FABRICATION AND CHARACTERIZATION OF POROUS NITI SHAPE MEMORY ALLOY BY ELEVATED PRESSURE SINTERING

A Thesis

by

ERIC LAYTON VANDYGRIFF

Submitted to the Office of Graduate Studies of Texas A&M University in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

May 2002

Major Subject: Aerospace Engineering
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May 2002

Major Subject: Aerospace Engineering
Shape Memory Alloys (SMAs) have emerged as a class of materials with unique thermal and mechanical properties that have found numerous applications in various engineering fields. Even beyond the shape memory characteristics inherent in dense SMAs, porous SMAs with a relatively low density would expand the applicability of SMAs. In addition to the large recoverable strains observed by SMAs, porous SMAs offer the possibility of undergoing greater overall strains as well as much higher specific energy absorption under dynamic loading conditions due to the possibility of wave scattering. Porous SMAs also offer the possibility of impedance matching by grading the porosity at connecting joints with other structural materials. In biomedicine, porous SMAs have been successfully used in such applications as bone implants and dental repairs. Despite their high potential for practical use, porous SMAs have not been sufficiently studied in the U.S., and techniques for their commercial production have not been adequately developed.

Currently, three methods are commonly used for producing porous NiTi SMAs from elemental powders. These methods include conventional sintering, Self-propagating High-temperature Synthesis (SHS), and sintering at elevated pressure via a Hot Isostatic Press (HIP). Conventional sintering requires long heating times and samples are limited in shape and pore size. SHS, which is initiated by a thermal explosion
ignited at one end of the specimen and propagates in a self-sustaining manner, usually results in an uncontrolled porous microstructure and impurities. Sintering at elevated pressures however results in a decrease in the necessary sintering time as compared to conventional sintering due to consolidation of the medium and offers more control over the fabrication process and phase composition than SHS.

In this work, dense and porous NiTi specimens with approximate porosity levels of 0\%, 42\%, and 50\%, respectively, are fabricated via HIPping and characterized in terms of composition and phase transformation characteristics. Mechanical behavior of the HIPped specimens is studied through quasi-static testing in both shape memory and pseudoelastic effect. Results for the porous NiTi in dynamic testing under compressive loading are also presented to illustrate the large energy absorption and strain recovery capabilities associated with porous NiTi SMA.
To my parents for their example and support and to my wife Carey for being my motivation and very best friend.
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Above all, I would like to thank my family for always supporting me in the decisions I make and for showing me by example. They have always taught me never to settle. Thanks goes especially to my wife, Carey, for always being by my side. I
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CHAPTER I

INTRODUCTION

As the requirements for many engineering applications tend toward a more compact and durable structure, Shape Memory Alloys (SMAs) are becoming a common ground as a multifunctional material, able to provide structural support as well as offer possibilities of actuation due to their ability to be deformed and return to a “memorized” shape. Over the last two decades, extensive studies have been completed which promote the use of SMAs in various engineering fields including a wide range of applications from naval functions, including underwater silent propulsion [1, 2], to aviation [3] and aerospace applications [4]. SMAs are also quickly finding their place in the medical field as biocompatible [5] medical devices, tools, implants and fixtures [6, 7, 8]. Interest in SMAs is also quickly growing in the petroleum field to exploit the usefulness SMAs as liners, couples and valves [9, 10]. These applications have mostly benefited from the ability of the inherent shape recovery characteristics exhibited by SMAs [11, 12, 13, 14]. In addition to the shape memory and pseudoe-elastic effects that SMAs possess [15, 16], there is also the promise of using SMAs in making high-efficiency damping devices [17] that are superior to those made of conventional materials, partially due to their hysteretic response.

A. Introduction to Shape Memory Alloys

SMAs are a unique class of metal alloys that undergo a solid-to-solid phase transformation which can exhibit large recoverable strains. This recoverable characteristic can be observed in two distinct manners known as Shape Memory Effect (SME) and

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Pseudoelasticity (PE) [15]. SME is generally observed at relatively low temperatures and occurs when a SMA is strained beyond the initial apparent elastic limit. In SME, the alloy does not recover its original shape until the temperature is raised above a specific activation temperature. In contrast, PE occurs when a SMA recovers the inelastic strain as the deforming stress is removed. Representative stress-strain plots showing a characteristic SME and PE response are shown in Figures 1 and 2, respectively.

Of the many SMAs available, NiTi has become one of the most widely used of the shape memory alloys due to its exceptional physical and mechanical properties, including large recoverable strains in polycrystalline forms [18]. The transformation and the shape memory effect in NiTi alloy with 50 at.% Ni was first discovered in 1962 by Buehler and coworkers at the Naval Ordinance Laboratory. Due to the origin of discovery, this alloy was appropriately named NiTiNOL, in honor of their workplace [19]. Because of these exceptional qualities, this research effort will focus on the fabrication and use of NiTi SMAs.

1. Structure and Transformations of NiTi SMA

To understand the reason behind the shape memory phenomenon of NiTi, it is beneficial to first understand the crystallography of this unique class of alloys. This phenomenon can be attributed to a diffusionless solid-to-solid phase transformation which occurs between the parent and martensitic phase. The crystal structure of the high-temperature parent phase, known as austenite (A), is an ordered body centered cubic (BCC) crystal form (B2) [20]. Upon cooling beyond a specific critical temperature, a thermoelastic martensitic transformation to a distorted monoclinic structure (B19\(^{\prime}\)) via a shear-like mechanism takes place, commonly referred to as martensitic plane variants. To accommodate the internal stresses caused by the transformation
Fig. 1. Typical stress-strain response of SMAs in SME
Fig. 2. Typical stress-strain response of SMAs in PE
to the B19’ phase, the formation of a combination of up to 24 multiple martensitic variants is possible, resulting in a twinned martensite crystal form, also known as self-accommodated martensite. Transformation to martensite (M) by twinning is completely reversible [21] and results in a thermoelastic hysteresis. In a polycrystalline structure, this transformation occurs over a temperature range due to the varying local stresses between grains. Four stress dependent parameters are used to characterize the start and finish temperatures required to cause a transformation in polycrystalline SMAs from austenite to martensite and martensite to austenite. These temperatures are often referred to as the transformation onset and finish temperatures and are defined as follows.

- $M_s$, martensite start temperature
- $M_f$, martensite finish temperature
- $A_s$, austenite start temperature
- $A_f$, austenite finish temperature

A two-dimensional schematic of this phase transformation without an externally applied stress is shown in Figure 3. It can be seen that upon cooling beyond $M_f$ the parent BCC austenite crystal structure is replaced by a self-accommodated monoclinic structure (twinned martensite). Without any external stresses, this phase change without a change in the overall material shape or volume is accomplished by introducing twins (twinned martensite) [22, 15]. Once the temperature of the alloy is again raised to above $A_f$, the thermal energy causes the atoms to rearrange themselves into an ordered BCC form.
Fig. 3. Stress-free thermally induced phase transformation in SMAs from Austenite to Martensite and vice versa.
2. Shape Memory Effect

As described in the self-accommodated martensite structure, the formation of multiple variants allows for changes from the BCC form of austenite to the B19' form of martensite without a macroscopic change in strain. However, applying an external stress to a self-accommodated martensite structure causes movement of the twin boundaries [23]. If the twinned martensite structure is stressed beyond a particular limit, these previously twinned crystal forms begin “flipping” their direction of tilt to match with neighboring tilted twins. This movement of the crystal structures causes the previously unaligned or twinned crystals to align themselves in the B19 form (detwinned martensite), resulting in an observable macroscopic change in shape (see Figure 4a). This process is known as detwinning of martensite. Fortunately for NiTi, the stress required to cause movement of the twinned boundaries is well below the critical stress of unrecoverable slip. Upon unloading to zero stress at temperatures below $A_s$, the detwinned crystal form remains (Figure 4b). Once the temperature of this deformed structure is again raised from below $A_s$ to above $A_f$, the detwinned martensite crystal structure transforms again to the BCC form and the cycle can be repeated. This cycle is referred to as one-way SME, or simply SME.

Just as there is a one-way SME, SMAs can also exhibit a phenomenon called two-way SME (also called two-way training) [24]. A two-way trained SMA is a SMA that has two different “memorized” configurations. Training is actually a result of limiting the number of variants of martensite that can form when the material is repeatedly heated and cooled below the critical temperature, causing limitations which inhibit the self-accommodation of the martensite and increases the internal strain. More simply, the limited number of possible variants result from stress fields due to the presence of dislocations introduced during cyclic deformation of a SMA. This be-
Fig. 4. Stress-temperature phase diagram with accompanying crystal forms of SMAs in SME: (a) detwinning of martensite under applied stress; (b) transformation of unstressed detwinned martensite into austenite upon heating
behavior is accomplished by repeatedly applying the same stress (same direction with respect to the specimen) to the SMA while it is cooled from the austenite to the martensite. Consequently, the stress favors the initial formation of particular variants of martensite, similar to the way that external stress favors the growth of certain variants in a preferred orientation.

a. Rhombohedral Phase in SMAs

The shape memory effect transformation from austenite to martensite can also be complicated by the presence of an R-phase (rhombohedral form) [25]. Normally, fully annealed near equi-atomic NiTi transforms from the austenitic phase directly to the martensitic phase. However, some factors such as aging [26], increased Ni content in alloying [27], thermomechanical treatment [28], and thermal cycling [29] can introduce and enhance the R-phase, or “pre-martensitic” phase, between the austenite to martensite transformation. The presence of the R-phase results in a completely reversible two step transformation, i.e., from the parent phase (austenite) to the R-phase and then to the monoclinic martensitic phase. Transformation to the R-phase differs from the martensitic transformation in that the martensite-austenite transformations involve a change in the microstructure (BCC to monoclinic). In contrast, a change from the austenitic phase to the R-phase consists only of small changes in the lattice parameters of the austenitic phase, resulting in a distortion of the original parent cubic phase. Otsuka and Wayman describe the R-phase as thin plates which take place by nucleation and growth, often initiated from dislocations [25]. According to Wayman and Airoldi and Rivolta [30, 31], the R-phase is always present in the transformation from austenite to martensite but is often overlapped by the martensitic phase transformation.
3. Pseudoelastic Behavior

As mentioned previously, another unique behavior observed in SMAs is known as pseudoelasticity. PE describes the mechanical behavior of SMAs at temperatures above $A_f$ when large apparent recoverable plastic deformation occurs (see Figure 2). Upon application of stress, the SMA has a stiffness representative of the elastic modulus of the austenitic phase ($E^A$). At a critical stress, the tangent modulus flattens as the parent BCC crystal form transforms to the detwinned martensitic crystal form. Once transformation has completed, the tangent modulus again increases to a stiffness representative of the elastic modulus of the martensitic phase ($E^M$). When the applied stress is removed, a similar process occurs in reverse order with an overall hysteretic response. A schematic of the crystal forms of this process is shown in Figure 5. The transformation from austenite directly to detwinned martensite is known as stressed-induced martensite (SIM). This can be accomplished by either increasing the applied stress or decreasing the temperature of the SMA, or a combination of these two parameters as shown by a generalized stress-temperature path represented by a double sided arrow in Figure 5. The PE response is completed when the stress is removed and the previously SIM transforms back to austenite.

A representation of the stress dependence of $M_s$, $M_f$, $A_s$, and $A_f$ are also shown in Figure 5. It can be seen that as the stress increases, the transformation temperatures increase as well. Similarly, an increase in the temperature of the SMA will also result in an increase in the stress required for transformation. For simplicity, this relationship is represented as a linear function.
Fig. 5. Stress-temperature phase diagram with accompanying crystal forms of SMAs in PE
4. Work Hardening, Heat Treatment, and Thermomechanical Cycling of SMAs

One of the difficulties in working with NiTi SMAs is the material dependency on the thermal and mechanical history of the alloy. Transformation temperature, recoverable strain, and material hardness can be directly affected by the previous conditioning steps, making the material sometimes difficult for consistent analysis, but useful in that manufacturing and process parameters can be slightly altered for many different engineering applications. In many cases, for example, it has been desirable to perform thermomechanical cycling in order to improve the PE response [32, 33]

a. Work Hardening of NiTi SMAs

There have been many studies pertaining to the work hardening of NiTi SMAs, and there are several material characteristics that are known to change as a result. It is well known that work hardening of NiTi increases the dislocation density as well as the residual (unrecoverable) strain [34]. This increase in dislocations restricts the growth of the martensitic phase and retards the development of detwinned SIM, ultimately resulting in a decrease of the martensitic and austenitic phase transformation temperatures [35, 28]. Besides generating internal stresses, dislocations act as nucleation sites for R-phase formation [25]. In addition to increasing the stress required for martensite transformation, increased dislocation density also causes an increase in the tangent modulus of the transformation region of the stress-strain response due to strain hardening.

b. Effects of Heat Treatment on NiTi SMAs

As mentioned previously, various heat treatments are another method for controlling the shape memory characteristics of NiTi SMA. The annealing of work hardened NiTi
alloys modify the effects of the dislocation density by rearranging the dislocations through recovery or eliminating the dislocations through recrystallization. Unlike work hardening, various heat treating methods of NiTi (T>350°C) have a tendency to raise the transformation temperature of the martensitic phase [36]. Treppmann et al. [36] and Thoma et al. [37] also report that the R-phase and austenite transformation temperatures remain nearly unaffected after annealing at temperatures between 300°C and 500°C.

As with many other alloys, the rate at which NiTi is cooled during heat treatment can have as large of an effect on the mechanical properties as the annealing temperature itself. In general, the slower the cooling rate, the higher the transformation temperature with less R-phase is observed [38]. This can be attributed to the fact that slow cooling rates allow the material to spend more time at intermediate temperatures, i.e. an aging effect. If the anneal temperature is high enough (>600°C), a slow cooling rate increases the possibility of the material to form other stable intermetallic neighboring phases. A rapid cooling rate on the other hand results in higher internal stresses, which in turn decreases the martensite transformation temperature.

c. Thermomechanical Cycling of NiTi SMAs

A very important practical consideration when using SMAs as actuators is the consistency or reproducibility of the shape memory behavior. As the use of SMAs as actuators increases, increasing studies on the thermomechanical behavior, useful mechanical cycles, and fatigue life are being conducted [28]. Similar to work hardening, thermomechanical cycling of NiTi alloys causes an increase in the dislocation density of the alloy and consequently, lowers the martensite transformation temperature. It has been shown however that the amount of change in thermal activation and hardening is dependent on the number of cycles performed. As the number of cycles
increases, the stress-strain behavior stabilizes, resulting in a more predictable and me-
chanically useful actuator. However, as with work hardening, a significant decrease in
the hysteresis loop is observed, possibly making the material less capable as a passive
damping device.

B. Porous Shape Memory Alloys

Due to the ability of SMAs to repeatedly withstand relatively large recoverable strains
coupled with their inherent large hysteretic response and variable stiffness, research
is being conducted to investigate the use of SMAs as damping devices and impact
absorbing components [39, 40, 41, 42, 43]. As described previously, the hysteretic
response of SMAs is associated with both the SME and PE. This hysteretic response
is due to the internal friction in the lattice structure as the material transforms from
one crystal structure to another, i.e. any combination of the transformations described
in the previous section, including austenite (BCC), R-phase (rhombohedral), twinned
martensite (B19'), and detwinned martensite (B19).

It is envisioned that these advanced materials could find their way into applica-
tions including self-healing lightweight armor, space launch vehicle payload isolation
[4, 43], and civil engineering applications including base isolation of elevated highway
bridges [44] and seismic protection devices [45, 46, 47, 48]. Encouraged by the pursuit
of these more advanced materials, the focus of the engineering community has given
recent attention to the fabrication of porous SMAs [49, 50, 51, 52, 53, 54]. Even be-
yond the energy absorption capabilities offered by conventional SMAs, porous SMAs
offer the possibility of higher specific energy damping capacity under dynamic loading
conditions and the possibility of wave scattering. With the additional possibility of
grading the porosity, porous SMAs could also be designed for impedance matching
at connecting joints with other structural materials as well.

Depending on the necessity of the application, porous SMAs could be manufactured with open or closed pore designs. Open porous SMAs are already beginning to find their way into biomedical applications as implants for bone reconstruction due to their permeability and reduced density [55, 56, 57, 58].

C. Objectives of this Work

The objective of this research effort is two fold: 1.) a novel method for fabricating porous NiTi from elemental powders via HIPping is developed, and 2.) various specimens fabricated using the HIP method are analyzed and characterized using several experimental techniques. Two different HIPping techniques are implemented to fabricate small and large pore NiTi SMA from elemental Ni and Ti powders via HIPping. Phase transformation characteristics and material composition of HIPped porous NiTi will be addressed through results obtained from thermal and microstructure analysis. The possibility of employing HIPped porous NiTi as single-component multifunctional shape memory and energy absorption devices (providing both structural stiffness and damping characteristics) will be demonstrated as results from quasi-static and dynamic tests performed under compression. The damage and failure characteristics of the porous SMAs will also be discussed from microscopic observation of the tested specimens.
CHAPTER II

LITERATURE REVIEW

A. Fabrication of Porous Metals, Specifically NiTi

Various methods for producing conventional porous metals and alloys currently exist, including casting, metallic deposition, and powder metallurgy [59]. One casting technique commonly used for producing metal foams includes the injection of gas into a metal melt, as described by Gibson and Ashby [60]. Other methods employ powder metallurgy techniques including conventional sintering, Self-propagating High-temperature Synthesis (SHS), and sintering at elevated pressure using a Hot Isostatic Press (HIP).

This research effort will investigate the fabrication of porous NiTi. Due to the high melting temperature (1310°C) and relatively high density of NiTi (6.45 g/cm³), fabrication challenges of injecting a gas into a NiTi melt are introduced that are not typically present with many other metal foams like aluminum. Also, conventional fabrication techniques of casting NiTi from a melt can be difficult due to the reactivity of the melt that often results in segregation defects [50]. In addition, it can be seen in the phase diagram of NiTi (Figure 6) [61] that the B2 phase region is very narrow at temperatures below 950°C and NiTi alloys have a tendency to decompose upon cooling, forming other stable intermetallics such as Ni₃Ti, Ni₄Ti₃, and NiTi₂, which do not exhibit the shape memory characteristics of binary NiTi. These difficulties have influenced the authors to utilize powder metallurgy techniques to produce porous NiTi SMA. Powder metallurgy offers the opportunity of employing either elemental or pre-alloyed starting powders. However, additional processing techniques required for producing pre-alloyed NiTi powders are both difficult and expensive. For this
reason, this research effort will mainly focus on fabrication of binary NiTi SMAs from elemental powders using the powder metallurgy techniques referred to above.

1. Conventional Sintering

Conventional sintering has proven to be a viable method of producing porous NiTi SMA [62] from powders. A cold compact of Ni and Ti powders are pressed from an elemental powder mixture to form a pellet compact, which is then sintered at near melting temperatures to produce a binary NiTi phase through diffusion of the two elements [52]. Using this method, porosity of the specimen is varied by the powder compaction pressure and the initial powder size and shape. Because the porosity results directly from the voids left between powder particles, the average pore size is relatively small and the overall pore volume is limited to a maximum porosity of nearly 40%. Some disadvantages associated with conventional sintering include long heating times (48 hours), small specimen sizes, and difficulties associated with other stable intermetallic phases. The long sintering times are a result of the voids that remain after pressing and during sintering. These voids act as gaps that in turn hinder the diffusion of the elemental powders.

2. Self-propagating High-temperature Synthesis

SHS, or combustion synthesis, has also been successful in the fabrication of porous SMAs from elemental powders [49, 63]. Combustion synthesis causes the solids to dissolve by introducing a liquid phase to promote the kinetics of mass transfer. Due to the exothermic reaction of Ni with Ti, the process is initiated by heating the entire specimen until reaction occurs or by a thermal explosion ignited at one end of the specimen, which then propagates through the specimen in a self-sustaining manner. Combustion synthesis has been successful in producing porous SMA with
Fig. 6. Phase diagram of NiTi
porosity counts as high as 65%. However, due to the explosive nature of the exothermic reaction through combustion synthesis, experimental control is limited once the reaction has initiated. Rapid heating rates and short heating times also make for a less consistent material due to the lack of particle diffusion and the formation of precipitates [64, 50, 65]. Also, the success of SHS is greatly dependent on the shape of the canister for a thorough reaction to occur.

3. Sintering at Elevated Pressure via HIPping

Another method for producing titanium foams from powders via a HIP was recently implemented by Kearns [66]. This work was later expanded on by Schwartz [67] and then by Davis et al. [68]. This technique utilizes a HIP to compress and trap Ar gas bubbles between neighboring metal powders which diffuse at elevated temperatures. The resulting compact contains high pressure Ar pores that became trapped between the metal powders during high-pressure diffusion. Subsequent sintering at reduced pressure causes the trapped gas to expand in the high temperature softened material. This method has been successful in producing components with relative densities as low as 50%.

Based on the HIPping technique, porous NiTi SMA was recently produced from elemental Ni and Ti powders in the Active Materials and Structures Laboratory at Texas A&M University [42, 53]. Some advantages of producing porous NiTi via HIPping include: 1) decreased solid state diffusion time, 2) control of pore size and volume fraction, 3) the ability to produce a variety of shapes, decreasing necessary machining time, and 4) a more stable and controllable reaction than offered by SHS. Some of the difficulties that may be encountered with the use of elemental powders to fabricate NiTi via HIPping are similar to those encountered using conventional sintering and include contamination from oxides and the formation of other stable
intermetallics. Using the HIP method, several NiTi specimens are fabricated with porosity levels ranging from 40-50% and are tested under quasi-static and dynamic loading conditions. This research effort will utilize slightly varying HIP techniques to fabricate two different types of porous specimens: small and large pore specimens.

Earlier work has been done by McNeese et al. in which a HIP was used to fabricate dense NiTi from elemental powders [69]. In his research effort, powders were hydraulically pressed into a stainless steel canister, vacuum purged, and sealed. The canister was then HIPped and any remaining voids left during compaction were compressed as the canister collapsed around the NiTi medium. Specimens with 99% relative density were fabricated. Similar to this method, dense NiTi specimens are also fabricated in this research effort for comparison with the porous specimens.
CHAPTER III

FABRICATION OF POROUS NITI SMA VIA HIPPING

In previous attempts by Kearns, Schwartz, and Davis to create porous titanium alloys from HIPping, a sealed canister design is employed in which the pore expansion is primarily carried out in the post-annealing process, whereas in this experimental effort, the greater part of the pore expansion is completed during the depressurization ramp of the HIP cycle. After HIPping, the specimen is annealed in a furnace to facilitate further diffusion of the elements and to enhance the porosity of the material. Through slight variations in the HIPping temperature and sintering time, specimens with relatively small and large pores are produced.

Elemental Ni and Ti powders obtained from Atlantic Equipment Engineers, Inc. were mixed together with a ratio of 50.6 at.% Ni [69]. A Beseler tumbler was used to mix the powders for approximately 12 hours. The powder was then loosely packed into a stainless steel canister. To promote diffusion, Ni and Ti particle sizes of <20 microns and >99% pure are employed. A summary of the chemical composition of the elemental powders are listed in Table I and Table II. For initial mixing of the elemental powders and during the packing of the powders in the canisters, no inert gas chamber was available and the powders were temporarily subjected to the atmosphere, however, after mixing and before storage, the containers which stored the elemental and mixed powders were placed into a vacuum chamber and purged with ultra high purity (UHP) Ar gas and sealed. In addition, during the tumbling process, an UHP Ar purged container was sealed to prevent contamination of the powders.

For HIPping, two different canister sizes are made from high temperature 316 stainless steel tubing. Both sizes are machined to be approximately 76.2 mm (3").
Table I. Chemical analysis of elemental Ni powders

<table>
<thead>
<tr>
<th>Component</th>
<th>Quantity (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>0.0390</td>
</tr>
<tr>
<td>O</td>
<td>0.0690</td>
</tr>
<tr>
<td>Fe</td>
<td>0.0030</td>
</tr>
<tr>
<td>S</td>
<td>0.0002</td>
</tr>
<tr>
<td>Ni</td>
<td>99.9999 (metals basis)</td>
</tr>
</tbody>
</table>

*Ni particle size < 20 μm*

long with an outer diameter of 15.88 mm (5/8”). Two different wall thicknesses are used, 1.59 mm (0.0625”) and 2.11 mm (0.083”), however, the difference in the wall thickness does not seem to make a difference in the outcome of the porous specimens. To seal the bottom of the canister, a cap is also machined from high temperature 316 stainless steel and sealed to the bottom of the canister using a Tungsten Inert Gas (TIG) weld. To remove any oxidation from welding, the canister is then bead blasted using a glass bead blasting cabinet. The canisters are then cleaned in an ultrasonic isopropyl alcohol bath to remove any residue or loose particles. A diagram and schematic of the thinner walled canister is shown in Figure 7.

After filling each canister with the loosely packed powders, the top cap is tack welded at two opposing sides ("open" canister design, not an air tight seal) and placed in the HIP for immediate purging with UHP Ar gas. The loosely packed powders have a relative density of approximately 50%. During the purging process, the HIP chamber is vacuum purged to 1 Torr, then backfilled with UHP Ar. This process is repeated 3 to 4 times to assure a clean environment, not only within the HIP chamber,
Table II. Chemical analysis of elemental Ti powders

<table>
<thead>
<tr>
<th>Component</th>
<th>Quantity (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>0.5690</td>
</tr>
<tr>
<td>N</td>
<td>0.0190</td>
</tr>
<tr>
<td>H</td>
<td>0.0397</td>
</tr>
<tr>
<td>Fe</td>
<td>0.2300</td>
</tr>
<tr>
<td>Si</td>
<td>0.0100</td>
</tr>
<tr>
<td>C</td>
<td>0.0200</td>
</tr>
<tr>
<td>Mg</td>
<td>0.0300</td>
</tr>
<tr>
<td>Mn</td>
<td>0.0100</td>
</tr>
<tr>
<td>P</td>
<td>0.0020</td>
</tr>
<tr>
<td>Al</td>
<td>0.0100</td>
</tr>
<tr>
<td>S</td>
<td>0.0030</td>
</tr>
<tr>
<td>Ti</td>
<td>99.7000% (metals basis)</td>
</tr>
</tbody>
</table>

*Ti particle size < 20 µm*

but also within the canister since it is not completely sealed.

The HIP chamber is then heated and pressurized to 200MPa. During the HIPping process, the temperature is raised to a minimum sintering temperature of 940°C and the pressure is increased to 200MPa. NiTi is created as a result of solid-state diffusion of Ni and Ti species. By maintaining a temperature below the melting point (see Figure 6 for melting temperature), compressed Ar gas remains between the diffused alloy. It is imperative that the HIP temperature remain below the melting temperature of NiTi, as a sintering temperature above the melting temperature of
NiTi would result in a melt in which the Ar bubbles would escape to the top of the NiTi medium. While in the HIP, the pressure is decreased, allowing pressurized Ar pores to expand in the still creeping NiTi medium. Processing steps will be presented in detail in subsequent sections for each type of HIPped porous specimen.

Initially, temperatures were selected according to previous work by McNeese [69] in which dense NiTi was fabricated from elemental Ni and Ti by HIPping. Through trial and error and depending on the desired results, these temperatures were refined for producing relatively small and large pore NiTi.

An Asea Brown Boveri (ABB) model QIH-3 hot isostatic press is used for elevated pressure sintering. The ABB HIP is controlled using a programmable microMAC 5000 controller and IBM PC/XT. The pressure, temperature, heating rates, and vacuum purging are controlled automatically by the controller, and manual overrides are available if a deviation from the set program is desired. The chamber is heated via a graphite furnace and the temperature is monitored using two platinum-rhodium thermocouples, positioned near the upper and lower portions of the chamber. The maximum operating temperature of the furnace is 2000°C and the maximum operating pressure is 217 MPa. The workload dimensions are 93.98 mm (3.7”) in diameter and 149.86 mm (5.9”) high. The ABB HIP and furnace chamber are shown in Figure 8.

For microstructure analysis of the dense and porous specimens, a portion of each specimen is cut using a low speed, low force 4 inch diameter diamond cutting saw and cleaned in an ultrasonic acetone bath. For casting, the specimen sample is set in an epoxy cast, placed in a vacuum chamber to remove bubbles from the epoxy, removed from the chamber, and cured. The epoxy mold with the embedded specimen is then ground and polished using a Struers Roto-Pol multiple specimen polisher to a 1/4 µm finish.
Fig. 7. HIP canister design: (a) diagram showing dimensions and parts (dimensions shown in inches); (b) schematic showing assembly of open canister design employing tack welds at top
Fig. 8. ABB QIH-3 hot isostatic press (HIP)
A. Small Pore NiTi Specimens

To produce porous NiTi specimens with relatively small pores, the HIPping temperature is initially raised to 800°C at 1 MPa to allow for the high pressure HIP seals to expand. From 800°C, the temperature is continually increased to 940°C and the pressure is raised to 200 MPa simultaneously. The pressure and temperature are held constant at 940°C and 200 MPa for 6 hours to allow ample time for solid-state diffusion between the species. The temperature and pressure are then simultaneously decreased and the specimen is removed from the HIP and annealed in a conventional furnace at 900°C in Ar for an additional 6 hours. Processing data from the HIP cycle is shown in Figure 9.

After sintering, the removal of the NiTi specimens from the stainless steel canisters is relatively simple. Due to the lower sintering temperatures, the Ni and Ti elements have a tendency to diffuse within each other, however, there did not appear to be any significant diffusion of the powders to the canister walls. Once the top cap is machined away, the newly diffused NiTi alloy is easily loosened by lightly impacting the sides of the canister with a hammer or similar impact tool. A picture of a HIPped small pore NiTi bar is shown in Figure 10.

The small pore specimens have an average pore size of approximately 20 μm and an open pore structure. Microscopic observations of the characteristic size and shape of the pores suggest that the pores are formed from voids left as a result of the spacing between the initial powders (similar to conventional sintering). Expansion of these voids upon decreasing the pressure may assist in the increase of the overall pore volume fraction if Ar has become trapped during the high-pressure diffusion, but is not the primary contributor to the overall relative density. This method has been successful in producing porous NiTi with relative densities as low as 50%. The
Porosity of the specimens is calculated by comparing the measured density of the porous NiTi to the theoretical density of solid NiTi (6.45 g/cm$^3$). Micrographs of the small pore specimens are shown in Figure 11.
Fig. 9. HIP cycle for fabricating porous NiTi SMA from elemental Ni and Ti powders (small pore specimen)
Fig. 10. Picture of a small pore bar fabricated via HIPping
Fig. 11. Micrographs of HIPped porous NiTi: (a) small pore, 10x; (b) small pore, 50x (pores are seen as dark regions)
B. Large Pore NiTi Specimens

For producing porous NiTi with relatively large pores, the HIPping temperature is initially raised to 940°C at 1 MPa to promote initial diffusion between the powders (Figure 12, part 1 and 2) and to allow the high pressure HIP seals to expand. Next, the temperature and pressure are then simultaneously increased to 1000°C and 200 MPa. As the pressure increases, the increasing temperature exceeds the eutectic and peritectic temperatures of NiTi₂ (942°C and 984°C, respectively) and approaches the melting point of Ni₃Ti (1118°C), causing partial melting of the diffusing powder mixture at sintering temperatures below the melting temperature of binary NiTi [61](see phase diagram, Figure 6). When sintering above these eutectic temperatures, a liquid forms, accelerating the diffusion process. The liquid disappears as the equilibrium NiTi phase is formed. As this occurs, open pores containing high pressure Ar begin to close, trapping the Ar in the diffusing medium. Continued increases in pressure cause these now closed pores to decrease in volume, promoting enhanced diffusion through consolidation of the medium (Figure 12, part 3, 4, and 5). This process causes a decrease in the overall volume of the initially 50% porous mixture, creating a closed pore microstructure with relatively high-pressure argon pores. At 1000°C and 200 MPa, the consolidated medium is then homogenized for 3 hours (Figure 12, part 5). The melting temperature of binary NiTi is 1310°C, however, due to the exothermic reaction of elemental Ni and Ti to NiTi, the HIPping temperature is kept well below the actual melting temperature. This exothermic reaction could cause the temperature of the alloying powders to melt, resulting in the escape of the trapped bubbles to the top of the medium. After 3 hours, the temperature and pressure are then decreased simultaneously, allowing the compressed argon pores to expand in the still creeping NiTi medium (Figure 12, part 6). After completing the
HIPping cycle, the specimen is then heated in a conventional furnace in Ar for 6 hours at 900°C to facilitate further diffusion of the elements and enhance the porosity of the material.

Using the same method as the small pore specimens to calculate the overall porosity, this method has been successful in producing porous NiTi with porosity counts as high as 42%. A simplified schematic of the pore evolution using this technique is shown in Figure 13. The encircled numbers in Figure 13 correspond to the various HIPping stages seen in Figure 12. A picture of a HIPped large pore specimen is shown in Figure 14. The large pore NiTi specimens have an average pore size of approximately 0.5 mm.

Observation of the size and characteristic shapes of the pores in the large pore NiTi specimens suggest that unlike the smaller pore specimens, the large pores are formed mostly upon the expansion of the Ar when the pressure is decreased. As the pores expand, many join, causing the formation of channel-like pores (Figure 15). It can also be seen in Figure 15 that many pores formed without joining. These two types of pore formations result in a mostly open pore structure interlaced with smaller closed pores.
Fig. 12. HIP cycle for fabricating porous NiTi SMA from elemental Ni and Ti powders (large pore specimen)
Fig. 13. Pore evolution of large pore NiTi using a HIP
Fig. 14. Picture of a large pore bar fabricated via HIPping: (a) specimen after removed from HIP canister; (b) axially cut section
Fig. 15. Micrographs of HIPped porous NiTi: (a) large pore transverse cut; (b) large pore axial cut (pores are seen as dark regions)
C. Dense NiTi Specimens

Nearly following the method described for fabricating large pore NiTi via HIPping, dense specimens were also fabricated for comparison with the porous specimens. Using the same canister design as was used for the porous specimens (refer to Figure 7), mixed Ni and Ti powders were packed using a hydraulic press and the canister was again tacked at the top so that it could be placed inside a vacuum chamber and purged with UHP Ar. The canister was then removed and immediately welded air tight to prevent the escape of Ar and the contamination by air. Following the HIP cycle for the large pore specimens (Figure 12), the sealed canister was placed in the HIP and the temperature was initially raised to 940°C at 1 MPa. The temperature and pressure were then increased to 1000°C and 200 MPa. Because the canister was sealed, the high temperature and pressure of the HIP chamber caused the canister to collapse, resulting in consolidation of the powders and a 99% dense NiTi specimen. The canister was then machined away, revealing the dense NiTi.
CHAPTER IV

EXPERIMENTAL RESULTS AND DISCUSSION

A. Material Analysis

1. Calorimetric Analysis

Next, thermal scans were conducted on the HIPped dense and porous SMA specimens using a Perkin Elmer Pyris 1 Differential Scanning Calorimeter (DSC). The Pyris 1 DSC is capable of measuring latent heat due to phase transformations within the temperature range of 600°C down to -65°C. It has a calorimetric accuracy and precision of ±1% and ±0.1% and a temperature accuracy and precision of ±0.1°C and ±0.01°C, respectively. Figures 16 and 17 show the results from thermal scans that were conducted on the dense and porous specimens. The upper curves shown in each graph represent the normalized heat flow (W/g) into the specimen during heating (endothermic) and the lower curves represent the heat flow out of the specimen upon cooling (exothermic). The existing crystal form for the transformation temperatures are also shown above and below the austenite and martensite finish temperatures to indicate the crystal form that is present at various temperatures. For measuring the onset, end, and peak temperatures, the software extrapolates a tangent line from each side of the transformation peak that intersects with a tangent line drawn from the baseline curve, resulting in an actual transformation peak that is slightly wider than reported by the onset and end temperatures.

The DSC results for the dense specimen indicate diffusionless solid-to-solid phase transformation at approximately 26°C (measured at transformation peaks) during heating (martensite-to-austenite) and -9°C (measured at transformation peaks) during cooling (austenite-to-martensite, see Figure 16). Therefore, depending on whether
the specimen was previously heated or cooled, either the martensite or austenite crystalline structure can be present at room temperature (22°C). Note that upon cooling from austenite, the first peak encountered upon cooling is indicative of a R-phase transformation (Wu and Wayman, 1989). The R-phase transformation can be an indication of other intermetallic precipitates as well as a result from thermal treatment.

The transformation peaks of the porous specimens were slightly higher than those of the dense specimen, occurring at approximately 44°C and 48°C (measured at transformation peaks) during heating (martensite-to-austenite) and -12°C and 11°C (measured at transformation peaks) during cooling (austenite-to-martensite) for the small and large pore specimens, respectively (Figure 17a and 17b). Similar to the dense specimen, depending on the thermal history of the specimen, either martensite or austenite can be present at room temperature. The porous specimens also indicate the presence of an R-phase transformation upon cooling from austenite to martensite.
Fig. 16. Thermal scan of HIPped dense NiTi
Fig. 17. Thermal scan of HIPped porous NiTi: (a) DSC results of small pore specimen; (b) DSC results of large pore specimen
2. Microprobe Analysis

In addition to the thermal analysis, further investigations to verify the composition of the HIPped specimens were conducted using an electron microprobe. A Cameca SX50 Electron Microprobe was used to verify the composition of the dense and porous specimens created from the HIPping process. By employing the electron backscattering capabilities of the microprobe, evidence of multiple intermetallic phases was revealed in the dense and porous specimens (Figures 18a, 19a and 20a). However, evidence of different phases was most prominent in the small pore specimens, with some of the phases occurring in areas as wide as 20 µm.

Next, a preliminary scan for elements was conducted on the HIPped specimens using an Energy-Dispersive X-ray Spectrometer (EDS). The results are shown in Figures 18b, 19b, and 20b for the dense, small, and large pore specimens, respectively. The EDS shows no evidence of elements other than Ni and Ti, except that of carbon in the small pore specimen from the epoxy casting that was used to cast and polish the specimens. The EDS results also aide in verifying the purity of the initial elemental powders as well as the prevention of contamination of the powders during mixing and the preparation of the HIPping canisters.

Further analysis of the dense and porous specimens using a Wave-Dispersive X-ray Spectrometer (WDS) was conducted on each phase seen in the backscattered electron (BSE) image for quantitative results. Upon analyzing the dense specimen, the greater part of the material was identified as equi-atomic NiTi (Table III). However, the dense NiTi specimens contain numerous needle-like structures (see Figure 18a) having a width on the order of 0.5 µm. These needle-like structures were too small to be analyzed using WDS techniques without significant interference from the surrounding medium. By analyzing some of the larger intersections of needle phases however,
Fig. 18. Microprobe analysis of HIPped dense NiTi: (a) BSE image showing various phases, i.e. NiTi matrix and Ni rich needle-like phase (rectangular shadow is a burn resulting from SEM); (b) EDS result of dense NiTi
Fig. 19. Microprobe analysis of HIPped small pore NiTi: (a) BSE image showing multiple phases (numbers correspond to Table III); (b) EDS result of small pore NiTi
Fig. 20. Microprobe analysis of HIPped large pore NiTi: (a) BSE image showing phases (NiTi and pores); (b) EDS result of large pore NiTi
it is presumed by a slight increase in the detected percentage of Ni that the needle phases are in fact Ni rich phases. These precipitates are most likely formed upon cooling as the NiTi phase is unstable below 950°C and decomposes by an aging reaction [70], resulting in the precipitation of other stable intermetallic phases. Similar needle-like precipitates have been seen in other works by Gall and Sehitoglu [71, 72] in which the precipitate is identified as Ni$_4$Ti$_3$. The formation of other stable and metastable intermetallics is also possible, such as Ni$_3$Ti and NiTi$_2$, and Ni$_3$Ti$_4$ [50]. Precipitation of other intermetallics as seen in the HIPped porous NiTi can cause two effects simultaneously. First, Ni rich phases result in a decreasing Ni-content of the matrix (at.% Ni) and will in turn increase the transformation temperatures. Second, the precipitate particles will act to impede propagation of martensite crystals, resulting in an increase in the stress required to complete SIM throughout the medium [73].

In the small pore specimens, five different phases, i.e., NiTi, Ni$_2$Ti, NiTi$_3$ and elemental Ni and Ti were identified, as shown in Table III. A magnified section of the BSE image from Figure 19a of the small pore specimen is shown in Figure 21b. Scanning electron micrographs of the elemental Ni and Ti powders showed the powder shapes and sizes to vary significantly. The Ni powders were mostly spherical and ranged in size from 2 µm to 20 µm. The Ti powders were more jagged and during grinding procedures of fabrication have the tendency to separate into plate-like shapes that ranged in size from 15 µm to 20 µm in length (see Figure 21a). Due to the random arrangement of Ni and Ti elemental particles throughout the initial powder mixture as well as a difference in average size and shape, it is likely that during high temperature diffusion, many local regions of the specimen do not contain the correct atomic percentage of the elements necessary to achieve complete diffusion to binary NiTi without consolidation of the medium. An example of this incomplete diffusion
can be seen in a titanium rich region where NiTi, NiTi$_2$, and Ti phases are present (Figure 21b).

Similar to the dense NiTi specimens, WDS analysis of the large pore specimens revealed that the greater part of the material was also identified as equi-atomic NiTi (Table III). Again, the presence of small needle-like precipitates was evident. Much like the dense specimen analysis, intersections of the needles indicate that these precipitates are a Ni rich phase and most likely form upon cooling.

Table III. Elemental and intermetallic phases identified by microprobe using WDS analysis (error: ±1%)

<table>
<thead>
<tr>
<th></th>
<th>Ni (at%)</th>
<th>Ti (at%)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>DENSE NiTi</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NiTi (matrix)</td>
<td>50.70</td>
<td>49.30</td>
</tr>
<tr>
<td>NiTi (needles)</td>
<td>52.14</td>
<td>47.86</td>
</tr>
<tr>
<td><strong>SMALL PORE NiTi</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(1) NiTi</td>
<td>51.81</td>
<td>48.19</td>
</tr>
<tr>
<td>(2) Ni$_3$Ti</td>
<td>75.51</td>
<td>24.49</td>
</tr>
<tr>
<td>(3) NiTi$_2$</td>
<td>33.37</td>
<td>66.63</td>
</tr>
<tr>
<td>(4) Ni</td>
<td>98.68</td>
<td>1.32</td>
</tr>
<tr>
<td>(5) Ti</td>
<td>0.65</td>
<td>99.35</td>
</tr>
<tr>
<td><strong>LARGE PORE NiTi</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NiTi (matrix)</td>
<td>50.46</td>
<td>49.54</td>
</tr>
<tr>
<td>NiTi (needles)</td>
<td>51.84</td>
<td>48.16</td>
</tr>
</tbody>
</table>

After identifying the different compositions contained in the HIPped specimens,
Fig. 21. Diffusion of elemental Ni and Ti powder species: (a) loosely packed mixture of Ni and Ti powders; (b) example of incomplete diffusion of elements in small pore specimen, consisting of NiTi, NiTi₂, and elemental Ti phases (magnification of encircled area from Figure 19)
the BSE images of the porous specimens are further analyzed using the commercially available Image-Pro image analysis software with the Materials-Pro add-on package. Using threshold adjustments and porosity calculation options, the area percentages of the phases as well as the pores are calculated. The area percentages of a small pore specimen are shown in Figure 22a and b and the area percentages of a large pore specimen are shown in Figure 23a and b. The reason for the presence of relatively large intermetallic phase regions in the small pore specimens can be explained by the lower fabrication temperature. By not reaching a temperature that causes the open pores to close due to partial melting, consolidation of the medium at elevated pressures is not achieved. In this case, the voids hinder the diffusion of the Ni and Ti species, ultimately leading to incomplete diffusion of the elemental powders. Using the HIPping method, consolidation of the partially melted medium at high pressure is a crucial component in achieving a homogenous alloy of NiTi.
Fig. 22. Quantitative analysis of phases from small pore BSE image: (a) phase analysis of BSE image after image enhancement; (b) percent area of pores and identified phases
Fig. 23. Quantitative analysis of phases from large pore BSE image: (a) phase analysis of BSE image after image enhancement; (b) percent area of pores and identified phases
B. Quasi-static Mechanical Testing under Compressive Loading

Mechanical testing was conducted on dense as well as small and large pore specimens in SME and PE. Both types of specimens were tested under compressive loading in quasi-static conditions using flat compression plates. The specimens were cylindrical and the ends were machined flat. A MTS 55-KIP hydraulic load frame with the Testar IIIm digital control software was used to apply load by displacement control at a rate of $1 \times 10^{-4}$ strain/sec and a resistive oven was used to elevate the temperature of the test section (see Figure 24). K-type thermocouples were placed in the heating chamber as well as on the specimens when tests were conducted at temperatures other than room temperature. The chamber temperature was monitored and controlled by Omron E5AX-A temperature controllers. When required, the same insulated chamber apparatus was used in conjunction with compressed CO$_2$ for tests conducted below room temperature. In such a case, the thermal controller was attached to a solenoid valve which would allow the flow of CO$_2$ into the chamber when the temperature deviated from a given temperature setpoint.

For measurement of strain, an extensometer with a 25 mm gauge length was used. Note that all of the mechanical tests performed for this study are under compression, therefore, compressive stress and strain are represented by positive values. The stress and strain values reported in this study for the dense and porous specimens are macroscopic values, neglecting the presence of pores. In addition, due to the fact that the overall strains are relatively small, the strain for each test is measured as the engineering strain.

In the following sections, HIPped dense and porous specimens will be quasi-statically tested under compression in the SME and PE regions. The testing temperatures are selected according to the transformation temperatures that were identified
Fig. 24. MTS 55-KIP hydraulic load frame outfitted with heating/cooling chamber
by the DSC. First, the SME response of the dense and porous specimens will be presented, followed by their PE behavior at elevated temperatures. The results obtained from the porous tests will be compared with the dense and the differences will be discussed.

1. Shape Memory Effect of HIPped NiTi

a. HIPped Dense NiTi

The stress-strain results presented for the dense specimen represent the material response after previous work hardening was performed. Multiple loading cycles were conducted on the dense NiTi specimens in an attempt to improve the shape memory characteristics. Finally, the specimen was annealed at 540°C for 1 hour, then quasi-static testing under compression succeeded. Tests conducted on the dense NiTi under quasi-static loading in SME are shown in Figure 25. To assure the crystal form of the specimen upon testing was twinned martensite, the specimen was placed in a freezer (-16°C), then set in the chilled insulated chamber at 5°C, well below $A_s$ (see Figure 16). The test was then conducted in isothermal conditions at 5°C. The dense NiTi exhibits an initial loading stiffness of the twinned martensitic phase ($E^{TM}$) of approximately 44 GPa, similar to commercially available NiTi [18], and almost immediately upon loading, begins transforming from twinned martensite to detwinned martensite, at which point the tangent modulus decreases to approximately 14 GPa. The dense NiTi is capable of being loaded to a strain of approximately 3% while the tangent modulus of the transformation region continually increases. Near 3% strain, the dense NiTi begins to show further strain hardening as the tangent modulus begins increasing more rapidly. Upon unloading, some recoverable strain is observed. This recoverable strain is most likely due to local stress concentrations throughout
the material due not only to the polycrystalline structure, but also to concentrations from multiple precipitates, as shown in microstructure analysis in the previous section. The presence of these local internal stresses will result in a decrease in the transformation temperatures when there is no externally applied stress. More simply, to assure complete transformation to martensite, local internal stresses will require that the specimen is tested at cooler temperatures to avoid any PE properties.

Once unloaded to zero stress, the specimen is heated to 150°C and nearly complete recovery is observed (see Figure 25, recovery at zero stress). A dotted line drawn along the tangent of the unload stiffness upon initial unloading is extended to the zero stress baseline. The total amount of recoverable strain can be measured by subtracting the residual strain of the specimen upon reheating from the value of strain where the tangent of the unload stiffness crosses the strain axis at zero stress. The total amount of recoverable strain due to phase transformation, $\varepsilon^t$, is measured to be approximately 2%.

Similar results for HIPped dense NiTi have been presented by McNeese et al. [69] In their work, the initial stiffness of dense specimens tested at room temperature in SME is closer to 30 GPa, slightly lower than the stiffness observed in this work. Work hardening, however, is evident in both studies and the tangent modulus increases throughout the stress induced transformation. Overall, there seems to be good qualitative agreement between the results obtained by both research efforts for HIPped dense NiTi.

b. HIPped Porous NiTi

For testing the porous specimens, cylinders were again chilled to -16°C, then allowed to warm to room temperature (22°C). For the porous specimens, the use of the chilled insulated chamber was not required since the transformation to austenite occurs well
Fig. 25. Quasi-static testing of HIPped dense NiTi under compressive loading in SME
above room temperature (see Figure 17). Two separate quasi-static load cycles are presented for both the small and large pore specimens. First, the initial load cycle will be presented, followed by the consecutive load cycles in an attempt to show the effects of residual strains and cycling on the HIPped porous material.

Figures 26 and 27 show the representative quasi-static results for the first cycle of the small and large pore specimens in SME. The initial stiffness ($E^{TM}$) upon loading is considerably less than that of the dense specimen, measured to be approximately 8 GPA for both specimens. It can be seen that a gradual decrease in the overall stiffness is continued until unloading. The small pore specimen was capable of being strained to almost 7.4% at 155 MPa, whereas the large pore specimen was strained to 4.25% at approximately the same maximum stress value. $\varepsilon^t$ for the small and large pore specimens is measured to be 3.4% and 2.4%, respectively. Similar to the HIPped dense NiTi, there is some recovery observed upon unloading to zero stress, again attributed to the presence of local internal stresses causing a decrease in the transformation temperatures when unloaded. The difference in the amount of maximum strain can most likely be explained by the difference in the pore wall thickness between the small and large pore specimens. The average pore wall thickness for the small pore specimens are 20 $\mu$m while the large pore specimens have pore wall thicknesses of up to 1/2 mm. After unloading, the porous specimens were heated to 150°C and additional recovery was observed. The residual strain for the small and large pore specimens after the first load cycle is measured to be approximately 2.1% and 0.8%, respectively.

Following recovery at elevated temperature, the specimens were again placed in a freezer, then removed and tested at room temperature. The second cycle of the small and large pore specimens in SME are shown in Figures 28 and 29. For the small pore specimen, the second cycle in SME considerably different. First, a gradual decrease
in the initial tangent stiffness of approximately 8 GPa is only dominant in the first
2% of strain, followed by a relatively linear hardening curve. At the same stress level
as the first cycle (≈ 150 MPa), the specimen strain is almost 5.5%, nearly 2% less
than the first cycle. However, recall from the first cycle that the residual strain is
approximately 2%. Upon unloading, partial recovery is again observed, followed by
near complete recovery when heated again to 150°C. The transformation strain for
the second cycle of 3.5% increased slightly over the first cycle (3.4%).

The second load cycle for the large pore specimen had similar results as the
small pore specimen. The large pore specimen was loaded to 150 MPa, equal to the
stress level of the first test. Similar to the small pore specimen, the initial tangent
modulus is approximately 7 GPa and a gradual decrease in stiffness is only observed
in the first 1% of the strain, following a relatively linear hardening path up to 4%
strain. Again, the difference in the amount of total strain from the first to the second
cycle is approximately equal to the residual strain of the first cycle (0.3%). The
unloading path shows partial recovery, and nearly complete recovery was observed
when reheated to 150°C. $\varepsilon_t$ for both cycles of the large pore specimen are almost
equal (2.4% and 2.6%, respectively), but there is a slight increase in the amount of
total transformation strain after the second cycle.
Fig. 26. Quasi-static testing of HIPped small pore NiTi under compressive loading in SME–1\textsuperscript{st} cycle (50% porosity)
Fig. 27. Quasi-static testing of HIPped large pore NiTi under compressive loading in SME–1\textsuperscript{st} cycle (42% porosity)
Fig. 28. Quasi-static testing of HIPped small pore NiTi under compressive loading in SME–2$^{nd}$ cycle (50% porosity)
Fig. 29. Quasi-static testing of HIPped large pore NiTi under compressive loading in SME–2nd cycle (42% porosity)
2. Pseudoelastic Effect of HIPped NiTi

a. HIPped Dense NiTi

Characterization of the HIPped NiTi samples was also performed above $A_f$ for a PE response. A stress-strain plot of a HIPped dense specimen is seen in Figure 30. This specimen was tested quasi-statically at 50°C, slightly above the $A_f$ temperature (refer to Figure 16). It can be seen by the results shown in Figure 30 that the PE response of the HIPped dense specimen is very similar to a characteristic response of commercially produced NiTi (see Figure 2). The stress required to induce martensite is similar to commercially available NiTi, occurring at approximately 500 MPa and the elastic stiffness of the austenitic phase ($E^A$) closely corresponds to the elastic stiffness normally attributed with the austenitic phase ($\approx 70$–$80$ GPa) [18]. One major difference between the HIPped and commercially available dense NiTi is the tangent modulus of the transformation plateau, which is relatively flat for commercial NiTi. The HIPped dense NiTi continually requires greater levels of stress for further stress induced transformation to occur. For this reason, the HIPped specimen cannot be strained much beyond 2.5% without considerable inelastic strains due to the additional force required. Upon unloading, the HIPped NiTi also exhibits a more gradual transformation from the stress induced martensite back to the austenitic phase. By tracing the initial unload stiffness and continuing to zero stress (dotted line), the difference between the elastic response ($\varepsilon^{el}$) and the PE response due to transformation ($\varepsilon^t$) can be estimated. For the HIPped NiTi, $\varepsilon^t$ is measured to be approximately 1.2%. As expected in PE, the recovery is almost complete in the HIPped specimen and exhibits only 0.2% of unrecoverable strain ($\varepsilon^i$). Overall, the HIPped dense NiTi material verified the successfulness of the HIPping method used for producing dense NiTi SMA by demonstrating recovery characteristics associated with NiTi SMA ob-
tained from more conventional fabrication methods.

Again, comparisons to results obtained by McNeese et al. [69] of HIPped dense NiTi in PE response are made. In their work, specimens above \( A_f \) are tested under compression to a maximum strain of approximately 3%. The elastic stiffness of the austenite is shown to be approximately 60 GPa, slightly lower than the stiffness observed in this study. The slope of the tangent modulus due to transformation to martensite in both works is greater than normally observed in commercially obtained NiTi samples, and can be attributed to other intermetallic phases as well as lack of mechanical processing. Again, the results obtained by McNeese are in good agreement with the results observed in this effort.

The same dense NiTi specimen that was tested in Figure 30 was then tested under cyclic loading for a representative stress-strain response. As previously, the specimen was tested at 50°C to assure a PE response and \( \varepsilon^i \) is carried over from the previous PE cycle, illustrated by the initial strain value of the first cycle (approximately 0.2%). The stress and strain were continually increased until the specimen began to buckle. It can be seen in Figure 31 that the dense specimen is capable of strains as great as 5.7% before the stress-strain response begins to plateau. Because of the deformation caused by buckling in the final cycle, measurements of \( \varepsilon^i, \varepsilon^t, \) and \( \varepsilon^{el} \) exclude the last cycle. It can be seen that the recoverable strain is approximately 1.6% and \( \varepsilon^i \) is 1.8%. Perhaps the largest difference between the HIPped and commercially available NiTi is the strain hardening that occurs during transformation for the HIPped specimen. In this result, the SIM begins near 500 MPa, however, hardening continues up to almost 1200 MPa before an observable yield limit is reached. This strain hardening is most likely due to stress concentrations throughout the NiTi medium caused by the precipitates observed in the microprobe analysis.

To verify that the final plateau seen in Figure 31 which begins near 6% strain is
in fact due to buckling, the critical buckling stress for a cylindrical bar is calculated. The formula described by Roark [74] for a uniform simply supported straight bar under end load ($P$) in which the bottom end is fixed and the top end is hinged and aligned with the point of inflection is used for calculating the critical buckling load, $P_{cr}$ (see Equation 4.1). In this estimation, the top of the specimen is not considered fixed because the upper compression plate is able to deflect slightly in the horizontal direction under significant load, mainly due to the length and complexity of the upper load linkage, including the crossbar, load cell, alignment spacers, tension washers, alignment collets, adapter collet, and compression plate. The lower portion is considered fixed because there is only the hydraulically actuated piston, which is directly connected to the lower compression plate, resulting in a horizontally rigid component (refer to Figure 24). The cross sectional area of the bar is $48.77 \times 10^{-6}$ m$^2$ (radius = 0.00394 m) and the length is 0.0329 m.

$$P_{cr} = \frac{9\pi^2 EI}{4l^2}$$

where $E$ is the tangent modulus of the dense specimen (13.5 GPa) and $I$ is the moment of inertia of the cross section about the central axis perpendicular to the plane of buckling. The critical stress ($\sigma_{cr}$) can be calculated by dividing $P_{cr}$ by the cross sectional area. Using this approximation, the dense NiTi bar should begin to buckle at 1.07 GPa. This value is slightly lower than $\sigma_{cr}$ observed experimentally which initiated at 1.18 GPa. This can be explained by the simplified assumption that the top of the specimen is hinged, however, the upper compression load linkage only allows slight horizontal movement of the compression plate under high loads and does offer some resistance to the rotation of the top surface.
Fig. 30. Pseudoelastic response of dense NiTi specimen in quasi-static conditions under compressive loading at 50°C (1st cycle)
Fig. 31. Pseudoelastic response of dense NiTi specimen in quasi-static conditions under compressive loading at 50°C (continued cycles)
b. HIPped Porous NiTi

The tests for the porous specimens were performed at a temperature of 60°C, just slightly above the austenite finish temperature ($A_f$) for both porous specimens (refer to Figure 17a and b). Each specimen was subjected to cyclic mechanical loading with an increasing magnitude of the maximum strain applied to each cycle. This was done such that a representative curve could be produced without destroying the specimen before unloading could be recorded as well as to observe the effects of cycling. Representative results for two specimens containing small and large pores are shown in Figures 32 and 33. It can be seen that after some initial elastic response, further loading of the specimens leads to a gradual deviation from elastic to inelastic response, indicative of a stress induced phase transformation from the austenitic phase to the martensitic phase. After each successive loading and unloading path, the strain shows recovery beyond the elastic recovery ($\varepsilon^{el}$), which shows evidence of a reverse phase transformation from stress induced martensite back to austenite (PE). However, only partial recovery is observed, which is attributed to permanent inelastic deformation ($\varepsilon^i$). Upon final unloading, the difference between the elastic and pseudoelastic response ($\varepsilon^t$) for the small and large pore specimens is approximately 1.5% and 2.1%, respectively.

It can be seen from Figures 32 and 33 that the quasi-static results for the porous NiTi differ from the HIPped dense NiTi stress-strain response. In the HIPped dense NiTi, the stress induced martensite transformation occurs throughout the entire medium at nearly the same stress level, resulting in easily identifiable regions of phase transformations in stress-strain data charts as commonly seen in dense NiTi fabricated using conventional techniques [32, 75]. In the porous NiTi samples however, a gradual change in the tangent stiffness beyond the elastic limit can be seen.
in Figures 32 and 33, indicating a gradual transformation of regions of austenite into stress induced martensite. This gradual transformation is most likely due to stress concentrations caused by the pores, resulting in local regions of varying stress values occurring at different locations around the pores of the porous NiTi.

The elastic stiffness between the porous specimens of the austenite and martensite regions are also very different. The tangent stiffness of the austenitic phase ($E^A$) in the large pore specimen is approximately 12 GPa (Figure 33), almost twice that of the tangent stiffness of the small pore austenitic phase of 7 GPa (Figure 32). This difference in stiffness may be partially due to the incomplete diffusion of the powders in the small pore specimen and the resulting partial adherence of the powder particles, as indicated by the microprobe analysis. The difference in the pore volume fraction of the two types of specimens also contributes to the difference in the observed initial elastic stiffness. Note that for both cases, the low value of the initial elastic stiffness may result from geometric effects due to porosity.

Efforts to improve the response of the porous NiTi by heat treating the material was also done. The same specimen from the quasi-static results shown in Figure 33 was annealed and machined for further testing. Portions of the specimen were also cut away and polished for microscopic observation (see next section). The remaining portion of the specimen was placed into a furnace at 540°C for 30 minutes, then quenched immediately after removal. After quenching, the specimen was again machined such that the ends were flat and parallel. Results from quasi-static tests for the specimen are shown in Figure 34.

It can be seen by the stress-strain results shown in Figure 34 that the tangent modulus of the large pore NiTi upon initial loading is reduced from 12 GPa to approximately 3.0 GPa. The specimen was continually loaded until the maximum stress level began a decreasing trend. Multiple isolated dips in the stress-strain response
Fig. 32. Pseudoelastic response of small pore NiTi specimen in quasi-static conditions under compressive loading at 60°C (50% porosity)
Fig. 33. Pseudoelastic response of large pore NiTi specimen in quasi-static conditions under compressive loading at 60°C (42% porosity)
along the upper portion of the curve caused by microcracks are present. As the stress/strain was increased, these isolated decreases in stress became more abundant, until the general trend of the stress-strain curve began to decrease near 13% strain. For comparison, the results from the first set of tests is represented by a gray curve while the heat treated specimen is shown in black. Upon unloading the final cycle, $\varepsilon^t$ is measured to be 4%. The overall inelastic strain, $\varepsilon^i$, is 7.6%, however, if only the final cycle is considered, $\varepsilon^i$ is 1.5% and the recovery of the non-elastic strain due to transformation is approximately 72%.

One major advantage of the porous specimens over the dense specimen in PE is the additional strain that can be exhibited. The large pore specimens are capable of withstanding almost 13% overall strain. In addition to the increased strain, the recoverable strain due to transformation is also greater in the porous specimens. The large and small pore specimens recovered an additional strain beyond the elastic recovery ($\varepsilon^{el}$) of 1.5% and 4.0%, respectively, compared to 1.6% for the dense HIPped specimen.

Efforts to model the effective thermomechanical response of porous SMAs have been made by Lagoudas et al. [42], Qidwai el al. [76], and Entchev and Lagoudas [77]. In these works the mechanical quasi-static behavior of porous NiTi was modeled using a micromechanics averaging model and Unit Cell Finite Element Method (UCFEM). The micromechanics modeling shows results compatible with the experimental observations, i.e., a reduction of $E^A$ and the onset of stress induced martensite due to porosity. In addition, the UCFEM results show a gradual phase transformation due to local stress concentrations caused by the introduction of pores into the matrix, similar to the experimental results.
Fig. 34. Pseudoelastic response of large pore NiTi specimen (42% porosity) in quasi-static conditions under compressive loading at 60°C before and after heat treating (gray and black curves, respectively)
3. Failure Characteristics of HIPped Porous NiTi Due to Quasi-static Loading

The manner of failure of the small and large pore specimens was also noticeably different. In PE testing, the large pore specimens failed gradually and had a tendency to form microcracks and cracking could be heard as the specimen was strained beyond 5%. This gradual failure is identified on the stress-strain curve where the stress decreases suddenly, forming dips as the stress/strain is increased (Figure 33). Micrographs showed that the cracks appeared throughout the specimen and did not propagate through more than just a few neighboring pore walls (Figure 35). In contrast, the small pore specimens fail catastrophically when strained near 6-7% in PE testing, forming large cracks that propagate throughout the specimen, causing the specimen to break into multiple fragments (Figure 36).

The sudden and catastrophic failure of the small pore specimens may be due to multiple reasons. First, some of the intermetallic and elemental phases identified using microprobe analysis embrittle the material. In the small pore specimen, almost 24% percent of the total cross sectional surface area (including pores) of the specimen consisted of phases other than NiTi (see Figure 22b). In contrast, the only other phase observed in the large pore specimens are the Ni rich needle-like precipitates occurring in 5–10% of the total cross sectional area. Second, the incomplete diffusion of the elemental powders in the small pore specimen and partial adherence of the powder particles also lead to decreased overall ductility of the porous material. Finally, the uniformity of the pore size observed in the small pore specimens, results in more evenly distributed stresses throughout the specimen. Thus, failure of a local region causes simultaneous failure of the neighboring regions and overall fracture of the specimen. On the other hand, due to the variety of pore sizes and shapes in the large pore specimens, failure of a local region in the specimen could cause the load to be
redistributed to neighboring regions which have not been critically stressed, resulting in local containment of damage.
Fig. 35. SEM micrographs showing microcracks in large pore HIPped NiTi after quasi-static testing under compressive loading (arrows indicate direction of loading).
Fig. 36. SEM micrographs showing fractured surfaces of small pore HIPped NiTi after quasi-static testing under compressive loading (arrows indicate direction of loading)
C. Dynamic Testing under Compressive Loading

Small and large pore specimens were also mechanically tested in compression under uniaxial dynamic loading conditions. However, due to the brittleness of the small pore NiTi, dynamic testing caused these specimens to crumble upon impact. For this reason, only dynamic loading results for large pore specimens have been obtained. Because the large pore specimens used for dynamic testing were fabricated in a separate batch from the specimens that were tested quasi-statically, a separate DSC test was completed for the dynamically tested large pore specimens as well. A slight variation in the transformation temperatures from the quasi-static specimens is present. The DSC results for the dynamically tested large pore specimens are shown in Figure 37.

Fig. 37. Thermal scan of HIPped large pore specimen used for dynamic impact testing
1. Split Hopkinson Bar Test Apparatus

Four of the large pore specimens were dynamically tested under compression at Los Alamos National Laboratory using a split Hopkinson bar apparatus (Figure 38). A split Hopkinson bar test is the most commonly used method for obtaining material properties at high rates of strain. The split Hopkinson bar apparatus consists of two long cylindrical bars that sandwich a shorter cylindrical specimen between them. Another shorter high velocity moving bar (referred to as a striker bar) is propelled, in this case by compressed gas similar to that of an air gun, towards the stationary input bar. Upon impact with the input bar, a stress wave is generated that immediately begins to travel towards the specimen. Upon reaching the specimen, part of the wave is reflected back towards the impact end of the input bar while the remainder of the wave transmits through the specimen and into the output bar. The transmitted and reflective waves are proportional to the specimen’s stress and strain rate, respectively. Using this data, the stress-strain properties of the specimen are calculated [78].

For testing porous NiTi, the specimen is placed between the impact faces of the bars. Strain gages are placed along the stationary bars to record the strain histories. The diameter of each of the cylindrical specimens was 13 mm. Each was approximately 5.5 mm long \((L_i)\). Before testing, each of the specimens was heated to 80°C, well above \(A_f\), then allowed to cool to room temperature, remaining mostly in the austenitic phase (refer to Figure 37). They were then tested at 22°C. This temperature is slightly above the martensite start temperature, \(M_s\). However, it can be seen from the DSC results that upon heating, some apparent transformation from martensite to austenite may in fact begin near 10°C, even though the bulk of the transformation occurs 20°C higher. This leads to a slight overlap of the \(A_s\) and \(M_s\). The results from the dynamic tests for the HIPped specimens can be seen in
Figures 39 and 40.

Fig. 38. Schematic of a split-Hopkinson bar apparatus used for impact loading of porous NiTi SMA.
2. Dynamic Loading of HIPped Porous NiTi

Figure 39 shows four consecutive impact tests performed on the same specimen (reheated to 80°C between each test). It should be noted that the specimen used for this test is the same as the second specimen shown in Figure 40, and therefore, the first cycle in Figure 39 is the same as the first cycle of the second specimen seen in Figure 40. A 127 mm striker bar was used for the impact load with a maximum strain rate of 3300/sec. The condition of the specimen prior to loading was a mixture of austenite and twinned martensite as a result of the initial testing temperature being slightly below $M_s$ (Figure 17b). Therefore, the first part of the stress-strain curves shown in Figure 39 corresponds to elastic loading of austenite and martensite, as well as detwinning of martensite, which progresses to a strain of about 4%. The first phase transformation to stress induced detwinned martensite initiates near a strain of 1% (Figure 39, region A). After this initial load plateau, a second plateau occurs near a strain of 6%, indicating further transformation to detwinned martensite and the formation of additional inelastic strains which could be attributed to plasticity in the SMA as well as possible damage (Figure 39, region B). Upon unloading, it can be seen that there is immediate partial shape recovery evident in the unloading path beyond the elastic response of approximately 2%. This partial recovery can be attributed to an increase in the temperature of the specimen to above $A_s$ due to latent heat released upon transforming from austenite to martensite and energy dissipation due to plasticity and damage.

After reheating the specimen to 80°C after each cycle, there was additional strain recovered, indicating that the temperature increase caused by the latent heat due to phase transformation as well as plasticity and damage was not sufficient to promote complete transformation back to austenite. In addition, the amount of strain recov-
ered by the specimens when heated to 80°C increased after each successive cycle. The lengths of the porous specimen before impact \((L_i)\), after impact \((L_f)\), and after reheating to 80°C \((L_r)\) were measured using a micrometer and are shown in Table IV. Note that the strain value in the stress-strain diagram is reset to zero for each cycle and the strain of each cycle is relative to the length of the specimen after reheating from the previous cycle. Adding the amount of unrecoverable inelastic deformation from each impact cycle that remained after reheating totals nearly 10% of the initial length. Further study of the stress-strain response reveals that the transformation from austenite to stress induced martensite, indicated by the first stress plateau (Figure 39, region A), also became more distinguishable as the impact cycles were repeated.

Table IV. Recovery of HIPped large pore specimen after cyclic impact loading

<table>
<thead>
<tr>
<th></th>
<th>(L_i) (mm)</th>
<th>(L_f) (mm)</th>
<th>(L_r) (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cycle #1</td>
<td>5.471</td>
<td>5.084</td>
<td>5.195</td>
</tr>
<tr>
<td>Cycle #2</td>
<td>5.195</td>
<td>4.932</td>
<td>5.000</td>
</tr>
<tr>
<td>Cycle #3</td>
<td>5.000</td>
<td>4.854</td>
<td>4.964</td>
</tr>
<tr>
<td>Cycle #4</td>
<td>4.964</td>
<td>4.800</td>
<td>4.929</td>
</tr>
</tbody>
</table>
Fig. 39. Dynamic stress-strain response of porous NiTi (42% porosity) under impact loading: 1 specimen, 4 cycles, 22°C (reheated to 80°C after each cycle)
Figure 40 shows the results of the first cycle of four impact tests conducted on four different specimens tested to different maximum stress and strain levels. The maximum strain rate for the specimens was 3300/sec for the 127 mm striker bar (Figure 40, specimens 1 and 2) and 3100/sec for the 250 mm bar (Figure 40, specimens 3 and 4). The transformation stresses and strains are very similar to the transformation stresses and strains shown in Figure 39. Again, two distinct plateaus occur at nearly the same stress and strain levels. Also similar to the results in Figure 39, the shape recovery beyond the elastic response is measured to be 2%. One noticeable characteristic of the HIPped porous NiTi is the ability to undergo considerable inelastic deformation (overall strain of 17% of specimen 4) under dynamic conditions and exhibit similar amounts of recoverable strain upon unloading. The repeatability of the transformation curve is consistent, even after the specimens have undergone considerable inelastic strain. Again, partial shape recovery is seen upon unloading, contributed to the temperature increase caused by the latent heat released from the phase transformation and energy dissipation due to plasticity and damage. The recovery of each specimen ($L_r$) is shown in Table V.

Table V. Recovery of HIPped large pore specimens under increasing impact loads

<table>
<thead>
<tr>
<th></th>
<th>$L_i$ (mm)</th>
<th>$L_f$ (mm)</th>
<th>$L_r$ (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spec #1</td>
<td>5.579</td>
<td>5.499</td>
<td>5.516</td>
</tr>
<tr>
<td>Spec #2</td>
<td>5.471</td>
<td>5.084</td>
<td>5.195</td>
</tr>
<tr>
<td>Spec #3</td>
<td>5.580</td>
<td>5.175</td>
<td>5.244</td>
</tr>
<tr>
<td>Spec #4</td>
<td>5.439</td>
<td>4.940</td>
<td>5.018</td>
</tr>
</tbody>
</table>
Fig. 40. Dynamic stress-strain response of porous NiTi (42% porosity) under impact loading: 4 specimens, 1 cycle each, 22°C (reheated to 80°C)
There are some noticeable differences between the material response of the large pore specimens tested under quasi-static and dynamic loading conditions. The most noticeable difference is the ability of the porous NiTi to withstand greater permanent inelastic strains than the specimens under quasi-static conditions. Furthermore, the amount of recoverable strain due to the pseudoelastic response (recovery during unloading) demonstrated by the specimen under dynamic loading appears to be independent of the inelastic strain. In addition to increased plastic deformation, the specimens under dynamic load initially recovered a strain of approximately 3% for each test and an additional strain recovery of 3% to 6% after heating above $A_f$, whereas the specimens under quasi-static loading conditions recovered a maximum strain of approximately 4%, as seen in Figure 34.

3. Failure Characteristics of HIPped Porous NiTi Due to Dynamic Loading

Figure 41 shows a micrograph of the large pore specimen that was tested in compression under dynamic loading after one cycle to a maximum strain of 8% (see Figure 40, specimen 1). It can be seen that microcracks formed at various locations in the specimen. Most of the cracks are small with lengths ranging from approximately 50-100 $\mu$m and did not normally propagate to adjacent pore walls. The magnified portion of the micrograph in Figure 41 shows an example of microcracks interconnecting adjacent pores.

A micrograph of the porous NiTi sample after being subjected to four consecutive impact load cycles (Figure 39) is shown in Figure 42. After the four impact load cycles, the porous NiTi has undergone much greater strain and more damage has occurred. The overall nominal strain of the specimen at the maximum strain level of the final cycle was approximately 20%. In the loading direction, it can be seen that many of the pores collapsed, causing the specimen to form microcracks throughout
the structure while enabling the specimen to withstand near equal amounts of overall applied stress for each successive loading cycle. It can be seen in comparison with the micrographs in Figure 41 that the microcracking induced damage is much more pronounced and the cracks are wider and longer. Even beyond the visible cracks, it is easily seen that the overall shape of the pores have been flattened well beyond their initial shape.

Fig. 41. Micrograph of fractured large pore NiTi due to dynamic loading after 1 load cycle to a maximum strain of 8% (see Figure 40, specimen 1)
Fig. 42. Micrograph of fractured large pore NiTi due to dynamic loading after 4 load cycles and an overall maximum strain of 20% (see Figure 39)
CHAPTER V

CONCLUSIONS AND FUTURE WORK

A. Summary and Conclusions

Using the established HIPping techniques, dense as well as porous NiTi with two different average pore sizes have been manufactured from elemental Ni and Ti powders. Small pore specimens were fabricated with 50% porosity with an average pore size of approximately 20 µm. By slightly varying some of the HIPping parameters, large pore specimens with 42% porosity and an average pore size of approximately 0.5 mm as well as fully dense NiTi were fabricated. The porous NiTi specimens have been characterized using thermal and mechanical tests and compared with results obtained from HIPped dense NiTi. The composition of the dense and porous material has also been analyzed using electron microscopy with microprobe capabilities. Results from microprobe analysis revealed only partial diffusion in the small pore specimens and complete diffusion of the elemental powders in the dense and large pore specimens.

Thermal analysis of the HIPped specimens was also completed and their respective transformation temperatures have been identified. For the small pore specimen, the martensite and austenite transformation temperatures occur at approximately -12°C and 44°C, respectively (measured at transformation peaks). The phase transformation temperatures for the large pore specimens were less widely spread and were measured to be 11°C and 48°C for the martensitic and austenitic phases (measured at transformation peaks). Lower transformation temperatures were observed for the dense specimen, occurring at -9°C and 26°C. This lower temperature is expected due to the increased dislocation density from previous thermomechanical cycles in addition to residual stresses from precipitates.
Microstructure examination of the HIPped dense and porous NiTi samples showed that the specimens consisted of mostly binary NiTi in addition to various other intermetallics in the small pore specimens and needle shaped Ni rich precipitates in the dense and large pore specimens. It is apparent that the decreased temperature necessary to produce the small pore specimens as well as the lack of powder proximity from loose packing of the initial powders causes a decreased rate of diffusion of the elemental powders and is not adequate to complete diffusion to the equi-atomic NiTi alloy. This is most evident by the elemental Ni and Ti phases present throughout the small pore specimens. At temperatures below 950°C, the NiTi phase region is very narrow and other phases such as Ni₅Ti and NiTi₂ remain stable, making the homogenization of the phases to NiTi difficult [79]. These difficulties can be greatly reduced in the HIP through consolidation of the medium during fabrication.

For the large pore specimens, it has been shown that consolidation of the elemental powders via HIPping combined with partial liquid phase assisted diffusion results in complete diffusion of the elements in reduced sintering times, as compared to conventional sintering. However, to reduce the presence of the Ni rich needle-like phases encountered in the dense and large pore specimens, an increased cooling rate may be necessary.

The incomplete diffusion of the Ni and Ti species to a binary alloy accompanied by intermetallics from other stable phases diminish the effective pseudoelastic and shape memory behavior of the porous NiTi SMA under quasi-static and dynamic loading conditions, including partial recovery upon unloading above the austenitic phase transformation temperature. However, both quasi-static and dynamic loading tests have shown promising results for the use of porous NiTi SMA as multifunctional components that are capable as static load bearing members as well as energy absorption joints between structures. Even beyond the amount of strain undergone
by porous NiTi in quasi-static testing conditions, dynamic tests demonstrated the increased amounts of strain that the porous NiTi was able to withstand without complete structural failure. The HIPped porous NiTi was dynamically tested to approximately 20% strain without a decline in the amount of applied stress.

B. Future Work

Based on the results of this research effort, future research will focus on improvement of material properties and transformation behavior by reducing the non-equi-atomic intermetallics, namely NiTi$_2$, Ni$_3$Ti, and elemental particles from incomplete diffusion, resulting in a more ductile porous SMA material. In addition to eliminating undesirable intermetallic phases, it has been shown by multiple cycles performed on the porous NiTi that the mechanical properties of the material can be improved through a variation of heat treating and thermomechanical cycling or work hardening.

1. Improving HIP Process and Post-fabrication Heat Treatments

In order to decrease the presence of other intermetallic phases due to incomplete diffusion of elemental powders, future work will focus on improvement of the current HIPping techniques and post-processing heat treatments. The use of elemental powders with more evenly shaped particles and nearer sizes could be used to improve the diffusion of the Ni and Ti species as well as create more evenly shaped and distributed pores. As mentioned previously, cooling rates, including quenching, will also be investigated to help reduce the presence of other intermetallics.
2. Mechanical Processes

It has been shown in this research effort that the mechanical properties of the porous NiTi specimens are very dependent on the mechanical history of the specimen. Future research will continue studying the effects of mechanical processes, both quasi-static and dynamic, on porous NiTi to improve the shape recovery characteristics of the material.

a. Marforming of Porous SMA

Recent studies have been made with respect to the activation and improvement of PE in NiTi material containing finely dispersed Ni rich precipitates. It has been found that by marforming and tempering, the PE response can be activated and enhanced in Ni rich compositions of NiTi. Marforming is a cold working process (often conducted in cryogenic conditions) that includes the plastic deformation of the NiTi SMA in the martensitic state. Depending on the amount of deformation, orientation and detwinning of martensite occurs, similar to SME as discussed previously. Increased amounts of deformation lead to the formation of additional dislocations and intra- and intermartensitic shear [80]. According to Wurzel, “rebetatising” at annealing temperatures between 350°C and 550°C is combined with recovery and provides a microstructure which leads to improved PE response in Ni rich NiTi SMAs. Future studies will research the effect of marforming and tempering on the HIPped porous NiTi to improve the PE response of the material.

3. Varying Porosities through Novel Techniques

Different HIPping techniques will also be investigated to fabricate porous NiTi specimens with different overall porosity levels. Increasing the initial pressure of the HIP
cycles may result in further expansion upon decompression, resulting in much higher overall porosity. Specimens with many different porosity levels would be invaluable in determining the effects of pore size and overall volume fraction on the mechanical and energy absorption properties of porous NiTi SMAs. In addition, NiTi with graded porosity will also be investigated for specific applications that would benefit from impedance matching at connecting joints with other structures.
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VITA

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