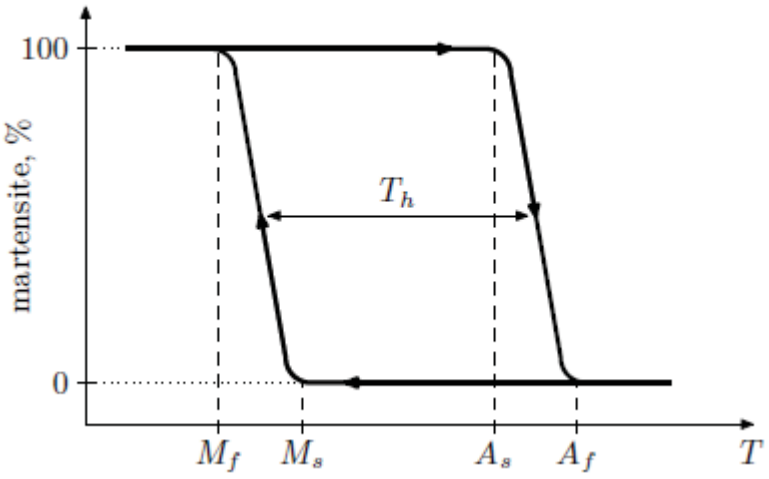


Fig.2: The temperature transformation curve of a NiTi alloy, Ms: martensite start temperature upon cooling; Mf: martensite finish tempetature upon cooling. The graph depicts the reverse transformation start temperature (As), upon heating; and the reverse transformation finish upon heating (Af). T is the transformation hysteresis. [8]

Post-processing treatments (e.g. heat treatment, cold working etc.) are generally required for NiTi manufactured parts to enhance the superelasticity and help improve biocompatibility [9-10]. Besides its superelasticity and unique properties for biomedical application the high nickel (Ni) content of the alloy (55 wt. % Ni) and its influence on the biocompatibility is a major concern [21]. However, the experimental results of Ryhanen *et al.* [13] with a fibroblast and osteoblast cell culture revealed that the high Ni content posed no threat of cytotoxicity. This is due to the fact that NiTi is a passive alloy, like titanium and stainless steel. A stable surface oxide protects

the base material from general corrosion. Titanium is not toxic when used in the human body, although nickel could be toxic when used in large amounts. Human tissue contains approximately 0.1 ppm of nickel, which is essential nutrition for the biological functionality of the human body [22, 23]. Fortunately, nitinol forms a passive titanium oxide layer (TiO_2) which acts as a physical barrier to nickel oxidation and protects the bulk material from corrosion. This layer is responsible for protecting nickel ions from leaking into the human bloodstream. It has been shown that the cytotoxicity of nitinol is comparable with other implantable alloys [24], such as 316 stainless steel and Ti6Al4V titanium alloy. Literature shows that that nitinol has no toxic effects on human tissue [25].

Nitinol could be confidently used for biomedical applications since it remains biologically innocuous inside living tissues [26]. It has also met the stringent requirement of the ASTM F86 [27] standards, which specifies that the various chemical and electrochemical surface treatments specified in this practice are intended to remove objectionable surface contaminants and to restore maximum corrosion resistance to the passive oxide film. Also the implant must not produce allergic reactions inside the host or release ions into the bloodstream. The biomechanical and biofunctional properties of nitinol have made it favoured in medical devices, e.g. surgical instruments, orthopaedic implants and cardiovascular devices [24], discussed below.

1.2 Surgical instruments

In recent years, the medical industry has focused on the concept of less invasive surgical procedures [28]. Following this tendency, nitinol shape memory surgical instruments have been developed (Fig. 3). Since nitinol has strains of (3% to 8%) they are preferably used in surgical endoscopic procedures, the recoverable deformation is primarily the key characteristic sought in these types of applications [4]. Instruments that are steer able, hingeless, kink resistant, and highly flexible and that provide constant force have all been developed [29].

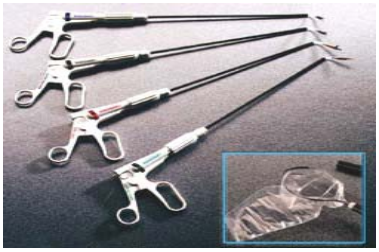


Fig 3. Laparoscopic instruments for minially invasive surgeries [24].

1.3 Orthopedic applications

NiTi has been used extensively for orthopedics and a lot of research has gone into various correction rods, compression staples and fracture fixators (Fig. 4). Orthopedic applications tend to be concerned with shape memory thermal recovery and the associated forces generated during recovery. SMA has a large number of orthopedic applications. The spinal vertebra spacer is one of them. The insertion of this spacer between two vertebrae assures the local reinforcement of the spinal vertebrae, preventing any traumatic motion during the healing process. The use of a shape memory vertebra spacer allows the application of a constant load regardless of the position of the patient, with some degree of motion. This device is used in the treatment of scoliosis [19].

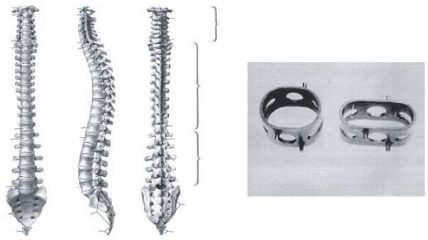


Fig 4. Sspinal vertebra spacers [24].

Another application in the orthopaedic area is related to the healing process of broken and fractured bones. Several types of shape memory orthopedic staples (Fig. 5) are used to accelerate the healing process of bone fractures, exploiting the shape memory effect. The shape memory staple, in its opened shape, is placed at the site where one desires to rebuild the fractured bone. Through heating, this staple tends to close, compressing the separated part of bones. It should be pointed out that an external device performs this heating and not the temperature of the body. The force generated by this process accelerates healing, reducing the time of recovery.

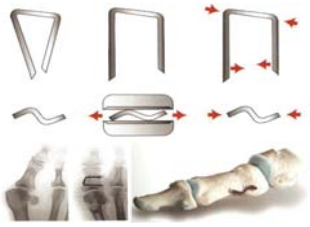


Fig 5. Bbiomedical staples [24].

1.4 Cardiovascular applications

The passing of catheters into arteries and veins has developed into a form of minimally invasive therapy known as interventional radiology. This therapy employs X-ray imaging techniques and magnetic resonance imaging (MRI) to guide different instruments and carry out advanced medical procedures. The atrial septal occlusion device (Fig. 6) is an alternative to the traditional surgery that is extremely invasive and dangerous because the thorax of the patient is opened and the atrial hole is sewn. This device is composed of SMA wires and a waterproof film of polyurethane. First, one half of the device is inserted through a catheter by the vena cava up to the heart, in its closed form. Then, it is placed on the atrial hole and opened, recovering its original shape. Next, the second half of the device is placed by the same route as the first one, and then both halves are connected. This procedure seals the hole, avoiding blood flow from one atrium to the other. A schematic diagram of the heart with the device in place is presented in Figure 6. [24]

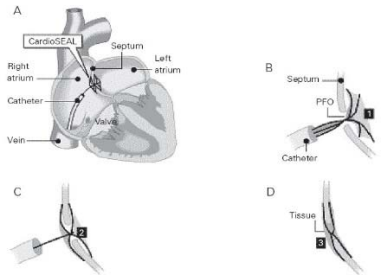


Fig 6. Atrial septal occlusion device, A) scheme of heart with the device, B) first half of the device placed in the left atrium, C) then the second half, D) then the catheter is withdrawn and the tissue closes. [24].

Angioplasty is a technique for treating occlusion of a blood vessel or heart valve. It is used extensively for the treatment of peripheral vascular disease to restore the correct blood flow and for the treatment of coronary heart disease. The procedure involves guiding a thin guide wire through the femoral artery until it is just past the blockage. Permanently implantable metal cylinders named stents made from nitinol are often used to support the walls of the vessel and maintain arterial lumen. The stent is shape set into the open condition, then compressed, and inserted into the delivery catheter. The deployed stent is prevented to completely recover its original shape and exerts a very gentle outside pressure against the vessel wall to keep it open and minimize its recoil [24] (Fig. 7).

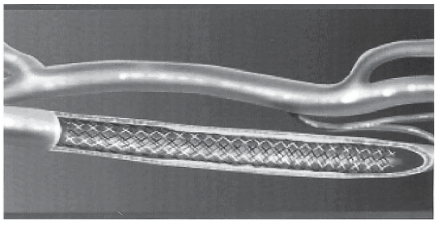


Fig 7. Showing stent in the internal carotid artery [24].

2. CONVENTIONAL METHOD OF MANUFACTURING NITINOL

The thermo-mechanical properties of NiTi are extremely sensitive to the alloy composition and the method of manufacturing [30]. Conventionally, NiTi is produced in ingots by self-propagating high-temperature synthesis (SHS), vacuum induction melting (VIM) or vacuum arc remelting (VAR) processes, which is followed by hot working and tooling until the required shape of the object is obtained. However, the arc melting requires multiple re-melting in a vacuum to obtain a near-homogeneous alloy. The induction melting can lead to carbon, and or oxygen contamination of the product [31]. The manufacturing and processing complications encountered when using the conventional methods to manufacture the NiTi alloy have the shortcoming of homogeneity in the microstructure, which affects the material's shape memory and superelastic behaviour. The method used to manufacture the NiTi alloy is crucial in that the manner in which the metallic powder is melted determined the quality, functionality, and behaviour of the NiTi alloy when in service [7]. The conventional methods which are normally used to manufacture Nitinol have obvious limitations, which affect the material's microstructure and mechanical properties adversely.

It is also reported that NiTi material's processing history and surface conditions are generally not well documented [7, 12, 21, 32]. Nickle-Titanium requires controlled processing to achieve optimal mechanical and thermal properties. Optimization of the thermo-mechanical processing provides good fatigue life and general mechanical properties to meet the stringent structural requirements of medical implants. Similarly, surface processing is required in order to promote optimal corrosion resistance and biocompatibility of the material [18,33]. The ASTM F86 [33] standard recommends surface improvements to improve the corrosion resistance of metallic surgical implants and also various chemical and electrochemical surface treatments are intended to remove objectionable surface contaminants. NiTi is a passive alloy like titanium and stainless steel and a stable surface oxide protects the base material from general corrosion. The surface is predominantly composed of titanium oxide and thus its passivity may be further enhanced by modifying the thickness, topography and chemical composition of the surface by selective treatments which cannot be conducted by the conventional methods [12, 21, 32]. The employed technologies need to be improved in order to produce parts with homogenous microstructures in cost-effective manners.

To further understand the fabrication of nitinol, its binary phase diagram needs to be studied. The phase diagram gives clarity on different phases of the alloy, especially if the material properties have to be adjusted during heat treatment processes. NiTi SMA is a near equiatomic (i.e. ~Ni 50.0 at. % Ti) with intermetallic compound $TiNi_3$ that forms eutectic during solidification, together with the Ni-rich solid solution. There are other compounds that are brittle in the system, Ti_2Ni, Ni_3Ti and Ti_3Ni, as shown in the Ni-Ti binary phase diagram (Fig.8) [34].

The intermetallic compounds which are detrimental to the mechanical properties of NiTi exist with other phases that form during ingot casting including titanium carbide (TiC), which form due to eutectic reaction with the graphite crucibles used in vacuum induction melting (VIM). During the reaction of NiTi the alloy undergo a peritectic reaction with oxygen due to higher reactivity of these metals. Even though the reaction happens in a vacuum atmosphere, peritectic reaction forms $Ni_2Ti_4O_X$, TiO oxides [35]. During the casting process, it was discovered that there were more carbides that form than oxides due to faster formation of eutectic reactions than peritectic reactions [34, 36]. These have a negative impact on the product formed, by causing the material to fracture and form particle void assemblies (PVA), which serve as a points of fracture after casting process [36, 37, 38, 39, 40, 41].

These limitations of conventional methods of producing NiTi have put materials scientits on the urge of using additive manufacturing (AM) technologies for better outcome.

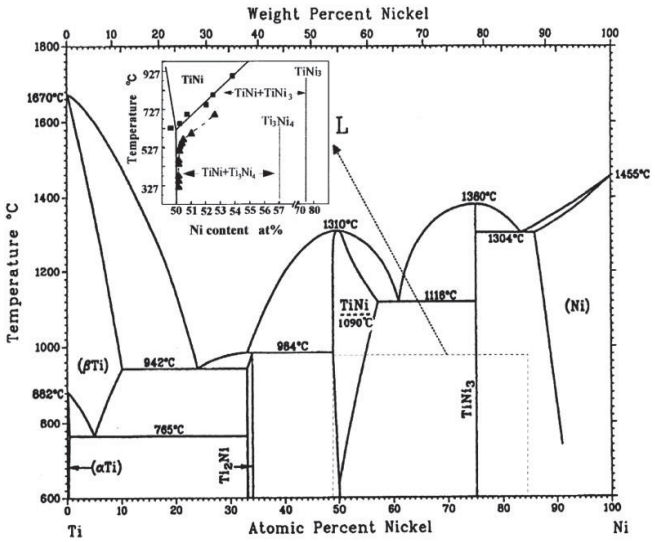
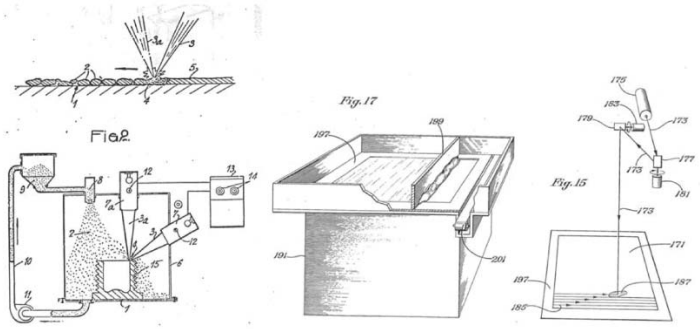


Fig.8: The Ni-Ti Phase diagram [42].

3. ADDITIVE MANUFACTURING OF NITINOL

Additive manufacturing (AM) is a process which is applied to build up objects in layer-by-layer from 3D CAD model [43]. The first patent of Laser Powder Bed Fusion (LPBF) concept was done by Pierre Cirauds in 1973, he described the creation of solid parts using a beam of energy to solidify powdered material (e.g., plastic or metal powder) onto a substrate [50]. Then in the 1980s, the LPBF concept was brought into practice by Dr. Carl Deckard and academic adviser, Dr. Joe Beaman at the University of Texas at Austin in the 1980s. The program was sponsored by the Defense Advanced Research Projects Agency (DARPA) [51]. Though similar process was patented by R.F Housholder in 1979, but never commercialized [51, 52]. Deckard, CR, thought the process will be better and will allow the manufacturing of complex parts from CAD models. He spent two and a half years thinking about how he would develop such a method. By the end of 1984, Deckard had come up with an idea of using a direct energy beam (such as a laser or electron beam) to melt particles of powder together to produce a three-dimensional object. The first machine Deckard built was called "Betsy", used a 100 W YAG laser (synthetic crystal yttrium aluminum garnet laser) to increase the power of the light emitted. Deckard filled a small box with power by hand using a device similar to a salt shaker while a computer ran the scanner on the table. "Betsy", was a success in additive manufacturing that which led to the development of other processes.



(a) **(b)**

Fig. 9: Cirauds invention (a) and Householders invention (b) [51].

By contrast to the conventional methods of fabrications, AM technology provides an almost unchallenged freedom of design without the need for part-specific tooling. AM is an Eco-Design topology optimization technology that allows very complex parts to be created monolithically [44] [45]. The high degree of freedom offered by AM technology of building complex geometries that would otherwise be difficult or impossible to produce using the conventional manufacturing process (casting, drilling, milling, vacuum induction melting, and vacuum arc re-

melting) makes it a preferable choice [46]. It is cost effective, energy efficient, most accurate and environmentally friendly manufacturing process.

The AM processes were classified into seven distinct parts (laser powder bed fusion, photopolymer vat, material extrusion, directed energy deposition, sheet lamination, material jetting, and binder jetting) by the American Society for Testing and Materials (ASTM) International F42 Committee on Additive Manufacturing Technologies [48,49]. The powder bed fusion process comprises Direct Metal Laser Sintering (DMLS), Selective Laser Sintering (SLM), Electron Beam Melting (EBM) and Laser Cusing (LC) – where the source of the thermal energy is either a laser or an electron beam. The powder bed fusion machines are the most commonly used for the creation of end-use parts for biomedical and other high-tech applications [47, 48].

Laser Powder Bed Fusion (LPBF) is a process capable of making metal alloy components that have mechanical properties comparable to wrought material. It is possible with LPBF to produce fully dense parts (up to 99.9%). The advantage of this process is that metal parts of complex geometric topology can be produced, which enables the production of customized components such as biomedical implants [49]. The efficiency of the process can also be attributed to the fact that there is no wastage of material. LPBF has opened a whole new world to the manufacturing industry; previously impossible designs and manufacturing concepts are now made possible with LPBF. Complex shapes and objects could be manufactured by utilizing the layer by layer scanning process of LPBF. Currently, much research and development are in progress to ensure optimal process parameters for a number of metal powders such as Nitinol. The new and innovative manufacturing technique (Fig. 10) of AM has seen massive sales growth in the past years.

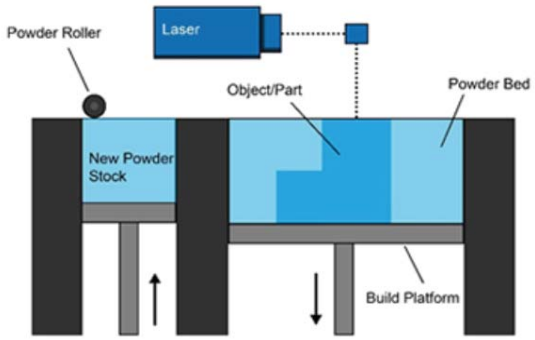


Figure 10: Schematic diagram of the laser powder bed fusion [53].

Cutting NiTi into desired size and shapes also posed a serious challenge due to the superelastic effect nature of the NiTi materials [54]. Using the versatility of AM technology such as laser powder bed fusion (LPBF) to produce biomedical objects of near-net shapes that would enhance the geometrical, technical and functional properties of the NiTi. The mechanical properties of a material are not the only determining factors for qualifying it for a specific application, but also the geometrical characterisation. This functional requirements of near-net shapes of complex geometries make additive manufacturing an attractive manufacturing technology to be exploited for manufacturing NiTi alloys with specific geometrical characteristics for biomedical applications. In addition, the AM processing routes are more promising to get more isotropic microstructures, since the building process takes place in an enclosed chamber it would eliminate any issues of contamination. It is a very cost-effective, energy efficient, and environmentally friendly manufacturing process [7].

AM, process parameters can be categorised into three categories:

(1) Machine based input parameters (laser, atmosphere, substrate etc.),

(2) Powder-related parameters (particle shape, size, density, distribution, layer thickness, etc.), and

(3) Process input parameters (laser, powder, design and strategy, and control unit) (Fig.11)

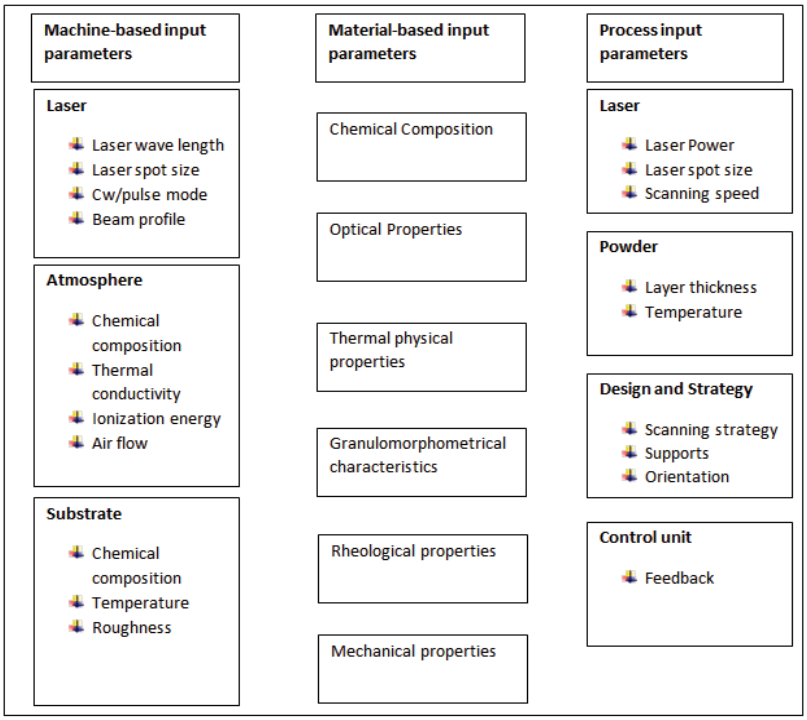


Figure 11: Factors influencing on LPBF process [55].

The product quality requires the development of a set of optimized processing conditions or parameters, which assure uniformity and control of microstructure in the associated mechanical properties and performance [56].

4. METHODOLOGY

A preliminary analysis will be conducted to determine the optimum process parameters for the selected alloy (55Ni-Ti) by forming and studying single tracks and single layers on a titanium substrate [57], according to well-known procedures [43, 58]. The optimum process parameters will be used to produce as-built samples for microstructural and mechanical properties investigations. The microstructural analysis would be conducted with optical and scanning electron microscopes. The mechanical property results obtained using LPBF will be compared to the properties of NiTi already found in literature. Based on the outcome of the comparison, conclusions will be drawn on the feasibility of using LPBF for producing NiTi samples for biomedical applications. More than one tensile test would be performed using a MTS Criterion model 43 Universal Test machine. The surface roughness of the samples will be measured with Surftest SJ-210 portable surface roughness tester accordingly to ISO 1997. EOSINT M 280 machine would be used for producing all the experimental samples.

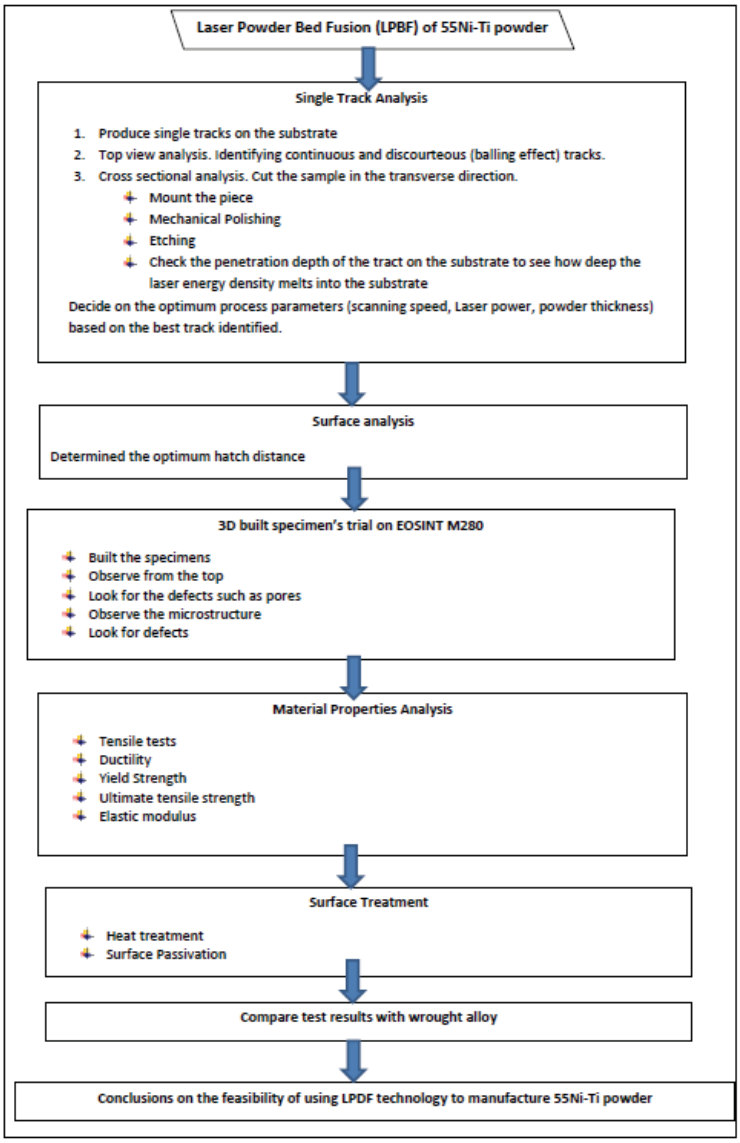


Fig. 12: Research Methodology.

5. CONCLUSION

From the literature review, it was revealed that the conventional methods have been used to manufacture NiTi for biomedical applications. However, the thermomechanical behaviour that gives Nitinol its superelastic properties are adversely affected due to the manufacturing limitations encountered when using the conventional methods of manufacturing. To solve the shortcomings brought by the conventional methods of manufacturing, additive manufacturing will be employed in an anticipation of producing biomedical objects with excellent biomechanical and biofunctional properties with complex shapes without contaminants.

The study intends to compare the mechanical properties of the LPBF NiTi samples to that of the conventionally manufactured samples. It is expected that the samples produced with the LPBF process would yield preferable mechanical properties and superelasticity. Literature shows that the elastic young modulus obtained from nitinol will be far less than that found in other biomedical titanium alloys, meaning nitinol will in the future help produce implants with appreciable mechanical properties to improve life of implant patients.

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