

This is to certify that the thesis entitled

NEW METALLURGICAL METHODS FOR JOINING NITINOL

presented by

JOHN W. FOLTZ IV

has been accepted towards fulfillment of the requirements for the

Materials Science Masters degree in Major Professor's Signature 8/24/07

Date

MSU is an affirmative-action, equal-opportunity employer





PLACE IN RETURN BOX to remove this checkout from your record. TO AVOID FINES return on or before date due. MAY BE RECALLED with earlier due date if requested.

DATE DUE	DATE DUE	DATE DUE
		1



NEW METALLURGICAL METHODS FOR JOINING NITI

By

John W. Foltz IV

A THESIS

Submitted to Michigan State University in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

Department of Chemical Engineering and Materials Science

ABSTRACT

NEW METALLURGICAL METHODS FOR JOINING NITI

By

John W. Foltz IV

Nickel titanium is an intermetallic alloy used in many applications because it demonstrates shape memory and pseudoelasticity at near room temperature. Historically, methods of joining nickel titanium have had limited success.

This thesis reports on a variety of preliminary experiments on creating metallurgical bonds with NiTi that take advantage of a pseudo-binary equilibrium system between NiTi and Nb. This system allows pure Nb to act as a melting point depressant for NiTi. Bonds between NiTi sections have exhibited high strength and ductility. The technique has been used to create low density honeycomb topologies capable of geometrically amplifying pseudoelastic and shape memory effects.

The liquid formed by this pseudo-binary is highly reactive, and aggressively wets many metallic and non-metallic surfaces. DC magnetron sputtered multilayers of NiTi and Nb can be used to control the reactivity of the liquid. These multilayers themselves exhibit shape memory and high transformation temperatures, which demonstrates achievement of good composition control. When combined with niobium cladding, multilayers also allow NiTi to be bonded with many other materials without the formation of undesired intermetallic compounds.

Copyright

JOHN W. FOLTZ IV

Dedication

To mom and dad. Thanks for the support.

ACKNOWLEDGEMENTS

I would like to acknowledge the many people whom I learned a great deal from while working on this thesis. Thank you Dr. Grummon, Dr. Shaw, Dr. Crimp, Dr. Case and Dr. Bieler. I would like to also thank the undergraduate students that have helped with this work, including Jason Carter, Neil Murphy, Corey O'Connell, Scott Gillard, Arthur Matteson and Jason Johnson. Finally, I would like to thank my family and Stacey Schroeder for supporting me through this process.

LIST	Г OF TA	ABLES	VIII
LIS	r of fi	GURES	IX
1	INTR	RODUCTION	1
	1.1	Shape Memory Processes	2
	1.2	Bonding NiTi	6
	1.3	Organization	
2	JOIN	ING SIMILAR NITINOL	17
		Discovery of	17
	2.1	NiTi-Nb reactive brazing with NiTi tubes	17
	2.2	Construction of pseudoelastic tubes in a low-density topolog	y28
	2.3	Construction of smooth corrugation honeycomb structures	
	2.4	Construction of hexagonal corrugation structures	
3	REA	CTION CONTROL USING MULTILAYERS	47
	3.1	Multilayers	49
	3.2	Application of multilayers to spot welding	56
4	BON	DING DISSIMILAR NITI SECTIONS	82
	4.1	Bonds between NiTi thin films and wrought Nitinol	83
	4.2	Thin film to Porous Nitinol	
	4.3	Thin film to Chemical Nitinol	
	4.4	Porous NiTi to Wrought Nitinol	
	4.5	Porous Nitinol to Chemical Nitinol	97
	4.6	Shape memory to pseudoelastic Nitinol	
5	JOIN	ING NITI TO OTHER MATERIALS	107
	5.1	Alumina	
	5.2	Molybdenum	112
	5.3	Cobalt Chrome	
	5.4	Fe ₂ AlV	
	5.5	Boron Carbide	
	5.6	Magnesium Oxide	
	5.7	Tantalum	140
	5.8	Ti-6Al-4V	144
	5.9	Tungsten	
	5.10	304 Stainless Steel	
6	CON	CLUSIONS	

TABLE OF CONTENTS

APPENDIC	ES	170
A.1	Brazing using Centorr Annealing Furnace	170
A.2	Brazing using MILA ULVAC rapid thermal heating system	171
A.3	Polyimide backed thin films	172
A.4	Freestanding thin film creation	
A.5	Multilayer creation	
A.6	Oxide Removal Etch	
A.7	Metallurgical Etch	
A.8	Tacking NiTi to Nb using AC spot welding	
A.9	Post Braze Heat Treatment	

LIST OF TABLES

Table 1: DSC results from post brazed pseudoelastic strip NiTi. 43
Table 2: DSC analysis of phase change temperatures in sample 111306A
Table 3: Experimental parameters covered in experiment series 121906A.
Table 4: Experimental procedure for AC spot weld samples 022107
Table 5: Experimental parameters for series 030107. 58
Table 6: Experimental parameters for series 040107. 59
Table 7: Experimental Procedure of experiment series 0412200763
Table 8: Experimental procedure and results of experiment series 0327200777
Table 9: Spot welding parameters for sample 03272007-577
Table 10: Transformation temperatures from DSC results corresponding to Figure 4684
Table 11: EDS analysis of spots shown in Figure 48. 90
Table 12: EDS results of chemical NiTi to thin film bond, shown in Figure 4994
Table 13: EDS analysis of X-ray scans shown in Figure 57.
Table 14: Sputtering conditions for sample 062306D118
Table 15: EDS analysis, in atomic percent, of X-ray spectra in Figure 70. 130
Table 16: EDS analysis of the areas shown in Figure 78. 143
Table 17: EDS analysis, in atomic percent, of spots indicated in .Figure 83151
Table 18: EDS Data collected from spots shown in Figure 89. 159
Table 19: EDS data collected from spots in Figure 90
Table 20: EDS semi-quantitative analysis corresponding to spots in Figure 92164
Table 21: Transformation temperatures for thin film 052307A. Obtained from DSC results displayed in Figure 99. 180
Table 22: Sputtering conditions for freestanding NiTi thin films. 184

LIST OF FIGURES

Figure 13: Etching effect of 127 μ m Nb wires cutting through the NiTi tubes, which is likely driven by capillary forces. Wires seem to have migrated and etched against the force of gravity, suggesting that gravity does not play a major role at the length scale of the wires
Figure 14: Schematic of the corrugation design for the NiTi strip material. This formation was termed the sine corrugation due to its resemblance to a sine wave, but it is defined by alternating circular radii
Figure 15: Schematic of corrugation construction using (a) 127 μ m Nb wires (b) 54 μ m Nb foils. While the foils are thinner, they are considerably wider than the wires, thereby supplying more Nb to the liquid. The foil does not cut through the NiTi, unlike wires34
Figure 16: (Top) Stress strain curves of cyclic loading of NiTi sandwich. The sample was strained up to 50% with little permanent deformation, demonstrating how the pseudoelastic effect can be geometrically amplified. (Bottom) Time versus strain plot, which shows the loading cycles for the sample
Figure 17: Typical heating schedule for initial sine wave corrugations. Furnace cooling continued until the sample was removed at room temperature
Figure 18: (a) Schematic of shape-set tool honeycomb corrugation made of stainless steel. All sides of the corrugation are 3 mm. At the intersection of the 3 mm lengths is a 0.18 mm kerf. (b) Stacking sequence showing 0.051 mm thick Nb pieces. (c) Final sandwich assembled and awaiting brazing
Figure 19: Sample 030805B, honeycomb assembled using a small thermocouple spot welding unit to tack the pieces of NiTi to Nb foil. The array was placed in a molybdenum fixture as shown, with a small weight applying a compressive load to ensure the NiTi strips were well aligned
Figure 20: This image shows the fixtures and set-up for sample 030805B, for honeycomb production. The honeycomb was encased in a molybdenum fixture with a molybdenum weight applying a compressive load to align the NiTi strips
Figure 21: Heating schedule for 030905D. As shown, the sample was heated to 1185° C for a dwell time of 5 minutes in the Centorr vacuum furnace. During this process, the pressure began at 4.4 μ Torr, and reached a maximum pressure of 24 μ Torr around 100°C before decreasing.
Figure 22: If the NiTi strips are misaligned, a meniscus forms as shown. The meniscus, being rich in Nb, has a shinier and smoother surface
Figure 23: SEI collage of 032805A. Bond taken from a honeycomb sandwich, which used a 54 μ m Nb foil to bond pieces of NiTi together

Figure 25: (a) Strain vs. time plot of sample 030905D showing the loading times and strains per cycle. Sample was strained to a maximum of 60% strain. Low permanent deformation from each loading cycle can be seen by the unloading area of the curve. After 60% strain, the sample had 8% permanent strain. (b) Stress-strain curve for each increasing cycle number. Note the sample pseudoelastically deforms even when compressed to 60% strain, which can be seen by little permanent deformation upon unloading. (c) (Top to bottom) Images of the sample before any compressive loading, deformed on cycle 12 to 60% strain, and unloaded from the 60% strain of cycle 12......46

Figure 34: Ni ₄ Ti ₃ precipitates in needle shaped morphology can be seen in the center of this SEI of sample 022107D. Niobium precipitates and residual porosity decorate the surrounding microstructure
Figure 35: Sample 010307A. Higher spot welding voltage causes increased residual porosity, grain boundary Nb precipitates and irregular shaped melting paths
Figure 36: AC spot weld from experiment 032307. Sample was tested in shear and failed throughout the weld area. The small lighter grey areas on the multilayer, visible on the left half, show the area that the electrodes melted. This area is smaller than the diameter of the electrode
Figure 37: Low magnification BEI of spot weld 010407D. Niobium mixed through the base metal towards the outer surface. There is evidence of convection currents mixing the multilayer into the base metal
Figure 38: High magnification BEI of Nb phase separation. Bright streaks inside the dark NiTi phase suggest solutionized Nb72
Figure 39: SEI of 053107A AC spot welding sample with niobium. Mixing of Nb with base metal suggests the multilayer foil is not critical for spot welding73
Figure 40: Specimen 053107D, AC spot weld without Nb. Melting occurred only near the interface between the NiTi pieces. The spot weld is approximately as wide as electrode contacts. The weld has melted more material to the right, suggesting the waveform of the power supply was non-symmetric
Figure 41: Specimen 03272007-5. Fracture surface at the edge of the spot weld. There is no oxide discoloration in the spot weld. Material ejected from the sample as a result of the electrodes pushing liquid from between the NiTi strips
Figure 42: Stress-strain curve for the strongest spot weld80
Figure 43:SEI of 040207. Niobium appears to be solutionized or pushed out of the spot weld. The niobium that can be seen has phase separated, as shown in the insert
Figure 44: Thin film bonded to wrought pseudoelastic NiTi. Film, originally the same width as the wrought NiTi, was tacked to top faces of corrugation. During brazing, the film sagged into contact with the wrought material
Figure 45: Thin film 012907A bonded to the inner surface of a NiTi pseudoelastic tube. The thin film was oriented with the 750 nm Nb coating facing towards the tube. The film was wrapped approximately 2.5 times around the inside of the tube, as shown at the top center of the image. Ti ₂ Ni is present at the bond line
Figure 46: DSC data from freestanding thin film 012907A. The film transforms from B2 austenite to R-phase to B19' martensite upon cooling, based on the two large upward peaks

Figure 47: NiTi low density closed cell foam brazed to SMA NiTi thin film91
Figure 48: Thin film bond to NiTi foam material. (<i>i</i>) Thin film, (<i>ii</i>) bond line between thin film and (<i>iii</i>) NiTi foam. (<i>iv</i>) Ti ₂ Ni phase is present, not the Nb phase92
Figure 49: SEI of sample 060107A, a thin film (top) bonded with chemical nitinol (bottom). The bond line between the film and bulk was probed using EDS at spots A and B. The thin film and bulk compositions were explored at points C and D respectively, as shown in Table 12
Figure 50: Sample KB052806. NiTi foam (top) bonded to wrought SMA plate Nitinol (bottom) using 54 µm Nb foil
Figure 51: Etched microstructure of NiTi foam (top) bonded with chemical NiTi (bottom). The eutectic microstructure can be clearly seen forming a bond between the materials and has filled some of the holes in the porous structure that are near the interface
Figure 52: Microstructure of chemical NiTi to chemical NiTi bond. Unmelted pure Nb foil remains in the center of the bond; eutectic NiTi and Nb have solidified between the Nb foil and NiTi base metal
Figure 53: Heating schedule for bimetal. The heating profile consists of a ten minute dwell time at 1190°C, then furnace cooled until below 100°C. The maximum pressure of 10.5 µTorr was reached at 900°C,
Figure 54: 39.2% cold rolling of sample 040605A. Eutectic has been compressed in the vertical direction 40%. No cracking is visible
Figure 55: Eutectic shows no major change in the microstructure. 40% compression in vertical direction. Niobium deforms easily without cracking
Figure 56: Metallurgical bond between pseudoelastic NiTi ribbon (top) and alumina (bottom) using multilayer 111306A. A eutectic microstructure of NiTi and Nb has formed between the Al2O3 and NiTi, with small precipitates of Ti_2Ni
Figure 57: X-ray scans corresponding to points shown in Figure 56
Figure 58: NiTi bonded to alumina (center), formed by a 0.504 mm thick Nb wire. Etching from the Nb wire can be seen on the left side of the image. Sample broke through alumina, as evident by the alumina fracture surface on the right side of the image. Scale divisions on the right are millimeters
Figure 59: Specimen 031607, showing the bond between molybdenum (top) and NiTi (bottom). A mixed two-phase microstructure between NiTi and Mo can be seen, which is a result of liquid formed by Nb lowering the melting point of the NiTi. Bright phases have high concentrations of Mo and almost undetectable levels of Nb. The linescan

across the bond begins on the left of the graph, with high counts moving to the right of the graph
Figure 60: Specimen 031607. Eutectic liquid is wetting the NiTi and forming a new morphology of two-phase microstructure. The Nb-rich phase contains most of the Mo, and is the bright phase in the two-phase region. The dark line between the NiTi and two-phase region is a polishing effect
Figure 61: Microhardness of sample 032107B, a bond between NiTi and Mo. A 50 gram load was used for the measurements. The hardness was the highest inside the bond. None of the indents chipped or showed any signs of microcracking
Figure 62: Heating profile of furnace. One minute dwell time at 1185°C. Sample 062806A, created from 062306D and 062306E119
Figure 63: Overview of CoCrMo fracture surface. Upper left corner was not brazed most likely due to capillary forces drawing the eutectic liquid away. Failure occurred inside the porous NiTi. The rough appearance of the CoCrMo (top left of CoCrMo) could be a result of significant Co sublimation during the brazing process
Figure 64: Composite image of pore and fracture surface. Note the different texture of the pore versus the fracture surface, implying fracture did not propagate through a pore. NiTi half of bond
Figure 65: Fracture surface in area that was brazed between NiTi pores and left material on CoCrMo side
Figure 66: Hardness data from CoCrMo material before and after brazing. The overall hardness increased by 13.7%, while the standard deviation in hardness decreased by 9.8 VHN. Many irregularly shaped indents were observed in both as-received and post brazed conditions
Figure 67: Global view of sample 031607A. The apparent wetting angle of the liquid by the NiTi has been changed compared with NiTi – NiTi bonds. Fe2AlV is adequately wetted by the liquid, and has filled cracks in the material
Figure 68: Low magnification SEI of 031607A. The solidification products of the bond appear different than the standard NiTi-Nb solidification products. The wetting angle of the Fe ₂ AlV is similar to other materials, however, the NiTi wetting angle is greater than 90°, suggesting a non-wetting condition. Fe ₂ AlV appears susceptible to microcracking, as suggested by a crack infiltrated with solidification product. This crack must have been present during the brazing process
Figure 69: Sample 031607A. The solidification product does not seem to be a cellular or dendritic structure. A third possible phase could be at the top of the image, appearing to have solidified from the Fe_2AIV

Figure 70: SEI and corresponding X-ray maps of NiTi-Fe ₂ AlV bond. Niobium content appears to be the largest chemical difference between the two solidification products. Titanium, aluminum and vanadium also appear different between the phases, while iron and nickel content are similar
Figure 71: SEI of microstructure. X-ray information was collected from points A-D and were analyzed in Table 15
Figure 72: Hardness data for specimen 032107-A. The NiTi phase has a lower hardness than the Fe_2AIV . The hardness of the bond was higher than the hardness of the parent phases; however no cracking was visible inside the bond
Figure 73: Optical image of NiTi side of NiTi- B_4C fracture surface. Units on the scale to the left is millimeters. (a) Area remained unbonded during brazing. (b) B_4C remains bonded with the NiTi. (c) Solidification product of the liquid134
Figure 74: Cross-section of fracture surface. While the base metal appears to be wetted by the eutectic liquid with a low contact angle, the brittle bond with the boron carbide fractured from thermal contraction
Figure 75: High magnification SEI of solidification product formed by NiTi-Nb liquid reacting with B ₄ C136
Figure 76: Mg rich region filled with fine Nb-based and Mg-based precipitates. The phases were too small to analyze using EDS. Based on EDS data, only the Mg-rich region appears to contain Mg
Figure 77: Stress-strain plot of the sample shown in the photo insert. Sample necked inside the tantalum, demonstrating the joint is stronger than the tantalum. (Low 2007) 142
Figure 78: Proeutectic NiTi eutectic Nb/Ta and NiTi fill the bond between NiTi and Ta. This SEI shows the simple eutectic between NiTi and Ta that results from brazing with an interlayer of $127 \mu m$ thick Nb foil. X-ray information collected at points A, B, C and D shown in Table 15
Figure 79: LOM of Nb coating, the bright phase on the right, on Ti-6Al-4V. The Nb film is approximately 10 μ m thick on sample 053007B, which was taken from the thin film deposition 051507B
Figure 80: LOM of (a) Ti-6Al-4V base alloy with (c) 30 µm Nb thin film deposited on it to prevent extra titanium from reaching (b) the eutectic between niobium and nickel titanium. Niobium successfully prevented Ni diffusion into Ti-6Al-4V. Four pieces of multilayer M032007A were placed between the niobium coating and the NiTi before brazing, serving as a liquid source
Figure 81: LOM of 060207C, (a) NiTi bonded to (b) Ti-6Al-4V with a dwell time of 1.5

minutes at a temperature of 1185°C. Niobium did not prevent the liquid from melting the

Ti-6Al-4V, which enriched the liquid in titanium, producing (c) Ti_2Ni upon cooling. The Ti_2Ni phase fractured during hot mounting
Figure 82: Sample 040607A. This BEI shows the transition in microstructure from BCC Nb (left, bright phase) to the tweed microstructure of Ti-6Al-4V. A two-phase region is seen between the thin film and base metal; differences in etching rate have produced a ledge that causes darkness at the interface
Figure 83: SEI of bond between NiTi (left) and Ti-6Al-4V (right). The coating of Nb appears to be well adhered to the Ti-6Al-4V as evident by Z-contrast in the B region. X-ray information from spot A, B and C were analyzed using an Oxford Instruments EDS software package
Figure 84: 042407A. NiTi to Ti-6Al-4V bonded without multilayers, only an Nb coating. This process was completed using a thick coating of Nb on Ti along with fast brazing times, especially above 1150°C
Figure 85: 040607A NiTi - Ti64: The microstructure of the solidified eutectic contains Nb and NiTi phases, along with a small phase fraction of Ti_2Ni , which is expected due to oxygen contamination on the multilayer foil
Figure 86: 040607A NiTi - Ti64. The Nb coating serves as a barrier for nickel diffusion from NiTi to Ti-6Al-4V. The soft Nb coating has proeutectic Nb solidified from the bond with NiTi using multilayer foils. The sputtered coating mixes with the Ti-6Al-4V in a two-phase region $\alpha+\beta$ region.
Figure 87: Microstructure of NiTi-W bond. (a) Unmelted NiTi base metal (b) Proeutectic NiTi phase coherent with unmelted NiTi (c) Proeutectic NiTi lamellae (d) Voids in the microstructure (e) Tungsten wire
Figure 88: LOM of sample 053007A. (a) Pseudoelastic NiTi bonded with (b) 254 μ m diameter tungsten wire and mounted in (c) Konductomet ® phenolic mount material. A small void is present in the bond between the NiTi and tungsten, as well as a eutectic microstructure and a proeutectic phase consisting of Nb and tungsten. Also, note the low wetting angle between the wire and eutectic liquid
Figure 89: NiTi side of 053007A. (a) Unmelted NiTi, (b) proeutectic coherent NiTi (c) eutectic solidified Nb phase. (d) Faceted precipitate. (e) Bright eutectic phase
Figure 90: Microstructure of 053007A near tungsten wire. (a) 'Matrix' phase that is dark grey, (b) tungsten wire approximately 15 μ m inside the wire, (c) dark precipitate phase, which could be based on Ti ₂ Ni, and (d) bright eutectic phase160
Figure 91: Low magnification SEI of post-fracture bond between NiTi and stainless steel. Bond was formed using Nb foil
Figure 92: Three distinct solidified microstructures in the bond between NiTi and 304 stainless steel

Figure 96: Collective results of cold rolling experiments. As rolling strain increases, the thermally recoverable strain also increases. 0.8% of the rolling strain is permanent. Cracking becomes present in thin films rolled beyond 6 to 7% strain, shown in Figure 97.

Figure 98: BEI of NiTi thin film on polyimide (bright stripe along bottom of film). The grain boundaries of the film appear to terminate roughly one μ m away from the polyimide film, which could be an etching effect or transition to amorphous NiTi.182

KEY TO SYMBOLS AND ABBREVIATIONS

Symbol	Unit of measure
°C	Degrees Celsius
mm	Millimeters
μm	Micrometers
mTorr	x 10 ⁻³ Torr
μTorr	x 10 ⁻⁶ Torr
MPa	x 10 ⁶ Pascal
EDS	Energy dispersive spectroscopy
XRD	X-ray diffraction
SEM	Scanning electron microscope
SEI	Secondary electron image
BEI	Backscattered electron image
LOM	Light optical micrograph
PID	Programmable interface device
NDC	Nitinol Devices Corporation, Inc.
Nitinol	Trade name for nickel titanium

1 Introduction

The interesting properties of the intermetallic alloy nickel titanium were first discovered between 1962 and 1963 at the United States Naval Ordinance Laboratories. After the alloy demonstrated shape memory, it was named Nitinol, which is an acronym for NIckel TItanium Naval Ordinance Labs. (Otsuka and Ren 2005; Memry 2006) Since its creation, nickel titanium has been used in many applications, due to its possession of several unique features: biocompatibility, pseudoelasticity, and shape memory transformation temperatures near human body temperature. (Memry 2006) Some alloys of NiTi can exhibit wide hysterisis, or a wide temperature difference between the austenite start (A_s) and martensite start (M_s) temperatures, which is useful for aerospace applications. (He and Rong 2004) In addition, NiTi is corrosion resistant at low temperatures, so it can be used in harsh environments. (Otsuka and Ren 2005) Finally, the unique physical properties of NiTi make it especially useful in electronic applications where large amounts of mechanical work must be developed using a small mass. (Gill, Ho et al. 2002) Sensors, motors and pseudoelastic antennas are just a subset of the potential electronic applications of NiTi alloys. (Memry 2006)

Nitinol is a near equiatomic formulation of nickel and titanium. Near room temperature, the material can undergo a phase change from a B2 (CsCl) austenite crystal structure to a B19' (monoclinic) martensite structure. This martensitic phase transformation is reversible and gives rise to shape memory and pseudoelastic effects. (Otsuka and Ren 2005)

The common oxide formed on NiTi alloys is Ti_4Ni_2O , which shares the same spacegroup and morphology as Ti_2Ni . For this reason, Ti_4Ni_2O and Ti_2Ni will be assumed interchangeable, because without TEM analysis, the two phases cannot be distinguished. (Otsuka and Ren 2005)

1.1 Shape Memory Processes

The single way shape memory effect (SWSME) encompasses the following transformation. First, the martensite is deformed, then, upon thermal reversion of the austenite the material will restore its previous shape. The crystallography of the phase change will be discussed later, but the effect is dependent on a rearrangement of reversible martensite variants under an applied external stress field. When the material is heated to above the austenite start temperature (A_s), the original austenite crystal structure is elastically restored due to the higher stiffness of the austenite. This effect is known to restore up to 7% strain in a polycrystalline material, and up to 10% in a single crystal. (Otsuka and Ren 2005)

Pseudoelasticity occurs when a material undergoes no permanent deformation when subjected to a strain substantially beyond the elastic limit of other metals. For monolithic polycrystalline NiTi, up to 7% strain can be elastically recovered by reversion of stressinduced martensite. During this martensite formation, the strain of the material increases dramatically, while the stress does not increase substantially. After the austenite phase is transformed to martensite, it can slip induce plastic deformation. (Hou 1998)

Pseudoelasticity can be observed during a strain controlled tensile test. If the material exhibits pseudoelasticity, only the endpoints of the loading and unloading curves are coincident, shown schematically in Figure 1.



Figure 1: Schematic stress strain curve of a pseudoelastic Nitinol. The upper curve is the loading curve, while the bottom is the behavior of the material upon unloading. Plastic deformation can begin at the completion of the pseudoelastic plateau on the stress strain curve.

1.1.1 Two-way shape memory effect

Two-way shape memory (TWSME) is another process that shape memory alloys, such as NiTi, can exhibit. In this process, an internal stress field drives material to a taught shape

in the martensite phase. When the Nitinol is heated into the austenite phase, it still shows the single-way shape memory effect. With this process, the material can remember two distinct shapes: one shape at low temperature and another at high temperature.

Cyclic thermo-mechanical treatments are used to induce a stress field into the nickel titanium. Exact procedures vary, but during this process the material is either under constant load and is cycled in temperature or is cycled both in load and temperature between the martensite and austenite phases. The TWSME is not as robust as the single-way shape memory effect, and shows less strain amplitude and less cyclic stability. Over time, the stress field can relax, which diminishes the effect. Typically, during the first few heating cycles, it is possible to get above 2% strain change, but after approximately 10 to 100 cycles, the effect diminishes to a asymptotic 1% strain change between cold and hot cycles. (Otsuka and Ren 2005) (Zhang 2006)

The TWSME effect can also be developed using external biasing of a SWSME. Here the material is redeformed upon cooling of the material by an external force. This is a less elegant form of the TWSME, but it can support higher maximum strain amplitude. (Foltz, Grummon et al. 2006)

1.1.2 Deformation systems

The functionality of Nitinol is dependent on a diffusionless, thermo-elastic, first order martensitic phase transformation. The B19' structure of Nitinol is a thermo-elastic martensite, which forms by inter and intra-martensite twinning. (Otsuka and Ren 2005)

The phase transformation must have a coherent phase front to create the martensite by shearing the austenite. Due to differences in lattice size between B19' and B2, this coherent phase front is accomplished through a Type II twinning process, which results in a twinned martensite. The strain associated with this shearing of the austenite is neutralized by other twin variants nearby. Due to this, martensite in Nitinol is referred to as forming by 'self accommodation'. (Otsuka and Ren 2005)

The B19' martensite has a monoclinic crystal structure, which is a low symmetry structure. The austenite phase is a high symmetry, CsCl, or B2 crystal structure. The austenite phase supports dislocation motion, making nickel titanium unusually ductile for an intermetallic. If the onset of slip plasticity is delayed using strengthening mechanisms, Nitinol can stress induce martensite, which is the basis for the pseudoelastic effect. (Otsuka and Ren 2005)

Stress inducing martensite is explained by the Claudius-Clapperyon equation. This relationship dictates that martensite transition temperatures rise as the shear stress in a material increases. Therefore, as the austenite is loaded, the start temperature of the martensite rises until the testing temperature is below the, now elevated, martensite start temperature. At this point, martensite stress induces and can deform by detwinning. Upon unloading of the sample, the detwinning and martensite nucleation reverses and leaves the Nitinol as austenite once more. (Otsuka and Ren 2005)

There is also a rhombohedral martensite (r-phase) which can form in Nitinol; it behaves differently than the monoclinic martensite, but still forms by self accommodated twinning. The strain-temperature hysteresis loop between austenite and the r-phase is smaller than the loop between austenite and B19' martensite. This has two important consequences: the r-phase completes the phase transformation at higher temperatures than B19', but has smaller recoverable strain. (Otsuka and Ren 2005)

1.2 Bonding NiTi

Several methods of joining nickel titanium have been developed in an effort to increase the complexity of devices. Thus far, some joining methods are acceptable in limited applications; while other applications, such as biomedical ones, do not have robust joining techniques due to biocompatibility problems. The following is a brief summary of some joining methods for nickel titanium.

1.2.1 Diffusion bonding

Joining nickel titanium has been historically difficult due to the slow diffusivity of both titanium and nickel in nickel titanium. According to Li and Rong, the bulk diffusivity of nickel in Nitinol is 1.5×10^{-12} at 1223 K, while titanium in Nitinol is 2.0×10^{-10} at 1223 K. (Li, Rong et al. 1998) A first order approximation of the time required to diffusion bond a NiTi surface with an average roughness of 10 µm is given by (Wert and Thomson 1970):

$$\sqrt{2Dt} = X$$

$$X^{2} = 2Dt$$

$$\frac{X^{2}}{2D} = t$$

$$\frac{0.001^{2}}{2 \cdot 1.5 \cdot 10^{-12}} = t = 333,333 \sec = 3.85 \ days$$

Equation 1: Approximation of average diffusion distance (Wert and Thomson 1970)

Where D is the average diffusivity, t is time and X is distance. With a lengthy high temperature process such as this, diffusion bonding leads to grain growth, and can cause precipitates to enlarge and lose their strengthening ability. This loss of strengthening can lead to easier slip plasticity in the austenite phase, poor pseudoelastic effect and poor strength. (Otsuka and Ren 2005)

1.2.2 Silver solders

There is some research on silver soldering of Nitinol. All published techniques require aggressive fluxes to remove the Ti_4Ni_2O complex oxide, which forms readily at elevated temperatures. These fluxes are generally not biocompatible and therefore cannot be used for biomedical devices. The strengths of these solders are low, usually between 150 and 250 MPa. (Memry 2006)

Three distinct soldering techniques have been explored by the Edison Welding Institute (EWI). Halogen based fluxes, used commonly for aluminum alloys, have limited success removing surface oxides in NiTi alloys, but must be mechanically removed after soldering. Nickel and other metals have been plated onto NiTi, which indirectly allows NiTi to be soldered to other materials. This technique, however, is difficult and time consuming due to the multiple stage process. The third method involves ultra-sonic soldering NiTi using tin. This technique is not biocompatible, and achieves low shear strength. The highest shear strength obtained among all three soldering techniques was 50 MPa. (Hall 1997)

1.2.3 Welding techniques

Welding and spot welding of Nitinol have provided reasonable success; but bond strengths of 550 MPa are the highest reported, which is approximately 50% that of the base metal. In metal inert gas (MIG) and tungsten inert gas (TIG) welding, nickel titanium bonds are typically brittle, and possess Ti₂Ni precipitates in the fusion zone, which is where the solidification takes place. (Falvo, Furdiuele et al. 2005; Li, Sun et al. 2006) Devices using these techniques are limited by the low bond strength, and the small cross sectional area of the weld, which reduces the functionality of the material near the weld.

Laser welding of NiTi sheet material using a Ng:YAG laser has provided positive results. Both shape memory and pseudoelasticity of NiTi plates can be preserved when joining them by laser welding with argon shielding gas. This method, however, can only be used for line-of-sight joining; not within a structure. (Schlossmacher, Hass et al. 1997)

1.2.4 Transient Liquid Processing

Transient liquid processing (TLP) is a method of joining materials that has existed for thousands of years. (MacDonald and Eagar 1992) Only in recent years has it begun to receive attention again, due to advancements in metallurgy. This joining method involves a liquid forming by a low melting temperature eutectic or peritectic reaction between two materials and an interleaved foil of reactive material. By way of solid state diffusion, the liquid slowly freezes as the atomic species of the interleaved foil diffuses into the bulk. The microstructure of the bond, upon solidification, is nominally the same as the parent materials, making the bond difficult to find later.

TLP requires high diffusivity of the minor species in the solid state of the parent phase, and a low melting eutectic or peritectic reaction between the two materials. (MacDonald and Eagar 1992) Without high diffusivity in the solid state, the processing time is prohibitive in terms of high cost and poor material properties. The process is not possible without the use of a low melting point peritectic or eutectic reaction; without this liquid formation, the process would be the same as diffusion bonding.

This process has been used in recent years to join NiAl and NiTi. (Gale and Guan 1997) TLP was mildly successful in joining these materials, however, the process greatly disturbed the transformation temperatures and microstructure of the NiTi material. The addition of a copper interlayer between the NiTi and NiAl allowed formation of a liquid, which later solidified from both the NiTi and NiAl sides. The bond contained excess Ti as a result of faster diffusion of Ti versus Ni in NiTi. As a result, the microstructure of

the NiTi was inhomogeneous as a function of distance from the bond. In addition to forming secondary phases, the process required over an hour of processing at 1150°C, which would cause excessive grain growth in the NiTi material.

To join NiTi to itself or other materials effectively and at a reasonable cost, the thermal exposure must be limited. This is due to the reduction of the mechanical properties of NiTi when exposed to temperatures above 500 °C, as well as the cost incurred by high temperature processing.

1.2.5 Ni-Ti-Nb ternary system

The Ni-Ti binary phase diagram, shown in Figure 2 is a complex system containing several intermetallics. The most important of these intermetallics is NiTi, but the stable intermetallic Ti₂Ni and the metastable Ni₄Ti₃ and Ni₃Ti₂ phases are important in determining the strength of NiTi alloys. Ti₂Ni is brittle and weak, and can embrittle and weaken NiTi alloys when it forms at grain boundaries. Ni₄Ti₃ and Ni₃Ti₂, however, can strengthen NiTi alloys by precipitation hardening if the particles are small and well dispersed in NiTi grains. Ni₄Ti₃, in particular, is commonly used as a strengthening mechanism against dislocation motion in the B2 phase of NiTi, which increases the pseudoelastic functionality of the alloy. (Otsuka and Ren 2005)

Niobium, a common alloying addition for NiTi, has low solubility in the B2 NiTi phase. With alloying additions above 10 at.% Nb, phase separation produces BCC niobium and B2 NiTi. (Piao, Miyazaki et al. 1992) The ternary system between Ni, Ti and Nb is shown in Figure 3. The nickel-rich half of the ternary system contains several ternary intermetallics, while the titanium-rich half contains no ternary intermetallics. (Gupta 1991; Prima, Tret'yachenko et al. 1995)

Literature suggests a possible quasi-binary eutectic between NiTi and Nb, shown in Figure 3, with a reported eutectic temperature of 1170°C with an atomic composition of 36Ni-38Ti-26Nb. (Piao, Miyazaki et al. 1992) (Gupta 1991; Prima, Tret'yachenko et al. 1995) The exact melting temperature of the quasi-binary eutectic point is only known to lie between 1150°C and 1170°C, because of the steep solidus surfaces in the ternary system. The quasi-binary eutectic temperature is roughly 140°C below the melting temperature of pure NiTi, and therefore could be used to join NiTi together in a process similar to TLP. Contact melting of niobium and NiTi will take place above 1150°C, joining the materials together. Upon solidification, based on the pseudo-binary eutectic, phase separation will occur and the bond will be composed of B2 nickel titanium and disordered BCC niobium. The key feature of these microstructures is that both phases in the eutectic are ductile.

Based on Ke Bin Low's work at Michigan State University, butt-joints made using the NiTi-Nb quasi-binary eutectic system have high breaking strengths, as shown in Figure 4. The fracture is comprised of a cup and cone type failure inside the solidified zone, which is most likely due to the ductile Nb phase. Microalloying the Nb phase with other elements could possibly lead to higher breaking strengths. (Low 2007)

The quaternary system between Ni, Ti, Nb and O is also of great importance to this joining method, which has not been studied in depth. If the eutectic liquid created by heating NiTi and Nb above 1150°C interacts with oxygen, even in a vacuum furnace, it stabilizes Ti₂Ni precipitates. Ti₂Ni precipitates that are solidified from the eutectic liquid can contain niobium, based on the Ti-Nb binary phase diagram. Niobium is assumed to substitute for Ti inside the Ti₂Ni precipitate. Without oxygen, a mixture of NiTi and Nb freezes into NiTi and Nb upon cooling. In the presence of oxygen, it is theorized that the liquid freezes into a 3 phase reaction plane consisting of NiTi, Nb and Ti₂Ni. Microstructural evidence for this hypothesis can be seen in Figure 5.



Figure 2: Ti-Ni phase diagram in atomic percent Nickel.



Figure 3: Ternary phase diagram between Ni, Ti and Nb displaying solidus surfaces and terminal phases.



Figure 4: Stress-strain response of a NTT butt-joint bonded using the Ni-Ti-Nb ternary system. Fracture surface shows ductile cup and cone type fracture, likely due to the Nb phase. (Low 2006)


Figure 5: SEM image of NiTi cross-section that has been wetted by NiTi-Nb liquid in a vacuum furnace. Upon freezing, faceted precipitates form, which are morphologically identified as Ti₂Ni.

1.3 Organization

The topic of this thesis is the creation and basic understanding of bonds between nickel titanium to itself and other materials. Numerous experiments were conducted for this thesis; these will be described in detail, with individual introductions, lists of materials and procedures. The results will be summarized after discussing all of the experiments.

2 Joining similar Nitinol

The first NiTi metallurgical joints made using Nb-based reactive eutectic brazing were made in 2004 by Shaw and Grummon, working at MSU, as an outgrowth of attempts to create low-density topologies in Nitinol. The first experimental joint was made along an axial contact line between a parallel pair of 3 mm NiTi tubes. Subsequent metallurgical analysis revealed the aggressive wetting capability of the liquid that was formed by contact melting, and the simple 2-phase eutectic structure in the solidification product. Preliminary mechanical tests suggested that the joint was mechanically robust.

2.1 Discovery of NiTi-Nb reactive brazing with NiTi tubes

2.1.1 Introduction

Brazing and diffusion bonding are the only processes that can create bonds on the inside of structures. By utilizing furnace brazing, nickel titanium requires none of the special equipment necessary for welding. Furthermore, brazing can bond large surfaces metallurgically, which is difficult to impossible with traditional welding techniques. This allows for tougher mechanical joints that can support higher loads and deformation without the high stress concentrations that can occur from welding.

The discovery of the NiTi-Nb reactive brazing process was one of accident while attempting to diffusion bond pseudoelastic NiTi tubes along an axial direction. The tubes were held in contact using a Nb wire, which melted during the experiment. After this discovery, the experiment was repeated, but a 0.508 mm wire of Nb was placed along the contact line of the tubes. The following section describes this initial attempt at using the Ni-Ti-Nb ternary system to join NiTi tubes.

2.1.2 Brazing

To make use of the reported quasi-binary eutectic between NiTi and Nb, two 3 mm diameter tubes of nickel titanium were joined together using a small supply of high purity niobium wire.

As-received NiTi tubes with an inner diameter of 3.2 millimeters were sectioned into 19 mm lengths. A single 19 mm length of 500 μ m diameter 99.995% pure Nb wire was placed between the tubes. The tubes were held in contact with a wrap of tungsten wire going around the circumferences of the tubes. The tubes were then suspended from the top of a Centorr vacuum furnace using another tungsten wire.

The tubes were joined by vacuum furnace brazing with a Centorr vacuum annealing furnace. The furnace was allowed to pump until the base pressure was below 10⁻⁵ Torr, after which it was heated to a temperature of 1185°C at an approximate rate of 20°C/minute. It was held at 1185°C for 5 minutes and then allowed to cool by turning off power to the heating elements. The temperature of the furnace was measured by an R type thermocouple attached to a Honeywell Versa Pro UDC 3000 thermocouple controller. The thermocouple registered below 500°C after approximately 15 minutes of cooling. Once cooled, the sample was heat treated in an air-furnace for 1 hour at a temperature of 400°C.

2.1.3 Results

The tubes were completely fused by formation of a low melting eutectic liquid as a result of the niobium braze filler. There was no discernable bond line in the cross section of the tubes, as shown in Figure 6. It is simple to determine the distance the liquid flowed by observing the color and shade of the NiTi tubes after being brazed. The liquid initially formed from contact melting between a single 500 μ m diameter Nb wire and the NiTi tubes. As the liquid formed, it filled the local capillary space nearby. The liquid crept up the sides of the tubes, to balance the surface energies by reducing the wetting angle between the nickel titanium and the liquid, as shown in Figure 6.

A tubular shape is one geometric configuration that can amplify the pseudoelastic effect of nickel titanium. The initial experiment to join the tubes using diffusion bonding was to create macroscopic transformation foams. To demonstrate the amplification of pseudoelastic effect, the sample was cyclically compressed with increasing compressive strain until fracture was observed, as shown in Figure 7. This fracture occurred at nearly 30% strain, measured by the initial height of the tubes, and was outside of the joined area. The pseudoelastic effect, which can be observed by the reversible strain upon unloading of the tubes, was above 20% on the final compressive loading curve.



Figure 6: Macroscopic bond of NiTi-NiTi using Nb filler metal. Note that the eutectic liquid wets the NiTi surface without fluxes or other wetting agents.



Figure 7: Compressive stress strain curve for a pair of joined NiTi tubes. Loading is shown as solid lines, unloading as dashed lines. The pseudoelastic effect of nickel titanium is amplified from approximately 7% reversible strain. Little permanent deformation was observed up to 30% compression.

The microstructure of the bond was especially useful in the attempt to verify the existence of the pseudo-binary eutectic reported in literature. The tubes were sectioned and polished to a mirror finish using silicon carbide grinding papers and alumina media on a polishing wheel. The final polish was conducted with 0.05 μ m diameter diamond paste, after which the specimen was observed using a scanning electron microscope.

One half of the bond between the NiTi tubes can be seen in Figure 8. A Hitachi S-2500C scanning electron microscope operating at 25keV and equipped with an Oxford Instruments EDS system was used to characterize the bond. The top left image in Figure

8 shows a low magnification secondary electron image of the bond. Below this image is a higher magnification image of the bond, where the dendritic solidification structure of the proeutectic NiTi phase is visible to the left and right of the central brighter area.

The dendrites are also present in the bottom right image of Figure 8. These dendrites of NiTi form as a result of the composition of the liquid; the liquid enriches in NiTi after the exhaustion of the Nb source. The liquid composition reaches the NiTi liquidus composition at the processing temperature, and upon cooling, the first phase to solidify is dictated by the two-phase region that the super-cooled liquid moves into, given by the phase diagram in Figure 9. The solidification of the melted NiTi of the tubes results in a dendritic structure, based on solidification rate. (Porter and Easterling 1989)

The bottom left image in Figure 8 also clearly shows the eutectic structure that forms below the eutectic temperature of 1170°C, which is a combination of Nb and NiTi phases. The morphology of the eutectic structure is consistent with furnace cooling in other alloy systems. (Sinha 2003)

To help understand the composition of the proeutectic NiTi and the eutectic mixture, X-ray fluorescence images were formed from the Nb L- α , Ni K- α and Ti K- α characteristic X-rays. As shown in Figure 8, the titanium concentration in the proeutectic NiTi is lower, and thus has a darker image, than the unmelted NiTi. Additionally, there is some Nb present in the proeutectic NiTi phase, but none is visible in the unmelted NiTi.

22

This implies that diffusion of Nb in solid state NiTi is slow, and that the Nb solidified into the proeutectic NiTi preferentially substitutes for Ti in the NiTi structure.

To obtain a fracture surface, another section was taken and the tubes were manually tore apart using pliers under moderate force. A low magnification secondary electron image of this fracture surface is shown in Figure 10. As indicated in the figure, dimples cover the fracture surface, implying a ductile tearing fracture mode and a tough bond. As seen in Figure 11, these dimples have coalesced into large voids, again implying a tough metallurgical bond. While the ductile tearing fracture by microvoid coalescence is commonly observed in the eutectic zone, the commonly observed fracture mode in nickel titanium is ductile cleavage.



Figure 3: (Top left) Secondary electron image of bond between NTT inbes using Nb filler metal. (Top right) Nb L-a X-ray fluorescence showing no significant solid state diffusion of Nb into NTI. (Center right) Ni K-a X-ray fluorescence shows a lower concentration of Ni inside the eutetic than inside the NTI. (Lower right) Lower concentration of Ti in the proeutectic phase than in the base NTI, which is shown using the Titanium K-e map. (Center Left) Low magnification SEI of the bond showing the presence of a eutectic structure and procutectic phase. (Bottom Left) High magnification image of eutectic structure and proeutectic phase.



Figure 9: Pseudo-binary eutectic between NiTi and Nb. The eutectic point lies at approximately 26 atomic percent Nb and a temperature of 1170°C. The maximum reported solubility of Nb in NiTi is near 6 atomic percent.



Figure 10: SEI of NiTi –NiTi bonded tube fracture surface. Dimpling present throughout the entire fracture surface implies a ductile tearing mode fracture.



Figure 11: High magnification SEI of fracture surface inside the bond area. Dimpling implies ductile fracture inside the bond.

2.2 Construction of pseudoelastic tubes in a low-density topology

2.2.1 Introduction

To further amplify the pseudoelastic effect, larger arrays of pseudoelastic NiTi tubes were bonded to one another using the NiTi-Nb reactive brazing technique.

2.2.2 Materials and Methods

Pseudoelastic NiTi tubes were purchased from NDC in an etched and polished condition to ensure no excessive surface oxides existed. These tubes were cut into 2.5 cm lengths and were stacked into a close packed array inside a molybdenum fixture. Three mm lengths of 125 µm diameter Nb wires were placed atop the junctions between NiTi tubes. The assembly was put in a Centorr vacuum furnace and was allowed to reach a base pressure of 10⁻⁵ Torr. The sample was then heated above 1185°C for 5 minutes and allowed to furnace cool to room temperature. The array was removed from the molybdenum fixture and was photographed and sectioned, as shown in Figure 12.

2.2.3 Results

As shown in Figure 12, the Nb wires used to form the eutectic liquid can chemically etch the walls of the NiTi tubes due to the shape and melting dynamics of the wire. As the Nb wires melt, the wires are pulled close to the NiTi tubes to minimize the surface area, and thus the free surface energy, of the liquid. To maintain equilibrium with both NiTi and Nb interfaces, the liquid continues to melt NiTi locally. As the Nb wires further melt the

28

NiTi tubes, the wires are drawn deeper into the newly formed crevice to minimize the surface energy of the liquid. In this manner, the Nb wires cut through the NiTi tubes, causing the etching effects visible in both Figure 12 and Figure 13. The effect does not seem due to the differences in density between the liquid and the niobium wires because many of the wires etched against the force of gravity. It is therefore suggested that on this length scale, tens to hundred of microns, gravity does not play an important role in determining melt dynamics.



Figure 12: Macro photo of close packed array of NiTi pseudoelastic tubes bonded with 127 μ m Nb wires. (A) Etching effect on Nb shown in the cross-section.



Figure 13: Etching effect of $127 \,\mu$ m Nb wires cutting through the NiTi tubes, which is likely driven by capillary forces. Wires seem to have migrated and etched against the force of gravity, suggesting that gravity does not play a major role at the length scale of the wires.

2.3 Construction of smooth corrugation honeycomb structures

2.3.1 Introduction

To improve the compressive properties of an array of pseudoelastic NiTi, thin strips of Nitinol were corrugated and stacked in an alternating structure. The corrugation was designed with two circular arcs, each with a radius of 2.54 mm, intersecting at tangential points defined by a 7.65 mm lateral separation between cycles. This design is shown in Figure 14.

2.3.2 Materials

The corrugations of pseudoelastic NiTi were shape set by clamping strips of material in a die and annealing the strips at 500°C for 15 minutes. The die was then quenched in water before the samples were removed. Both before and after the anneal, the nickel titanium strips were acid etched as discussed in Appendix A.6. The etch removed the surface oxides, which can embrittle the metal at high temperatures.

Following etching, the corrugations were tacked together using a small custom-built AC thermocouple spot welder. For the initial experiment, specimen 071604A, 127 μ m diameter, 3 mm, Nb wires were placed between the corrugations, as shown in Figure 15 (a). Once these corrugations were tacked together, as discussed in Appendix A.8, the assembly, also known as a sandwich, could be manipulated without the corrugations breaking apart. The sandwich was then placed in a Centorr vacuum annealing furnace, and was allowed to reach <10⁻⁵ Torr before brazing. In initial experiments, the dwell period was 10 minutes at 1200°C, which was reduced to 2 minutes at 1185°C once it was

discovered how quickly melting occurred. The heating schedule for the initial experiments is shown in Figure 17.

The sandwiches were then post-braze annealed in an air furnace for 1.5 hours at 350°C to restore the pseudoelastic functionality of the NiTi. This anneal has been reported to reprecipitate metastable Ni-rich phases that are solutionized above 800°C. (Saburi)

2.3.3 Results

The sample was sent to Dr. John A. Shaw at the University of Michigan for compression testing. The sample was cyclically compressed with increasingly compressive strains from 5% strain to 50% strain. The results of this test can be seen in Figure 16.

From the testing, it was shown that the compressive strain to failure of the sine wave corrugated NiTi strips was superior to the strain to failure in the NiTi tubes. The pseudoelastic effect of NiTi was further amplified by the corrugations compared with the tubes. The density and stiffness of the array also decreased.

Niobium wires used in initial specimens etched holes in the NiTi, which decreased the mechanical properties of the array. To eliminate this problem, later samples were constructed using Nb foils and multilayer films that altered the contact geometry as discussed in Section 2.2.3. The schematic design for later specimens is shown in Figure 17 (b).



Figure 14: Schematic of the corrugation design for the NiTi strip material. This formation was termed the sine corrugation due to its resemblance to a sine wave, but it is defined by alternating circular radii.



Figure 15: Schematic of corrugation construction using (a) 127 μ m Nb wires (b) 54 μ m Nb foils. While the foils are thinner, they are considerably wider than the wires, thereby supplying more Nb to the liquid. The foil does not cut through the NiTi, unlike wires.



Figure 16: (Top) Stress strain curves of cyclic loading of NiTi sandwich. The sample was strained up to 50% with little permanent deformation, demonstrating how the pseudoelastic effect can be geometrically amplified. (Bottom) Time versus strain plot, which shows the loading cycles for the sample.



Figure 17: Typical heating schedule for initial sine wave corrugations. Furnace cooling continued until the sample was removed at room temperature.

2.4 Construction of hexagonal corrugation structures

2.4.1 Introduction

Nickel titanium honeycombs with hexagonal corrugations were designed to further amplify the pseudoelastic effect in Ni-rich NiTi strips at a lower density than sine wave corrugations.

2.4.2 Materials and Methods

In a process very similar to that described in Section 2.3, strips of NiTi were acid etched, shape set and assembled as shown in Figure 18. At the contact points between NiTi strips, small 2 mm x 4 mm squares of 0.051 mm thick Nb foil were tacked into place as described in Appendix A.8. A molybdenum fixture was used to hold the sandwich inside the vacuum furnace, as shown in Figure 19 and Figure 20. The entire honeycomb assembly was then brazed using the method described in Appendix A.1. The heating schedule of the process is shown in Figure 21.

The sample was then given a post braze anneal to restore the pseudoelasticity of the alloy. The sample was heated in an air furnace for 1 hour at a temperature of 450°C. The honeycombs were finally sent to Dr. John A. Shaw at the University of Michigan for compression testing.



Figure 18: (a) Schematic of shape-set tool honeycomb corrugation made of stainless steel. All sides of the corrugation are 3 mm. At the intersection of the 3 mm lengths is a 0.18 mm kerf. (b) Stacking sequence showing 0.051 mm thick Nb picces. (c) Final sadwich assembled and avaiting brazing.



Figure 19: Sample 030805B, honeycomb assembled using a small thermocouple spot welding unit to tack the pieces of NiTi to Nb foil. The array was placed in a molybdenum fixture as shown, with a small weight applying a compressive load to ensure the NiTi strips were well aligned.



Figure 20: This image shows the fixtures and set-up for sample 030805B, for honeycomb production. The honeycomb was encased in a molybdenum fixture with a molybdenum weight applying a compressive load to align the NTI strips.



Figure 21: Heating schedule for 030905D. As shown, the sample was heated to 1185° C for a dwell time of 5 minutes in the Centorr vacuum furnace. During this process, the pressure began at 4.4 μ Torr, and reached a maximum pressure of 24 μ Torr around 100°C before decreasing.

2.4.3 Results and Discussion

The geometry of the honeycombs allows Nb foils to be placed between the contact nodes of the individual pieces of strip NiTi. This deviation in Nb geometry from wires previously changed the melt dynamics; Nb no longer chemically etched through the NiTi. As shown in Figure 22, the bond between NiTi and NiTi using Nb foil produces a low wetting angle meniscus between the individual strips. This can also be seen in the SEM, as shown in Figure 23. The liquid is also capable of spreading out and moving along surfaces for several hundred microns. Several honeycombs were made throughout this work at Michigan State University. Of particular interest, 030805D was a large hexagonal array produced for compression testing. As shown in Figure 25, sample 030805D was subjected to increasing strain every cycle of testing. The maximum compression strain for sample was 60%, with only 8% permanent strain after unloading. The density of the honeycomb was estimated by the mass and volume measurements to be just under 0.5 g/cm³. With such a large deformation and a low density, this honeycomb could also be described as an open celled, transformational NiTi foam.

The high temperature brazing process does change the thermo-mechanical properties of the base alloy. Samples of the alloy before and after the brazing process were sent to the Composite Center at Michigan State University to find the transformation temperatures of the material using a DSC. A third sample was sent to the Composite Center after an in-air heat treatment at 350°C for 1.5 hours in an attempt to restore pseudoelastic functionality. The transformation temperatures acquired from the tests are shown in Figure 24 and are summarized in Table 1. Based on these results, the austenite start (A_s) and finish (A_f) temperatures change significantly, raising the potential for a significant phase fraction of martensite at room temperature. The martensite start (M_s) and finish (M_f) temperatures also increase during and after brazing, compared with the as received material.

Step	Mf	Ms	As	Af
As Rec	N/A	N/A	-24°C	-1°C
Post Braze	N/A	-12°C	-26°C	11°C
Post heat treatment	N/A	-16°C	8°C	26°C

Table 1: DSC results from post brazed pseudoelastic strip NiTi.



Figure 22: If the NiTi strips are misaligned, a meniscus forms as shown. The meniscus, being rich in Nb, has a shinier and smoother surface.



Figure 23: SEI collage of 03205A. Bond taken from a honeycomb sandwich, which used a 54 µm Nb foil to bond pieces of NiTi together.



Figure 24: DSC results from pseudoelastic NiTi. From top to bottom, the austenite start and finish temperatures shift as thermal processing continues.



Figure 25: (a) Strain vs. time plot of sample 030905D showing the loading times and strains per cycle. Sample was strained to a maximum of 60% strain. Low permanent déornamicn from each loading cycle can be seen by the unloading area of the curve. After 60% strain, the sample had 8% permanent strain. (b) Stress-strain curve for each increasing cycle number. Note the sample pseudoelastically déforms even when compressed to 60% strain, which can be seen by little permanent déformation upon dunoláng. (c) (Top to bottom) Images of the sample before any compressive loading, deformed on cycle 12 to 60% strain, and unloaded from the 60% strain of cycle 12.

3 Reaction control using multilayers

Many film deposition techniques exist, such as DC magnetron sputtering, radio frequency magnetron sputtering, co-sputtering, plasma spray, and thermal evaporation. In sputtering, atoms are electrically attracted towards the cathode by an electrical field. These atoms ballistically knock atoms from the cathode; these released atoms attach to the substrate. (Hou 1998) Sputtered nickel titanium films, if grown at room temperature, are amorphous and require annealing to crystallize. NiTi films are commonly deposited between 673-873 K in a crystalline form, which obviates the need for a post-deposition crystallization heat treatment. (Fernandes, Martins et al. 2002; Cho, Kim et al. 2005) Amorphous films have been reported to crystallize above 400°C when annealed for one hour or more. (Fernandes, Martins et al. 2002) Once deposited, NiTi thin films can perform a multitude of tasks including work generation and fatigue life improvement. (Grummon, Nam et al. 1992)

Many researchers have attempted to make NiTi thin films from multi-layers of pure components. (Cho, Kim et al. 2005) These films are later heat treated to synthesize NiTi from the pure elemental nickel and titanium. Unfortunately, local fluctuations in chemistry create Ti₂Ni, Ni₂Ti, Ni₃Ti and Ti₃Ni₄ precipitates that reduce the performance of these films.

Others have examined the performance of single-layer Ti-rich NiTi thin films deposited at above room temperature. (Zhang, Sato et al. 2005) These films were examined using transmission electron microscopy to observe the evolution of Ti-rich precipitates in the Nitinol films. Small Gunier-Preston zones of Ti_2Ni were observed inside the NiTi grains and at grain boundaries. These precipitates changed the twinning mechanism in the film and strengthened by precipitation hardening.

DC magnetron sputtering is complicated by composition fluctuation over the life of the cathode. Film composition can also vary based on the lateral distance away from the center of the cathode due to different take-off angles of different elements. The differences in take-off angles can be amplified by varying the distance between cathode and substrate. (Hou 1998; Zhang 2006) These fluctuations can substantially change the phase transition temperatures of the film and the mechanical properties.

Thin film adhesion is critical for many applications; if a film delaminated, it could decrease fatigue life or lower functionality of the device. Surface oxides and oils must be removed in order to develop high interfacial strength. (Zhang 2006) A final sputter cleaning of the substrate inside the vacuum chamber prior to deposition can improve adhesion. To sputter cleaning, the conductive sample is placed at a highly negative electrical potential so that ionized argon atoms will be attracted to the substrate. During the argon - substrate collision, the kinetic energy of the argon atoms is imparted to the substrate surface, which etches the surface.

Thin film deposition techniques for the creation of multilayers were taken from another work at Michigan State University. (Foltz, Grummon et al. 2006) Ductile thin films of NiTi that demonstrated shape memory at room temperature were deposited on polyimide.

48

These films were later cold co-rolled to develop uniaxial strains that could be thermally recovered. These works, and the conditions necessary for creating ductile thin films of NiTi, are included in Appendix A.3.

3.1 Multilayers

3.1.1 Introduction

When brazing nickel titanium to itself and other materials it is often desirable to form a liquid of NiTi and Nb from a single source, rather than multiple sources. As previously described, capillary forces can draw liquid away from its origin to other areas, which can create structural flaws in a component. This can be eliminated if the eutectic liquid is created by a filler material, rather than a foil of pure niobium and NiTi.

Additionally, if the eutectic liquid source were rich in NiTi, it could deposit unmelted NiTi to an area, potentially strengthening sections of a device. Conversely, if the liquid were rich in Nb it would remove NiTi from the surrounding area, which could potentially remove small amounts of surface oxides. There are several ways to manufacture such a eutectic liquid source. With the equipment available at Michigan State University, DC magnetron sputtering of thin films to create a multilayer of NiTi and Nb was the most practical. The term multilayer film (ML) will be used to describe alternating layers of the NiTi compound and the Nb phase. This method of creation has the added benefit of drastically increasing the interfacial area between NiTi and Nb, on which melting is dependent. With discrete thin layers of NiTi and Nb in intimate contact, the melting rate of a multilayer should be orders of magnitude faster than a single layer Nb foil (Low 2007).

3.1.2 Materials

Several multilayer films of alternating NiTi and Nb layers were made using DC magnetron sputtering according to Appendix A.5. The first sets of multilayer films, specimen 111306A, were made from a sputtering cathode of $Ti_{53.5}$ -Ni_{46.5} at a working distance of 51 mm. The films were grown at ambient temperature with a base pressure of 3 µTorr and a working pressure of 4 mTorr of high purity argon gas.

The substrates for these films were glass microscope slides, which were cleaned with acetone before deposition. The Nb was sputtered onto the substrate for two minutes at 145 W, while the NiTi was sputtered for three minutes at 228 W. The films were designed to have 127 alternating layers of NiTi and Nb, with Nb on the top and bottom of the film.

After deposition, the films were removed from the sputtering chamber and post crystallized in a Centorr annealing furnace for 3 hours at 575°C. The films were checked for crystallinity using a Scintag 2000 XDS equipped with a Cu-K α X-ray source operating at -35keV. The results of a 2- θ angle scan can be seen in Figure 26. Based on the two-theta scan, the films showed a crystalline structure. Using a glass cutter, the glass slides were broken in half and the films were manually delaminated.

3.1.3 **Results and discussion**

A section of film 111306A was imaged in cross-section using a Camscan SEM, operating at 17 keV, equipped with a backscattered electron detector. As shown in Figure 27, the sample contains alternating, discrete layers of NiTi and Nb. The volumetric ratio of NiTi to Nb was calculated using SEM imagery to be approximately 2.2:1, which is very close to the 2.18 volumetric ratio needed to produce the eutectic composition. Using the SEM and a conventional micrometer, the thickness of the film was found to be 34 μ m. The multilayer exhibited the shape memory effect in a 'pinch test', where the film is pinched and then placed on a hotplate. The foil was sent to the Composite Center at Michigan State University for DSC analysis. The film was found to exhibit both B19' and R-phase transformations. The transformation temperatures for the film are shown in Figure 28 and Table 2.

A piece of specimen 111306A was placed between two pieces of pseudoelastic NiTi strip material, and brazed in a Centorr vacuum furnace at the same time as an identical sample with a 25 μ m thick Nb foil. The results of the comparative microstructure can be seen in Figure 29. The overall microstructures are the same, but the thickness of the multilayer bond is significantly smaller because the 25 μ m Nb foil creates 80.7 μ m of liquid, while the multilayer creates only 34 μ m. The bonds are thinner than the calculated thicknesses because of capillary forces pulling material away, however the cross-section confirms the approximate volume ratio of NiTi:Nb to be approximately 2.2:1.
In addition to serving as a braze foil for NiTi – NiTi bonds, the multilayer foil could be used for joining NiTi to dissimilar materials that have been coated in an inert, but wetable material.





Figure 26: X-ray diffraction results from sample 111306A after annealing for 3 hours at 550°C. Theoretical Nb and NiTi (B2) X-ray peaks are shown at the top, while actual results are on bottom. There are no significant amorphous peaks, and based on thermal shape recovery, the sample appears crystalline.



Figure 27: BEI of a cross-sectioned piece of specimen 111306A using a 25keV field emission gun. The bright phase inside the multilayer film is niobium and the darker grey phase is nickel titanium. In total, the film is made of 127 discrete layers and is 34 µm thick.

Table 2. DSC analysis of phase change temperatures in sample 111500A.								
Mf	Ms	R _f	Rs	As	Af			
7°C	22°C	48.5°C	57.5°C	62°C	76°C			

Table 2: DSC analysis of phase change temperatures in sample 111306A.

DSC Results of 051407A



Figure 28: One exothermic peak upon heating (bottom half of curve) showing the austenite start and finish temperatures. Two endothermic transformations occur during cooling, which can only be interpreted as formation of the R-phase upon cooling between 60°C and 40°C, followed by the B19' martensite phase between 25°C and 5°C.



Figure 29: Comparison between eutectic structures produced by 25 μ m Nb foil (top) and a 34 μ m multilayer film (bottom). The eutectic region is larger in the Nb foil due to the base metal NiTi melting during the brazing process.

3.2 Application of multilayers to spot welding

3.2.1 AC Spot welding

3.2.1.1 Introduction

Rapid thermal processes that limit thermal exposure to local areas are very attractive from a financial and production standpoint. In addition to removing the need for furnaces, spot welding units have high production rates and consume less energy. Alternating current (AC) spot welding is a method of joining metals where pieces of metal are locally joule heated using large currents and low voltages of electricity. The electricity is applied to the sample through electrodes that are usually made from copper based alloys having low electrical resistivity and high thermal conductivity. The electrodes are designed to conduct the heat away from the outside of the sample so that melting is limited to the interface between the two halves of the sample. This is schematically shown in Figure 30.

Spot welding relies on two types of resistance for heating: resistivity of the material and resistance of the interface between the two halves. While the resistivity of the material can be calculated and assumed consistent from sample to sample, the interface resistance is dependent on many factors and must be considered a dynamic value. A proper spot weld relies on both of these sources of resistance to heat the sample: the inherent resistance of the alloy locally heats the sample near the melting point, and the interface resistance resistance raises the temperature at the interface to just above the melting point. Heavy reliance on only one of these mechanisms can produce inconsistent welds. While the

56

inherent resistance of the material cannot be altered, the interface resistance can be drastically altered by surface preparation and by adjusting the applied compressive load. Contact resistance is an inverse function of compressive stress. Therefore, having a large compressive force on the sample can reduce the interface resistance such that spot welds become consistent; and relying mostly on the resistivity of the base metal. (Karagoulis 1991)

3.2.1.2 Materials and Methods

In this section, all samples were made from strips of 0.180 mm thick, pseudoelastic NiTi. All multilayers that used were taken from sample 111306A. An SEWA AC spot welder with a 5 kA power supply was used to create lap shear specimens for tensile testing.

A baseline for experimental parameters was established in sample 121906A. This sample was made with round 1.588 mm diameter copper wire electrodes. The experimental parameters for this sample are shown in Table 3. A second sample, 010407D, was later created to examine the microstructural effects of longer pulse times and higher pulse power settings.

14010 J. L	Twie 5. Experimental parameters es eres in experiment beries 1219001.									
Sample	Applied	Applied	Pulse 1	Pulse 1	Pulse 1	Dwell	Pulse 2	Pulse	Pulse 2	
	Load	Voltage	ramp up	time, sec	Power,	time, sec	ramp up	2 time,	power,	
			time, sec		Amp		time, sec	sec	Amp	
121906A	0.1 kg	3.5 V	0.0833	0.5	700	0.167	0.0833	0.5	300	
010407D	0.1 kg	3.5 V	0.483	1.65	550	0.333	1.65	1.65	550	

Table 3: Experimental parameters covered in experiment series 121906A.

The first series of experiments was designated 022107, and used dissimilar-shaped copper electrodes. The top electrode was spade shaped, measuring 5 mm wide by 1 mm long. The bottom electrode was an 8 mm diameter electrode. The experimental parameters of experiment series 022107 can be seen in Table 4.

Sample	Volts	Pressure	Ramp up	Pulse 1	Pulse 1	Dwell	Pulse 2	Pulse 2	Ramp down
		(kg)	time, sec	Time,	Power,	Time	Time, sec	Power,	time, sec
				sec	Amps			Amps	
022107A	3.5	0.1	0.0833	1.65	550	0.167	1.65	550	0.25
022107B	3.5	0.1	0.0833	1.65	500	0.167	1.65	500	0.25
022107C	3.5	0.1	0.0833	1.65	450	0.167	1.65	450	0.25
022107D	3.5	0.1	0.483	1.65	550	0.333	1.65	550	1.65
022107E	4.5	0.1	0.483	1.65	550	0.333	1.65	550	1.65
022107F	4.5	10	0.483	1.65	550	0.333	1.65	550	1.65

Table 4: Experimental procedure for AC spot weld samples 022107.

A second series of experiments, 030107, was conducted after consultation with Dr. Michael Karagoulis. Ramp up and down times were eliminated to simplify the waveform. New electrodes were designed and machined with a symmetric, hemispherical shape with a 3.2 mm diameter flat at the contacts. These electrodes were used in all subsequent AC spot welding. The electrodes were made from a chromiumcopper, Alloy 182, 15.88 mm diameter rod purchased from McMaster-Carr. The electrodes can be seen schematically in Figure 30. Experimental parameters for 030107 can be seen in Table 5.

Table 5: Experimental parameters for series 030107.

	Applied Load	Electrical Current	Applied Voltage	Pulse 1 Time, sec	Pulse 2 Time, sec
Min	41.5 kg	250 A	2.5 V	0.167	0
Max	41.5 kg	450 A	2.5 V	0.666	0

Series 040107 was a third and final experiment designed to find the optimum parameters. The bounds for experiment 040107 are in Table 6.

	Applied Load	Electrical Current	Applied Voltage	Pulse 1 Time, sec	Pulse 2 Time, sec
Min	41.5 kg	750 A	2.5 V	0.333	0
Max	41.5 kg	1200 A	2.5 V	0.333	0

Table 6: Experimental parameters for series 040107.

3.2.1.3 Results and Discussion

Sample 121907A was made from a small piece of multilayer 111306A, described in Section 3.1, placed between NiTi strips. The results of the spot welds can be seen in Figure 31 and Figure 32. Near the center of the spot weld, the multilayer mixed with the molten base metal, as evident by traces of niobium near the surface. Near the edge of the spot weld, in Figure 32, poor adhesion between the multilayer and the base metal was observed. Joule heating in the multilayer was greater than in the base metal due to the number of metallurgical interfaces. Heat conduction away from the weld zone in the base metal was high; however, the conduction from the multilayer to the base metal was low. This resulted in poor adhesion between the multilayer and base metal. From literature, this suggests that the contact pressure of the electrodes should be increased to improve the heat conduction from the thin film to the base metal. (Karagoulis 1991)

In sample 010407D, niobium appears to be solutionized in some areas, and phase separated in other areas, shown in Figure 37 and Figure 38. The backscattered electron images show that the base metal has significantly mixed with the multilayer, meaning the sample was heated above the melting temperature. This strongly suggests that the heating time should be reduced, the current increased and the electrodes redesigned for more efficient thermal conduction. (Karagoulis 1991) In an attempt to discover the microstructural dependencies of each setting, the first series of experiments varied power, voltage and pressure according to Table 4. Compared with other samples in this series, the multilayer adhered to the base metal better in sample 022107D and had less residual porosity. This is because the sample used a higher power setting, which melted the multilayer and surrounding base metal more than other samples.

The resulting microstructure of 022107D can be observed in Figure 33. The sample was imaged after breaking in a lap shear test. While the sample featured a eutectic solidified area and higher strength than other samples, it was not an optimal spot weld. Some large, brittle precipitates of Ni₄Ti₃ grew during the process, as shown in Figure 34; these precipitates are undesirable because they are too large to strengthen against dislocation motion.

At 3.5 V and 0.1 kg pressure, sample 022107B showed the best strength. Specimens 022107E and 022107F, which were made with 4.5 V, did not join the multilayer to the base metal as well as 022107B, and contained more microvoids than the other samples. Sample 022107F contained grain boundary Nb that grew out perpendicular from the multilayer because of increased voltage, shown in Figure 35.

Experiment 032307 adjusted the power and time length, to try to improve the microstructure of the spot welds. Throughout this experimental series, as power

increased, the breaking strength of the spot welds increased. All the specimens fractured through the spot weld in a tensile fashion, as shown in Figure 36.

To better match the power settings of DC spot welding, experiment 04122007 used shorter pulse times and larger applied currents. Twenty-eight samples were made, each with an identical five spot weld pattern. The experimental results from this series can be seen in Table 7. Specimen 04122007-13 had the highest breaking strength at 500N, or 591 MPa, using an applied current of 950 amps.

A sample was made for metallurgical inspection using a 950 amp power setting, shown in Figure 39. The multilayer film has mixed with the base metal, suggesting that spot welding can be completed without the multilayer. However, the power required for spot weld with the multilayer foil is lower than that required without the multilayer, which is a result of the increased joule heating inside the multilayer and at the contact interfaces. By increasing the resistance of the sandwich, the spot weld using the multilayer foil requires less power to heat the above the melting point.

During experiment 032307, it was speculated that the multilayer was not required to spot weld NiTi pieces together. Based on this hypothesis, samples 04122007-27 and 04122007-29 were made without any multilayer foil. Specimen 04122007-29 had the highest breaking strength, 510 N, with a power setting of 1200 amps.

61

A sample was made without a multilayer film, using a 1200 amp current pulse for metallurgical, shown in Figure 40. The spot weld has a non-symmetric nugget, suggesting the waveform of the power supply was biased to one half of the AC sine wave. The nugget does not penetrate more than halfway through the NiTi base metal, which is an improvement from initial results and suggests good adhesion in the bond. However, to reduce residual void porosity inside the nugget, a higher pressure should be applied through the electrodes.

Based on the AC spot welding results from 04122007, it is unnecessary to use the multilayer film to join NiTi. The multilayer increases the resistance in the spot weld due to the metallurgical interfaces, which lowers the required current to make a spot weld. There is insufficient temperature control in spot welding to melt only the multilayer while heating the base metal for good adhesion. Multilayer films do not improve the strength of AC spot welding, and would add significant manufacturing cost.

Sample#	AC Current, amps	Thickness, µm	M <u>ax Load</u>	Breaking Tensile Stress, MPa	
1	700	182	100	117	1
2	720	177	165	199	1
3	740	185	270	311	1
4	760	181	95	112	1
5	780	180	125	148	1
6	800	186	35	40	1
7	820	182	285	334	1
8	840	183	235	274	1
9	860	182	250	292	1
10	880	185	250	288	1
11	900	183	395	461	1
12	920	183	360	420	1
13	940	180	500	591	1
14	950	175	270	328	1
15	960	182	500	586	1
16	980	184	400	463	1
17	1000	193	340	376	1
18	1050	178	370	442	1
19	1000	182	410	481	1
20	1050	185	410	472	1
21	950	184	260	301	1
22	950	187	250	284	1
23	950	180	375	443	1
24	950	183	275	321	1
25	950	182	385	450	1
26	1100	189	430	484	1
27	1100	188	460	522	No ML foil
28	1200	181	500	589	
29	1200	182	510	598	No ML foil

Table 7: Experimental Procedure of experiment series 04122007.



Figure 30: Schematic drawing of spot welding design. (A) Spot weld nugget (light grey) formed by local melting at the interface between the two pieces of the sample (B). Melting is limited to the interface by rapid heat conduction (lines) through the electrodes (C). The electrodes apply a compressive stress to the sample.



Figure 31: Grain boundary niobium phases and small precipitates of Nb inside the NiTi base metal of 121906A. Temperatures exceeded 1300°C locally, melting the base metal. Black spots are etch pits.



Figure 32: Sample 121906A2 (A) SEI of multilayer transitioning from unmelted to fully melted, demonstrating the processing temperature gradient. (B) The multilayer did not adhere well to the base metal, which could be a result of increased heat conduction or less joule heating in the base metal.



Figure 33: SEI of post-fractured 022107D. Specimen broke at the edge of the spot weld. Eutectic solidified multilayer can be seen at the fracture surface. This implies that the spot weld heated outside of the electrodes (overheated).



Figure 34: Ni₄Ti₃ precipitates in needle shaped morphology can be seen in the center of this SEI of sample 022107D. Niobium precipitates and residual porosity decorate the surrounding microstructure.



Figure 35: Sample 010307A. Higher spot welding voltage causes increased residual porosity, grain boundary Nb precipitates and irregular shaped melting paths.



Figure 36: AC spot weld from experiment 032307. Sample was tested in shear and failed throughout the weld area. The small lighter grey areas on the multilayer, visible on the left half, show the area that the electrodes melled. This area is smaller than the diameter of the electrode.



Figure 37: Low magnification BEI of spot weld 010407D. Niobium mixed through the base metal towards the outer surface. There is evidence of convection currents mixing the multilayer into the base metal.



Figure 38: High magnification BEI of Nb phase separation. Bright streaks inside the dark NiTi phase suggest solutionized Nb.



Figure 39: SEI of 053107A AC spot welding sample with niobium. Mixing of Nb with base metal suggests the multilayer foil is not critical for spot welding.



Figure 40: Specimen 053107D, AC spot weld without Nb. Melting occurred only near the interface between the NiTi pieces. The spot weld is approximately as wide as electrode contacts. The weld has melted more material to the right, suggesting the waveform of the power supply was non-symmetric.

3.2.2 DC Spot welding

3.2.2.1 Introduction

Direct current (DC) spot welding is also commonly used in industry. This form of spot welding can be more reliable because the waveform of the power output more precisely controlled. The DC spot welding supply used for this research could only adjust between 1 and 9 millisecond pulse times, compared to 0.0833 to 1.5 second pulses in AC spot welding.

3.2.2.2 Materials and Methods

Initial attempts at DC spot welding used niobium foil to join NiTi to itself, which proved unsuccessful. It was hypothesized that the niobium foil could not melt sufficiently, because of the very short heating times involved, which resulted in poor adhesion. To solve this problem, the multilayer sample 111306A was created, which was designed to melt much faster. The interfacial area between NiTi and Nb was drastically increased by the number of alternating layers of Nb and NiTi. The melting rate of the film is dependent on the interfacial area, so the foil should melt several orders of magnitude faster than an Nb foil of similar thickness. The film also supplies the necessary NiTi to create the liquid. If the temperature of the spot weld remained below 1310°C, mixing of the base metal and the liquid should not take place. Spot welds utilizing the multilayer film had much higher adhesion than spot welds using Nb foils. A series of experiments was run to determine the best power settings for the DC spot welds. Using a set of copper-chrome electrodes with hemispherical ends and an applied pressure of 40.5 kg, the power settings were adjusted from 300 amps to 2700 amps. The electrical pulses delivered by the power supply started at 8 ms pulses, and were increased to 9 ms pulses to strengthen the bonds. Experimental details can be seen in Table 8.

Sample	P4	T3	Thickness	Max load (N)	
1	0.93	7	0.353	495	
2	0.93	9	0.358	500	
4	0.95	7	0.369	480	
4a	0.95	7	0.367	560	
5	0.95	9	0.373	575	
5a	0.95	9	0.367	485	
7	0.97	7	0.356	275	
7a	0.97	7	0.367	520	
8	0.97	9	0.367	325	
8a	0.97	9	0.368	440	
10	0.99	7	0.361	410	
11	0.99	9	0.363	460	
13	1.01	7	0.372	325	
14	1.01	9	0.367	460	
16	1.03	7	0.334	215	
17	1.03	9	0.357	510	

Table 8: Experimental procedure and results of experiment series 03272007.

3.2.2.3 Results and Discussion

The optimum DC weld conditions were determined for the 0.190 mm thick pseudoelastic strip material, which can be seen in Table 9. A lap shear sample, 03272007-5, was made with these conditions. The actual pulse current applied using the DC power supply was 1.7 kA, not the selected 0.95 kA. The resulting fracture surface from the tensile can be seen in Figure 41; the associated stress-strain curve can be seen in Figure 42. The sample broke with the force of 575 N inside the base metal. The calculated tensile stress in the metal at failure was 644 MPa, based on the cross section of the strip NiTi.

Tuble 7. Spot wording parameters for Sample Contractor of									
Applied Load,	Applied Load, Pulse Time, msec		Pulse Current, Thickness, mm		ML thickness,				
kg		amps			μm				
41.5	9	1700	0.190	4.7	34				

Table 9: Spot welding parameters for sample 03272007-5.

Specimen 040207 was made for metallography using the same spot welding conditions as previously described. The spot weld process appears to have pushed the liquid from the multilayer away from the spot weld, as seen in Figure 43. The niobium that remained in the spot weld has phase separated.

Optimum AC and DC spot welds melt significant fractions of the base metal. The multilayers are not necessary because the base metal melts. Spot welding NiTi to NiTi without Nb or a multilayer should be possible; using higher power settings would increase the joule heating in the base metal.



Figure 41: Specimen 03272007-5. Fracture surface at the edge of the spot weld. There is no oxide discoloration in the spot weld. Material ejected from the sample as a result of the electrodes pushing liquid from between the NITI strips.



DC Spot Weld Tensile Strengths

Figure 42: Stress-strain curve for the strongest spot weld.



Figure 43:SEI of 040207. Niobium appears to be solutionized or pushed out of the spot weld. The niobium that can be seen has phase separated, as shown in the insert.

4 Bonding dissimilar NiTi sections

Establishing a reversible shape memory effect is critical in many designs where actuation or a pre-programmed response is required. Reversible shape memory, or two-way shape memory, can be created in a variety of ways. One approach is to train the nickel titanium by inducing plastic deformation in a controlled manner, which will result in a self-biasing effect in the material. When the material heats up, it will form one shape, and when it cools down, the nickel titanium will remember a different shape. This can develop large forces, but rather small displacements because this type of reversible shape memory is roughly limited typically to 1% strain.

Shape memory alloys can also be biased using other materials like steel; at a low temperature, Nitinol is more compliant than steel and visa versa at high temperature. Larger strains can be developed using this method, up to the elastic limit of the biasing spring, which can be mechanically amplified. Examples of this have been shown in devices such as the Krulevitch microgripper and the Johnson valve. (Johnson, Gupta et al.) (Lee, Ciarlo et al. 1996)

The ultimate biasing spring would be one that elastically deforms much beyond the typical 1% strain of most engineering metals: a pseudoelastic metal. It is therefore important to examine the capability of the niobium brazing system in order to join dissimilar Nitinol formulations. In addition to transformational shape memory and pseudoelastic Nitinol, NiTi can also be created as a thin film, a non-transforming porous foam or a fully dense non-transforming 'chemical' Nitinol. Both porous and chemical

Nitinol contain impurities and usually do not transform into the B19' phase upon cooling, these formulations of nickel titanium are very important for biomedical applications. Porous nickel titanium is a biocompatible, high compliance, low-density structure that allows tissue growth inside the pore structure. Chemical Nitinol is less expensive than other forms of NiTi, and could be used in biomedical devices that do not require pseudoelasticticity or shape memory. The latter form of nickel titanium could be used as a structural material to join Nitinol sections together without drastically raising the price compared with using active Nitinol. (Grummon, Shaw et al. 2003; Chu, Chung et al. 2005; Greiner 2005)

4.1 Bonds between NiTi thin films and wrought Nitinol

4.1.1 Introduction

Bonds between macroscopic sections of NiTi and thin films are important in the production of MEMS devices and other thin film applications for NiTi. Without bonds between thin films and macroscopic materials, installation and assembly of thin film devices can be difficult. These bonds must possess microstructural stability and ductility, but do not require high strength.

4.1.2 Materials

Shown in Figure 44, thin films of NiTi can be bonded to bulk NiTi alloys. This specimen was made from 0.254 mm thick wrought pseudoelastic strip NiTi bonded to a SMA freestanding thin film approximately 10 µm thick. The film was cut to the same width as

83

the strip NiTi and was tacked to the top faces of the strip NiTi using a small AC spot welder. The sample was brazed using the MILA ULVAC furnace with a heating rate of 30°C per second and a dwell time of 30 seconds. After cooling below 300°C, the sample was removed from the furnace and quenched in water.

Thin films can also be rolled and bonded to the inner faces of pseudoelastic NiTi tubes. A section of the same thin film was bonded inside NiTi tubes using the heating process as previously described above. The sample was then sectioned, mounted and polished for metallurgical examination. An etchant, described in Appendix A.7, was used sparingly to develop contrast between the phases, as shown in Figure 45.

Table 10: Transformation temperatures from DSC results corresponding to Figure 46.

					8	
Sample	M _f	Ms	R _f	R _s	A _s	A _f
012907A	5°C	26°C	57°C	61°C	66°C	77°C

The bond is filled with Ti_2Ni , rather than eutectic NiTi and Nb. Based on the transformation temperatures of the thin film shown in Table 10, it is unlikely the film is rich in titanium. The NiTi tube is nickel rich, so the bond must contain Ti_2Ni as a result of oxygen stabilization of the Ti_2Ni phase. EDS data from the area also supports this theory; niobium is found in the Ti_2Ni , which might further stabilize the phase.



Figure 44: Thin film bonded to wrought pseudoelastic NiTi. Film, originally the same width as the wrought NiTi, was tacked to top faces of corrugation. During brazing, the film sagged into contact with the wrought material.



Figure 45: Thin film 012907A bonded to the inner surface of a NiTi pseudoelastic tube. The thin film was oriented with the 750 nm Nb coating facing towards the tube. The film was wrapped approximately 2.5 times around the inside of the tube, as shown at the top center of the image. Ti₂Ni is present at the bond line.





Figure 46: DSC data from freestanding thin film 012907A. The film transforms from B2 austenite to R-phase to B19' martensite upon cooling, based on the two large upward peaks.

4.1.3 Results and Discussion

The films used in both Figure 44 and Figure 45 were made from DC magnetron sputtering using $Ti_{53.5}Ni_{46.5}$ and 99.999Nb cathodes, as described in Appendix A.3. In Figure 45, the microstructure of the bond shown is dominated by Ti_2Ni , but small phase fractions of NiTi and Nb are also present. Without considering oxygen, these terminal phases normally are only in equilibrium if the local alloy composition is rich in titanium and not located on the quasi-binary eutectic. With the high transformation temperatures shown in Table 10, it is possible that the thin film could be rich in titanium. Another indication the film is rich in titanium is the presence of the R-phase, shown in Figure 46, which Ti-rich thin films typically form upon cooling from the B2 austenite crystal
structure before forming the B19' martensite. (Otsuka and Ren 2005) Ti_2Ni can also be stabilized by oxygen, which could also make it a more favorable solidification product.

The bond between the thin film and the bulk wrought material is similar to the bond between two wrought pieces of Nitinol. The bond might be further improved if the phase fraction of Ti₂Ni was reduced by either better vacuum control or the addition of extra nickel to compensate for Nb substituting for Ti and forming Ti₂Ni. Higher vacuum is difficult, so the simple solution would be adding extra nickel to the multilayer source.

The mechanical performance of the thin film was lowered by the brazing process. The formation of Ti_2Ni dulled the surface finish of the film, and increased the stiffness of the film.

4.2 Thin film to Porous Nitinol

4.2.1 Introduction

Complex biomedical implants may eventually employ thin films that work as pumps, valves or even artificial muscles. These devices may be physically attached to bone or tissue by cellular material filling the pores. Bonds between these thin films and foam materials must be strong, tough, and able to resist damage from high cycle fatigue and corrosion. The first step in producing devices like this is demonstrating that NiTi foams can be bonded metallurgically to thin films.

88

4.2.2 Materials

Specimen 040607A was created by brazing a Nb-coated thin film to a closed-cell type NiTi foam received from NDC. A small section was taken from a 3.8 cm diameter round stock of NiTi foam and was ultrasonically cleaned for 5 minutes in cyclohexane. The thin film was sectioned from sample 013007A, which was made by DC magnetron sputtering. NiTi was deposited at room temperature from a $Ti_{53.5}Ni_{46.5}$ sputter target for 8 hours at 200W, followed by 10 minutes of Nb deposition at 200W. The base pressure of the deposition was 3 µTorr, while the working pressure of the sputtering guns was below 4.5 mTorr throughout almost the entire deposition. The films were deposited on glass microscope slides, which were a distance of 50 mm away from the cathode. To help delaminate these films from the slides, the working pressure of the sputtering guns was maintained at 7 mTorr during the first 5 minutes of the deposition, Following deposition, the films were post-crystallized in a Centorr vacuum annealing furnace at a temperature of 575°C for 1.5 hours before being peeled away from the glass slides.

To create sample 040607A, the 3 mm square of thin film was placed on top of the foam inside the MILA ULVAC vacuum furnace. The furnace was allowed to pump to low vacuum, 0.1 mTorr, before heating. The temperature of the sample was determined with a direct contact thermocouple probe placed beside the foam NiTi. The sample was heated to 1185°C in 40 seconds, held at 1185°C for 10 seconds and then furnace quenched by turning off the infrared heating elements. Once the sample was cooled below 300°C, it was removed from the furnace and quenched in water. The sample can be seen in Figure 47.

89

4.2.3 Results and discussion

The sample was cross-sectioned for metallurgical examination in the Hitachi S2500-C SEM. The niobium coating on the thin film was in direct contact with the foam and created a volume of liquid approximately 2.5 μ m thick. This liquid fluxed the surface oxides and formed a mixture of Ti₂Ni, Nb and NiTi phases upon solidification. The Nb from the film substituted for the titanium in the Ti₂Ni phase rather than forming a niobium rich phase, as seen in Figure 48. Based on EDS information shown in Table 11, the bond and the film appear to be rich in titanium. Traces of niobium can be found in both the film and the bond, but not in the porous material. These observations are consistent with the film being rich in titanium and forming Ti₂Ni, with the Nb substituting for Ti in Ti₂Ni.

Spot	Ti	Ni	Nb	
Α	55.00	44.53	0.5	
В	48.22	51.62	0.16	
С	50.39	49.10	0.51	
D	52.84	46.83	0.33	
Е	55.66	43.92	0.41	
F	53.94	45.57	0.49	
G	51.83	48.19	0.00	
Н	47.48	52.57	0.00	
I	47.06	52.96	0.00	

Table 11: EDS analysis of spots shown in Figure 48.



Figure 47: NiTi low density closed cell foam brazed to SMA NiTi thin film.



Figure 48: Thin film bond to NiTi foam material. (i) Thin film, (ii) bond line between thin film and (iii) NiTi foam. (iv) Ti_2Ni phase is present, not the Nb phase.

4.3 Thin film to Chemical Nitinol

4.3.1 Introduction

Bonds between NiTi thin films and chemical, or non-transforming, NiTi could be important in building advanced biomedical implants that make use of thin film valves. Scaffolding would fix the valve in place; bonds between chemical NiTi and NiTi thin films could provide the mechanical and electrical connections necessary for a complex device. If the mechanical requirements of the scaffolding were low, chemical NiTi would offer a lower cost alternative than bonding the thin film to pseudoelastic or shapememory NiTi.

4.3.2 Materials

Sample 060107A, a 40 μ m DC magnetron sputtered film bonded to a piece of chemical Nitinol, was made based on the procedure in Appendix A.2 with a dwell time of 30 seconds at a time of 1185°C. The film was taken from sample 013007A, which was a freestanding film of approximately 40 μ m of NiTi and 1 μ m of Nb. Both NiTi and Nb were deposited at 200 W; the NiTi was deposited for 8 hours using a Ti_{53.5}-Ni_{46.5} sputtering cathode, and the Nb for 10 minutes. The sputtering followed the procedure listed in Appendix A.4. The chemical Nitinol was cut from a used sputtering cathode with a composition of Ti_{53.5}-Ni_{46.5}. Following brazing, the sample was sectioned and metallurgically mounted and polished.

4.3.3 Results and Discussion

Sample 060107A can be seen in Figure 49. The microstructure of the joint between the film and the bulk material is filled with Ti_2Ni , which is stabilized by the presence of oxygen. The EDS data supports the morphological evidence for Ti_2Ni , as the titanium content inside the bond is significantly higher than in the film or the base metal. When Ti_2Ni forms, it often changes the local chemistry of the metal, enriching the NiTi with Ni atoms. If some level of surface oxides stabilized the Ti_2Ni phase, Nb could substitute for Ti in Ti_2Ni , helping force the phase in the bond.

While the Ti_2Ni phase does limit the strength of the bond between bulk NiTi and a thin film, this could be overcome with the proper design considerations. Additionally, metallic foams have limited strength, so low bond strength would be expected and acceptable.

Spot	Ni at%	Ti at%	Nb at%
Α	43.79	56.04	0.13
В	45.16	54.67	0.16
С	50.81	49.04	0.15
D	51.53	48.46	0.008

Table 12: EDS results of chemical NiTi to thin film bond, shown in Figure 49.



Figure 49: SEI of sample 060107A, a thin film (top) bonded with chemical nitinol (bottom). The bond line between the film and bulk was probed using EDS at spots A and B. The thin film and bulk compositions were explored at points C and D respectively, as shown in Table 12.

4.4 Porous NiTi to Wrought Nitinol

NiTi foams can be bonded to wrought NiTi using Nb to stimulate local melting of the interfaces, as shown in Figure 50. This sample, KB052806, was formed using the procedure given in Appendix A.1, with a dwell time of 2 minutes and a temperature of 1185°C. As shown, the 54 µm Nb foil formed a liquid that infiltrated some of the lower pores of the foam, which appear brighter in the figure. These types of bonds could

provide biomedical implants with strength and pseudoelastic or shape memory performance in one area, while allowing tissue infiltration in another area. Such an implant could be useful in the replacement of bones that require both tissue infiltration and strength. These bonds do not significantly differ from microstructures seen in NiTi foams bonded with chemical NiTi.



Figure 50: Sample KB052806. NiTi foam (top) bonded to wrought SMA plate Nitinol (bottom) using 54 μ m Nb foil.

4.5 Porous Nitinol to Chemical Nitinol

4.5.1 Introduction

Bonding fully dense sections of NiTi to porous NiTi foams may be useful for biomedical implants, because cellular growth can occur in the porous structure while the fully dense, structurally active NiTi protects the body by dampening loads. Similarly, bonding porous NiTi to chemical NiTi, which does not transform but is less expensive than traditional NiTi due to processing standards, could help lower the overall cost while improving the functionality of biomedical implants. Chemical NiTi traditionally is less expensive than transformational NiTi because it contains higher concentrations of impurities. The purpose of this experiment is to determine if chemical NiTi's higher impurity level could lower the strength of the NiTi brazing process by forming Ti₂Ni or other undesirable intermetallics.

4.5.2 Materials and Methods

Chemical Nitinol can be bonded to NiTi foams using either niobium foils or multilayers. Bonds between these materials are stronger than the porous material, and thus are untestable using standard mechanical tests. Due to the inherent inability to test it, this combination of materials was only briefly explored. A piece of chemical NiTi was bonded to porous NiTi, received from NDC, using a small piece of multilayer film, specimen 111306A. The sample was processed in the MILA furnace as according to Appendix A.2, with a set temperature of 1185°C and a dwell time of 1 minute. The

97

sample was sectioned, polished and metallurgically etched using the procedure in Appendix A.7, and was observed in a Hitachi S-2500C SEM operating at 10 keV.

4.5.3 **Results and Discussion**

As shown in Figure 51, a eutectic of NiTi and Nb phases fills the bond between materials. This eutectic structure is similar to the microstructure of chemical NiTi to chemical NiTi bonds, shown in Figure 52, and SMA NiTi to SMA NiTi bonds. The microstructure is different, however, than the Ti₂Ni that is observed in thin film to foam bonds, shown in Figure 48. This difference in microstructure is not due to by surface preparation techniques, as all samples with visible black layers of surface oxides were etched clean. The difference could, however, be due to the differences in oxygen content between the multilayer and the 40 µm film.



Figure 51: Etched microstructure of NiTi foam (top) bonded with chemical NiTi (bottom). The eutectic microstructure can be clearly seen forming a bond between the materials and has filled some of the holes in the porous structure that are near the interface.



Figure 52: Microstructure of chemical NiTi to chemical NiTi bond. Unmelted pure Nb foil remains in the center of the bond; eutectic NiTi and Nb have solidified between the Nb foil and NiTi base metal.

4.6 Shape memory to pseudoelastic Nitinol

4.6.1 Introduction

Bonding shape memory NiTi to pseudoelastic NiTi is an attractive method of producing a thermally reversible bimetal actuator that employs a small temperature range, unlike traditional bimetal actuators that require large temperature changes.

Shape memory NiTi can be fastened to other metals, so that a spring can re-deform the Nitinol during cooling, creating a biased shape memory effect. The amount of deformation capable in these devices is limited however, to the stiffness and local strains inside the biasing material. Utilizing a thin plate of pseudoelastic Nitinol to bias the shape memory NiTi could provide a larger reversible strain.

4.6.2 Materials and Methods

Two pieces of 1.588 mm thick plate SMA NiTi and two SE NiTi pieces were EDM cut into 12.5 mm by 45 mm coupons. These coupons were then shape set flat, in a die held at 500°C for 30 minutes. The samples were subsequently etched to remove any surface oxides.

To create bimetal plates, the pseudoelastic plate was placed atop the shape memory plate, with 127 μ m Nb foil between the contacting faces of the materials. The samples were loaded into a Centorr vacuum annealing furnace and degassed at a temperature of 375°C for 12 hours to obtain a base pressure of 2.6 μ Torr. A brazing schedule of 10 minutes at 1190°C was desired; the actual heating profile is shown in Figure 53. Following 10 minutes of brazing, the sample was allowed to furnace cool in a vacuum chamber to below 100°C. In air, the sample was post annealed at a temperature of 350°C for 1.5 hours to restore pseudoelastic functionality in the nickel-rich half of the sample.



Figure 53: Heating schedule for bimetal. The heating profile consists of a ten minute dwell time at 1190°C, then furnace cooled until below 100°C. The maximum pressure of 10.5 µTorr was reached at 900°C,

4.6.3 Cold rolling thin plates for actuators

The samples created in 4.6.1 were subsequently cold rolled to induce a two-way shape memory effect in the material. As the sample is heated, the shape memory half of the plate should transform to austenite, which is significantly stiffer than the prior martensite. As this happens, the pseudoelastic material, which is softer than the austenite in the SMA half, should deform by twinning mechanisms to martensite. This apparent 'flip' of the microstructures will allow the bimetal to straighten towards the original flat shape. Upon cooling, the material should re-deform as the SMA material converts back to martensite and the some stress is relieved from the pseudoelastic NiTi, causing it to convert back to austenite. Through this entire process the bond between the halves of the bimetal must be able to transfer the stress from one half to the other without yielding. If the bond is too thick it could deform significantly, and allow one half of the bimetal to slip. The bond must also accommodate any bending strains that might arise from the unbalanced elastic modulus in the material.

Specimen 041406A was cold rolled to 3% strain by a Fenn cold rolling mill. At this point the specimen curled towards the martensite, which could have been a result of unbalanced roller speed in the mill. The sample was then cross-rolled perpendicular to the prior rolling direction, which did not change the overall curl of the sample. Upon heating to 100°C, the sample did not change shape. This could have many causes, including improper straining of the material, plastic versus elastic deformation of the pseudoelastic material during cold rolling, or improper transference of the stress through the bond. The sample was then rolled to 7.7% strain; at which point it curled towards the SMA half slightly less than before. The sample was also hot, approximately 45°C, upon exiting the mill. Upon heating to 100°C the sample did not recover the stored curl, but did reduce in length by 0.52 mm, or 1% strain. This implies that the curvature of the specimen was imposed by improper cold rolling; unbalanced strain in the sample could

103

develop if the rollers of the mill moved at different rates then an unbalanced strain could develop throughout the specimen.

The sample was subsequently rolled to 12.3% strain and still curled towards the SMA half of the sample. Finally, the sample was taken to failure at 39.2% strain, where it failed violently in shear with a rapid release of energy. As a note to readers, cold rolling should be done with extreme care following all available safety precautions.

The sample was sectioned along transverse and longitudinal directions for metallurgical inspection. The sample was observed using a Hitachi S-2500C SEM; the unfractured bond can be seen in Figure 54 and Figure 55. Additionally, the microstructure is compressed in the vertical direction, which demonstrates that the bonding process is compatible with subsequent forming techniques. Forming techniques, including cold rolling, could be used to design bimetals that demonstrate reversible shape memory.



Figure 54: 39.2% cold rolling of sample 040605A. Eutectic has been compressed in the vertical direction 40%. No cracking is visible.



Figure 55: Eutectic shows no major change in the microstructure. 40% compression in vertical direction. Niobium deforms easily without cracking.

5 Joining NiTi to other materials

Bonding nickel titanium to dissimilar metals and nonmetals, such as titanium or alumina, is exciting from a technological standpoint as it allows complex devices with either transformational pseudoelasticity or shape memory to make use of the strengths of other materials. An example would be combining the high wear resistance of alumina with the low density and high stiffness of titanium and the pseudoelasticity of NiTi.

NiTi was bonded to numerous materials using niobium to form a liquid. The resulting bonds were examined, and compared to NiTi;NiTi bonds in terms of the presence of second phases and wetability of the materials. Through this investigation, two materials were commonly used: 0.180 mm thick pseudoelastic NiTi strip material and 1.588 mm thick pseudoelastic plate nickel titanium.

When bonding with some materials, like alumina, the eutectic liquid created by Nb and NiTi melting above 1170°C wetted the surface of the dissimilar material without substantially melting it. With other materials, secondary phases precipitated quickly due to melting of the dissimilar metal. In the latter case, creative solutions are needed to bond the dissimilar metal to NiTi while keeping the eutectic liquid from reaching the dissimilar metal. The solution is a multilayer film composed of alternating layers of NiTi and Nb, made as described in Appendix A.5.

5.1 Alumina

5.1.1 Introduction

Alumina (Al₂O₃) has frequently been used for fixturing experiments, and has been accidently bonded to NiTi several times. NiTi and Al₂O₃ can be bonded with either Nb or a multilayer foil placed between them. The bond is formed by only NiTi and Nb melting; not Al₂O₃. One accidental bonding was during an attempt to make a butt joint in pseudoelastic strip NiTi material, where Al₂O₃ was used for fixturing. The butt joint was successful, as shown in , but Al₂O₃ was also bonded with the specimen as shown in Figure 56.

5.1.2 Materials and Methods

The sample was made in the MILA ULVAC furnace using a dwell time of 1 minute and a set temperature of 1185°C, following the procedure described in Appendix A.2. Two pieces of 0.180 mm thick NiTi strip material were placed adjacent to one another with one 35 μ m multilayer foil and one 10 μ m NiTi thin film tacked to each side of the butt joint. The sample was loaded into a MILA ULVAC furnace with a small piece of Al₂O₃ placed underneath as a fixture. Following the brazing process, the Al₂O₃ was joined with the NiTi. The sample was mounted and metallurgically polished to reveal the butt joint and the bond between Al₂O₃ and NiTi.

5.1.3 Results and Discussion

The sample was observed with a Hitachi S-2500C SEM using an accelerating voltage of 10 keV. EDS information from the bond between NiTi and Al_2O_3 was taken using an Oxford Instruments X-ray detector that was equipped with a beryllium window capable of detecting elements as light as boron.

In Figure 56, the dark line between the eutectic microstructure and the Al_2O_3 in the bond, at the bottom of the image, is a ledge caused by differences in hardness during polishing. X-ray spectrums, shown in Figure 57, were taken from the spots shown in Figure 56. EDS semi-quantitative analyses of these X-ray spectrums are listed in .

The Ti_2Ni in the bond between NiTi and Al_2O_3 is similar to Ti_2Ni found in the butt joint between the NiTi pseudoelastic materials shown in . The Ti_2Ni in the NiTi: Al_2O_3 bond is most likely not related to the alumina; therefore it is probably stabilized by oxygen content in the multilayer film.

Mechanical tests of NiTi bonds with Al₂O₃ have not yet been designed, in part due to the inherent low tensile and shear strength of alumina. Based on the microstructure however, the bond should be strong. This has been confirmed by fracture surfaces produced by manually breaking bonds between NiTi and Al₂O₃, as shown in Figure 58. While some of the Al₂O₃ remains bonded to the NiTi, fractured occurred with little strength. This tends to imply that the alumina is somehow weakened by the process, presumably by a form of microcracking.

109



Alumina

Figure 56: Metallurgical bond between pseudoelastic NiTi ribbon (top) and alumina (bottom) using multilayer 111306A. A eutectic microstructure of NiTi and Nb has formed between the Al2O3 and NiTi, with small precipitates of Ti_pNi.

Spot	Ni at%	Ti at%	Nb at%
A	53.40	46.22	0.367
В	41.30	56.70	1.986
С	47.10	50.66	2.229

Table 13: EDS analysis of X-ray scans shown in Figure 57.



Figure 57: X-ray scans corresponding to points shown in Figure 56.



Figure 58: NTT bonded to alumina (center), formed by a 0.504 mm thick Nb wire. Etching from the Nb wire can be seen on the left side of the image. Sample broke through alumina, as evident by the alumina fracture surface on the right side of the image. Scale divisions on the right are millimeters.

5.2 Molybdenum

5.2.1 Introduction

Molybdenum (Mo) is a common refractory metal used for fixturing materials in vacuum furnaces. On several occasions, NiTi-Nb eutectic liquid has encountered Mo inside a furnace and bonds have accidentally been created upon cooling. This Mo:Nb:NiTi bond is difficult to break, and as a result, it could be an important bond in joining NiTi to ceramics, that might require a diffusion barrier to prevent formation of undesired intermetallics.

5.2.2 Materials and Methods

To examine this bond, a diffusion couple was made between NiTi and Mo with a 54 μ m thick Nb foil as the liquid source. For this diffusion couple, a dwell time of two minutes at a temperature of 1185°C was used in a MILA ULVAC vacuum furnace at a pressure less than 0.2 mTorr. The procedure followed is listed in Appendix A.2. The sample was sectioned, metallurgically mounted and polished to examine the microstructure and hardness of the bond.

5.2.3 Results and Discussion

The sample was observed using secondary electrons with a Hitachi S-2500C SEM. The bond between NiTi (bottom) and Mo (top) can be seen in Figure 59, with a linescan overlaid upon the image. From the linescan, the two-phase mixture appears to be made of NiTi and Mo phases. Niobium is almost undetectable in the linescan and occupies the same location as Mo. This is expected because Nb and Mo have similar atomic radii and both have BCC crystal structures at room temperature. (William D. Callister 2003) Additionally, Mo is miscible in Nb according to the binary phase diagram, so it is unlikely to have any non-terminal phases if bonded to nickel titanium using a niobium braze. (Massalski 1986) The Mo appears to change the overall morphology of the solidified eutectic, as shown in Figure 60. The solidified structure appears to have higher phase fractions of proeutectic NiTi.

Vicker's microhardness testing was used to compare the hardness of the bond with the base metals using a load of 50 grams. As shown in Figure 61, the hardness of the bond is

higher than either base metal, and no cracking or chipping was observed following the indentation. Based on these observations, this robust metallurgical bond with NiTi warrants further investigation.



Figure 59: Specimen 031607, showing the bond between molybdenum (top) and NiTi (bottom). A mixed two-phase microstructure between NiTi and Mo can be seen, which is a result of liquid formed by Nb lowering the melting point of the NiTi. Bright phases have high concentrations of Mo and almost undetectable levels of Nb. The linescan across the bond begins on the left of the graph, with high courts moving to the right of the graph.



Figure 60: Specimen 031607. Eutectic liquid is wetting the NiTi and forming a new morphology of twophase microstructure. The Nb-rich phase contains most of the Mo, and is the bright phase in the two-phase region. The dark line between the NiTi and two-phase region is a polishing effect.



Figure 61: Microhardness of sample 032107B, a bond between NiTi and Mo. A 50 gram load was used for the measurements. The hardness was the highest inside the bond. None of the indents chipped or showed any signs of microcracking.

5.3 Cobalt Chrome

5.3.1 Introduction

Cobalt chrome (CoCrMo) is an important material for biomedical implants, as well as tribological applications. Several experiments were conducted to find the optimum method of brazing NiTi to CoCrMo. In a vacuum chamber at elevated temperature, the cobalt in CoCrMo has a significant vapor pressure; often times coating the fixtures in a thin film of Co. This proved to be a challenge for bonding NiTi to CoCrMo; thin film coatings put on CoCrMo had poor adhesion. In addition to poor adhesion of thin films at ambient temperatures, thin films depositions were attempted at 400°C, which completely failed to adhere to the CoCrMo, most likely due to outgassing of the CoCrMo.

5.3.2 Materials and Methods

A bond between porous NiTi and CoCrMo was made to examine the resultant microstructure. This sample was made before NiTi-Nb multilayers, and was an initial attempt in preventing other elemental species from melting into the eutectic liquid. CoCrMo samples were provided by Nitinol Devices & Components, and were polished to colloidal silica before deposition. Sputtering conditions are summarized in Table 14. 20 µm of NiTi were initially deposited onto the CoCrMo. Ten µm of niobium were then deposited on the CoCrMo and porous NiTi.

Samples were sectioned with a diamond saw, cleaned and placed in a Centorr vacuum furnace. A section of porous NiTi was set directly above a section of the CoCrMo, with

the two niobium coated faces toward one another. The furnace was degassed for fifteen hours at 150°C to reach a base pressure of 5 μ Torr. The heating profile is shown in Figure 62, and follows the procedure given in Appendix A.1.

The bond did not fully wet both materials. Following brazing, the sample was fractured in 3-point bend to observe the fracture surface without collecting data on the stresses involved.

Base Pressure	< 3 µTorr		
Power	200 Watts		
Working Pressure	<4.5 mTorr		
Nb Sputtering Rate	7.5 μm/hr		
NiTi Sputtering Rate	4.4 μm/hr		
Working Distance	50 mm		
Deposition Temperature	Ambient, ~18°C		

Table 14: Sputtering conditions for sample 062306D





Figure 62: Heating profile of furnace. One minute dwell time at 1185°C. Sample 062806A, created from 062306D and 062306E.

5.3.3 Results and Discussion

As shown in Figure 63, the interface between NiTi and CoCrMo was only partially wetted by the liquid. It appears that most of the liquid was pulled into capillary space in the porous NiTi rather than spreading across the bond interface. Additional multilayers of NiTi and Nb might solve this problem by forming more liquid.

The fracture surfaces were examined using a Camscan SEM. Fracture surface features from the CoCrMo side can be seen in Figure 63 and Figure 65, while a portion of the NiTi half of the fracture surface can be seen in Figure 64. As shown in Figure 63, most of the CoCrMo material was not bonded with the NiTi. Figure 65, however, was taken in the area that bonded with the NiTi and shows that the fracture occurred in the NiTi, not at the bond.

The hardness of the CoCrMo was tested before and after brazing. The materials hardness raised by the brazing process, but the standard deviation in hardness decreased. Hardness data is summarized in Figure 66.

The difficulty of bonding CoCrMo with other materials is the high vapor pressure of Co inside a vacuum chamber. If an adherent thin film of niobium were able to coat the CoCrMo and remain adherent at 1170°C or higher, multilayers could provide liquid for metallurgical bonding with CoCrMo.



Figure 63: Overview of CoCrMo fracture surface. Upper left corner was not brazed most likely due to capillary forces drawing the eutectic liquid away. Failure occurred inside the porous NiTi. The rough appearance of the CoCrMo (top left of CoCrMo) could be a result of significant Co sublimation during the brazing process.



Figure 64: Composite image of pore and fracture surface. Note the different texture of the pore versus the fracture surface, implying fracture did not propagate through a pore. NiTi half of bond.



Figure 65: Fracture surface in area that was brazed between NiTi pores and left material on CoCrMo side.


Figure 66: Hardness data from CoCrMo material before and after brazing. The overall hardness increased by 13.7%, while the standard deviation in hardness decreased by 9.8 VHN. Many irregularly shaped indents were observed in both as-received and post brazed conditions.

5.4 Fe_2AIV

5.4.1 Introduction

Thermoelectrics are currently researched materials designed to reclaim wasted heat in engines and other devices. These materials, however, usually have low toughness and are susceptible to failure in environments that have large vibrations and applied loads. Pseudoelastic materials, such as nickel titanium, could be used as a support structure capable of dampening these forces, thereby protecting the thermoelectrics.

5.4.2 Materials and Methods

Bonds between Fe₂AlV were made using a MILA ULVAC vacuum furnace following the procedure in Appendix A.2. Multilayer films of NiTi and Nb, taken from sample 111306A, served as the liquid source. The samples were brazed for 30 seconds at a temperature of 1185°C, followed by a rapid furnace quench. The bonds were subsequently sectioned and metallurgically polished and etched for SEM microscopy.

5.4.3 **Results and Discussion**

The resultant microstructure can be seen in Figure 67, Figure 68, and Figure 69. The microstructure inside the bond consists of two phases, both intermetallics. These phases were characterized using EDS, the results of which are shown in Table 15. Both phases appear to be rich in nickel and titanium, but without crystallographic data it is difficult to further identify the phases.

As seen in Figure 68, the NiTi-Nb eutectic liquid readily wets the thermoelectric, which is the material on top. It is interesting to note is that the low wetting angle observed in NiTi:NiTi bonds was not observed in this sample.

The thermoelectric material appears microcracked in Figure 67 and Figure 68. One of the cracks contains solidification product from the bonding process, suggesting the crack was created before the brazing process. Other cracks do not contain solidification products, which suggests they were formed by the rapid heating and cooling of the braze. It should be noted that the rapid heating and cooling of the sample in this experiment was done for convenience, and not as a preplanned heat treatment.

X-ray mapping shows the variation in composition between the two solidification products in Figure 70. Nb and Ti have the most notable differences in composition. The phase that appears light in Figure 69 appears to have significantly more Nb than the dark phase; conversely, the dark phase appears to have significantly more titanium than the light phase.

The hardness of the NiTi, Mo and the bond were all examined using Vickers microhardness indentation; the results are shown in Figure 72. The hardness of the bond was higher than the hardness of the parent materials, but the bond did not show any signs of microcracking or chipping. The Fe₂AlV microcracked from the thermal processing, while the solidification product between the Fe₂AlV and NiTi did not crack.

125

The results of this investigation demonstrate that the thermoelectric is more susceptible to damage from thermal shock than the bond or NiTi. Further identification of the phases present in the solidified microstructure is needed, but the bond appears stronger than the thermoelectric material. As identified in Figure 71, thermal shock of the material can result in fracture of the thermoelectric in the vicinity of the bond, which could be a result of a mismatch in coefficients of thermal expansion. In future studies, a similar sample should be created and allowed to heat and cool at a more moderate rate.







Figure 68: Low magnification SEI of 031607A. The solidification products of the bond appear different than the standard NiTi-Nb solidification products. The wetting angle of the Fe₂AlV is similar to other materials, however, the NiTi wetting angle is greater than 90°, suggesting a non-wetting condition. Fe₂AlV appears susceptible to microcracking, as suggested by a crack infiltrated with solidification product. This crack must have been present during the brazing process.



Figure 69: Sample 031607A. The solidification product does not seem to be a cellular or dendritic structure. A third possible phase could be at the top of the image, appearing to have solidified from the Fe₂AIV.



Figure 70: SEI and corresponding X-ray maps of NiTi-Fe₂AlV bond. Niobium content appears to be the largest chemical difference between the two solidification products. Titanium, aluminum and vanadium also appear different between the phases, while iron and nickel content are similar.



Figure 71: SEI of microstructure. X-ray information was collected from points A-D and were analyzed in Table 15.

Spot	Ti	Ni	Nb	Al	V	Fe
A	41.42	49.22	5.865	1.095	1.137	1.258
В	49.61	47.74	0.797	0.543	0.159	1.151
С	47.89	52.10	0	0	0	0
D	0	0	0	24.62	24.13	51.23

Table 1.3. LDS analysis, in alonne beleent of A-lay spectra in Figure /	Table 15: EDS analysis, in atomic percent, of X-r	ray spectra in Figure 70
---	---	--------------------------

032107-A Microhardness



Figure 72: Hardness data for specimen 032107-A. The NiTi phase has a lower hardness than the Fe_2AIV . The hardness of the bond was higher than the hardness of the parent phases; however no cracking was visible inside the bond.

5.5 Boron Carbide

5.5.1 Introduction

For specimen fixturing in research and industrial production, it is important to find materials that do not react with the eutectic liquid. Boron carbide, B_4C , was bonded to NiTi to determine if materials with strong covalent bonds would react with the eutectic liquid.

5.5.2 Materials and Methods

A small, fully dense piece of boron carbide was bonded to NiTi inside the Centorr vacuum furnace using a 34 μ m thick multilayer foil, specimen 111306A. The heating schedule followed the procedure listed in Appendix A.1. The dwell time of the sample was two minutes at a temperature of 1185°C. Upon opening of the chamber to retrieve the sample, the B₄C had broken off from the NiTi bond. It is likely the sample fractured due to thermal stresses, which occur because of different thermal expansion coefficients. The NiTi half of the sample was mounted in cross section and polished and examined with a Hitachi S-2500C SEM.

5.5.3 Results and Discussion

The nickel titanium half of the fracture surface is shown in Figure 73. The boron carbide was partially bonded to the NiTi, and the fracture occurred through the bond. A mixture of the two parent materials appears to have adhered to the base NiTi metal around the

fracture surface, which can be seen in cross section in Figure 74. The bond between the NiTi and the solidification product shows a low angle wetting with the NiTi, but a high wetting angle with the solidification product. Furthermore, the microstructure of the solidification product, shown in Figure 75, shows a complex morphology, from which no meaningful X-ray data could be obtained due to interaction volume and difficulties quantifying boron. From the microstructure, it is speculated that the solidification product is most likely a complex non-terminal solidification product that has nearly no toughness or strength. This bond is the least adherent and interacts the least of all the materials bonded to NiTi thus far.



Figure 73: Optical image of NiTi side of NiTi-B₄C fracture surface. Units on the scale to the left is millimeters. (a) Area remained unbonded during brazing. (b) B₄C remains bonded with the NiTi. (c) Solidification product of the liquid.



Figure 74: Cross-section of fracture surface. While the base metal appears to be wetted by the eutectic liquid with a low contact angle, the brittle bond with the boron carbide fractured from thermal contraction.



Figure 75: High magnification SEI of solidification product formed by NiTi-Nb liquid reacting with B₄C.

5.6 Magnesium Oxide

5.6.1 Introduction

The bond between NiTi and magnesium oxide, MgO, was examined in the attempt to find a material that does not bond to the eutectic liquid. Similar to boron carbide, magnesium oxide has strong covalent bonds, and a high melting point. Magnesium oxide was chosen based on magnesium having a higher affinity for oxygen than titanium, which was assumed to be a limiting factor in producing new solidification products with oxygen. (Gaskell 1995)

5.6.2 Materials and Methods

Reagent A.C.S. magnesium oxide powders, from Matheson Coleman & Bell, were spread across a multilayer foil, specimen 111306A, that was on top of a piece of 3.127 mm thick pseudoelastic NiTi. The sample was carefully placed in the MILA ULVAC furnace, which was gently evacuated to avoid disturbing the powder. The sample was brazed for two minutes at 1185°C in the furnace, followed by a quench according to the procedure listed in Appendix A.2. Upon opening the furnace, much of the powder remained unbonded to the multilayer. These loose particles subsequently blew away during sample removal. Some particles did attach to the NiTi, as evident by the rough texture of the free surface. The sample was mounted in cross section and polished.

5.6.3 Results and Discussion

The microstructure of the bond, shown in Figure 76, appears similar to that of the solidification products in a NiTi – NiTi bond. A eutectic structure of NiTi and Nb is still observed in the material, as well as Ti₂Ni, from the liquid forming on a free surface and oxidizing. Magnesium oxide agglomerates have been infiltrated by the eutectic liquid. The solidification products inside the magnesium oxide agglomerates are too small to quantify using the SEM, and thus are assumed MgO, Nb and NiTi based on phase contrast. If MgO powders have been infiltrated by the eutectic liquid, it is an example of a metal matrix composite. Based on the microstructure in Figure 76, this bond should be recreated using fully dense magnesium oxide to better understand the solidification products.



Figure 76: Mg rich region filled with fine Nb-based and Mg-based precipitates. The phases were too small to analyze using EDS. Based on EDS data, only the Mg-rich region appears to contain Mg.

5.7 Tantalum

5.7.1 Introduction

Cheng, Cai and Zheng used tantalum as a surface modification for NiTi implants to improve radiopacity for viewing of medical X-rays. (Cheng, Cai et al. 2006) Coating the NiTi surface with approximately 3 μ m of tantalum resulted in higher implant visibility within the body when imaging using X-rays. Additionally, this reduced the nickel release rate of the NiTi by over an order of magnitude.

5.7.2 Materials

Ke Bin Low made a butt joint between pseudoelastic NiTi and tantalum using the Centorr vacuum annealing furnace at Michigan State University, following the procedure in Appendix A.1 (Low 2007). A foil of 127 μ m Nb was placed between the NiTi and Ta, which subsequently melted and bonded the materials when brazed at 1185°C for two minutes. After standard furnace cooling, the sample was sectioned using a diamond saw for mechanical testing.

5.7.3 Results and Discussion

Results of the tensile test, conducted at a strain rate of 0.1 mm/sec, can be seen in Figure 77 (Low 2007). Necking occurred in the Ta, showing that the butt joint between the tantalum and nickel titanium is stronger than Ta alone. The maximum engineering stress experienced by the sample was roughly 210 MPa, which was the ultimate tensile strength of the Ta. This implies that if Ta coatings on NiTi had poor adhesion, the Ta could be

brazed to the nickel titanium using an intermediate layer of Nb. An intermediate layer on Nb would melt when heated above 1170°C and improve the interface between the thin films and the NiTi by removing any porosity and oxides present.

A portion of the bond between Ta and NiTi was mounted and polished for inspection. The sample was imaged using secondary electrons on a Hitachi S-2500C SEM. As shown in Figure 78, the resultant braze microstructure is a simple eutectic with proeutectic NiTi and Ta phases. As suggested by the completely miscible binary phase diagram between Nb and Ta, the image morphologically demonstrates that niobium and tantalum have phase separated from the NiTi, producing a eutectic microstructure. (Massalski 1986) EDS analyses of the phases, Table 16, show that the Nb and Ta have phase separated from the NiTi. Due to the X-ray interaction volume, EDS could not accurately quantify the eutectic phases.



Figure 77: Stress-strain plot of the sample shown in the photo insert. Sample necked inside the tantalum, demonstrating the joint is stronger than the tantalum. (Low 2007)



Figure 78: Proeutectic NiTi eutectic Nb/Ta and NiTi fill the bond between NiTi and Ta. This SEI shows the simple eutectic between NiTi and Ta that results from brazing with an interlayer of 127 μ m thick Nb foil. X-ray information collected at points A, B, C and D shown in Table 15.

Spot	Ti	Ni	Nb	Ta
Α	51.37	48.27	0.12	0.23
В	46.70	52.94	0.13	0.22
С	46.06	53.55	0.14	0.24
D	54.0	34.0	5.45	6.49
E	49.5	25.8	11.0	13.5

Table 16: EDS analysis of the areas shown in Figure 78.

5.8 Ti-6Al-4V

5.8.1 Introduction

Ti-6Al-4V is an important biocompatible alloy used extensively due to its low density, high strength and high corrosion resistance. Complex devices combining these features with the pseudoelastic or shape memory effects of NiTi could usher in a new generation of implants. From the Ni-Ti phase diagram, nickel titanium and titanium contact melt above 942°C and can produce equilibrium mixtures of titanium, Ti₂Ni and NiTi upon cooling.

5.8.2 Materials and Methods

To prevent the formation of Ti_2Ni , coupons of Ti-6Al-4V were coated with 30 μ m of Nb by DC magnetron sputtering at a temperature of 400°C. (Lütjering and Williams 2007) Heating the titanium to 400°C improves adhesion by allowing the titanium alloy to reduce the surface oxide, thus allowing a metallurgical bond with the Nb film. The titanium alloy was sectioned with a diamond saw after the film deposition.

Samples were created using four squares of 34 µm thick multilayer foils to bond a pieces of pseudoelastic NiTi strip material to a piece of 1.588 mm thick Ti-6Al-4V plate material. The pieces of multilayer, specimen 111306A, were tacked to the NiTi, and placed against the Nb coated face of the titanium alloy. The assemblies were heated in the MILA ULVAC vacuum furnace to 1185°C in one minute and were held at 1185°C for 10 seconds before furnace quenching. Sample 042407A was held for 1 minute at

1185°C. During the dwell, the multilayer melted and the Nb coating on the titanium came in direct contact with the liquid. Upon cooling, the liquid solidified, forming a metallurgical bond between the NiTi and Nb, while the Nb and Ti-6Al-4V metallurgical bond remained. The samples were later sectioned and metallurgically mounted and polished.

5.8.3 Results and Discussion

The process formed a metallurgical bond between NiTi and Nb, and a sputtered metallurgical bond between Nb and Ti-6Al-4V. The bond was polished and etched; it was imaged in a light microscope shown in Figure 79. The sample was coated with only 10 μ m of Nb, which appears intact after the brazing process. This means that the liquid did not significantly melt the Nb coating on the titanium. A lower magnification image of the joint between NiTi and an Nb coated section of Ti-6Al-4V can be seen in Figure 80, which shows the low wetting angle of the liquid on the NiTi and Nb coating. Furthermore, the low magnification image shows that capillary action drew the NiTi close to the Nb coating near the bottom of the image without significantly affecting the coating itself. Figure 81, shows a sample that was brazed too long, allowing Ni atoms to penetrate the Nb coating. When this happened, the Ti-6Al-4V and NiTi formed Ti₂Ni in the bond, which resulted in cracking and uncontrolled melting of the sample.

DC magnetron sputtered thin films can have porosity and pinholes from irregularities during sputtering. It was important to examine the bond between the Nb and Ti-6Al-4V to determine if any nickel was able to penetrate the Nb layer through holes. In a higher

magnification SEI, Figure 82, a transition from the BCC Nb to BCC and HCP Ti-6Al-4V can be seen, however no Ti₂Ni appears to be present. This transition is further characterized by EDS along the Nb to Ti-6Al-4V bond line, which did not detect nickel, as shown in Figure 83 and Table 17. In Figure 84, the X-ray linescan performed across the image shows a simple transition from NiTi to eutectic with NiTi and Nb, to the Nb coating and then the Ti-6Al-4V. No nickel is detected beyond the Nb coating. A small two phase region between the Nb and Ti-6Al-4V, shown again by the linescan, demonstrates the metallurgical nature of the bond between the Nb coating and Ti-6Al-4V. The bond between Nb and Ti in also appears to be well mixed based on the Zcontrast in the titanium side of the interface. The bright features in the interface between Nb and Ti are differences in secondary electron emission at a ledge from different etching rates between Ti and Nb. The dark interface shown in the BEI of Figure 82 demonstrates that beta-stabilizing elements in the titanium, such as vanadium, diffuse faster into the niobium than the niobium diffuses into the titanium. This results in a higher volume fraction of the α -titanium phase at the bond than in the bulk of the sample.

In Figure 85, the solidified microstructure of the braze and Nb coating can be observed. Proeutectic Nb, identified by Z-contrast in the lamellar structure, appears to have solidified from the Nb coating. This demonstrates that melting of the Nb coating can be controlled by properly designing the thickness of the film for the intended thermal exposure above 1150°C. By using rapid cooling, samples that do not use multilayers produce similar solidification microstructures as samples with multilayers. For comparison, a specimen was made using the same brazing technique mentioned earlier, but did not contain multilayer foils. The microstructure of this bond can be seen in Figure 86. The braze interface appears identical near the niobium, but this is a result of the rapid cooling. With conventional furnace heating and cooling rates, NiTi and Nb would continue to melt until the Nb interlayer was exhausted. The multilayer establishes a large diffusion distance between the pure NiTi and pure Nb layers, over which diffusion is slow. This prevents severe dissolution of the Nb coating, which protects the Ti-6Al-4V from nickel atoms.



Figure 79: LOM of Nb coating, the bright phase on the right, on Ti-6Al-4V. The Nb film is approximately 10 μ m thick on sample 053007B, which was taken from the thin film deposition 051507B.



Figure 80: LOM of (a) Ti-6Al-4V base alloy with (c) 30 µm Nb thin film deposited on it to prevent extra titanium from reaching (b) the eutectic between niobium and nickel titanium. Niobium successfully prevented Ni diffusion into Ti-6Al-4V. Four pieces of multilayer M032007A were placed between the niobium coating and the NITi before brazing, serving as a liquid source.



Figure 81: LOM of 060207C, (a) NTTi bonded to (b) Ti-6A14V with a dwell time of 1.5 minutes at a temperature of 1185°C. Niobium did not prevent the liquid from melting the Ti-6A14V, which enriched the liquid in titanium, producing (c) Ti₂Ni upon cooling. The Ti₂Ni phase fractured during hot mounting.



Figure 82: Sample 040607A. This BEI shows the transition in microstructure from BCC Nb (left, bright phase) to the tweed microstructure of Ti-6A1-4V. A two-phase region is seen between the thin film and base metal; differences in etching rate have produced a ledge that causes darkness at the interface.



Figure 83: SEI of bond between NiTi (left) and Ti-6Al-4V (right). The coating of Nb appears to be well adhered to the Ti-6Al-4V as evident by Z-contrast in the B region. X-ray information from spot A, B and C were analyzed using an OXford Instruments EDS software package.

Table 17: EDS analysis, in atomic percent, of spots indicated in .Figure 83.

Spot	Ni	Ti	Nb	
Α	None Detected	46.65	53.35	
В	None Detected	46.65	53.35	
C	48.77	47.35	3.87	



Figure 84: 042407A. NiTi to Ti-6Al-4V bonded without multilayers, only an Nb coating. This process was completed using a thick coating of Nb on Ti along with fast brazing times, especially above 1150°C.



Figure 85: 040607A NiTi - Ti64: The microstructure of the solidified eutectic contains Nb and NiTi phases, along with a small phase fraction of Ti₃Ni, which is expected due to oxygen contamination on the multilayer foil.



Figure 86: 040607A NiTi - Ti64. The Nb coating serves as a barrier for nicked diffusion from NiTi to Ti-6Al-4V. The soft Nb coating has proeutectic Nb solidified from the bond with NiTi using multilayer foils. The sputtered coating mixes with the Ti-6Al-4V in a two-phase region α + β region.

5.9 Tungsten

5.9.1 Introduction

The niobium brazing process also wets tungsten, a commonly used refractory metal.

Tungsten is attractive because it could possibly act as a diffusion barrier to prevent other

materials from being attacked by the reactive liquid.

5.9.2 Materials and Methods

To explore the metallurgical interaction between NiTi and tungsten, a small piece of 0.180 mm thick NiTi strip material was bonded to 254 μ m diameter tungsten wire using a 3 mm square of 34 μ m thick multilayer foil taken from sample 111306A. The sample was created using the MILA brazing furnace, with a dwell time of 2 minutes at a temperature of 1185°C. See Appendix A.2 for more information on the brazing process.

The sample was cross sectioned, metallurgically polished and then etched following the procedure described in Appendix A.7.

5.9.3 Results and Discussion

The sample was photographed using a Nikon D70 digital camera attached to a Nikon reflection microscope. Figure 88 is a collage of light optical micrographs showing the microstructure of the bond. Some microvoids were present inside the bond, which could ultimately lower the strength of the bond. These voids were not interconnected however, so the hermetic qualities of the bond are probably not compromised. This image also shows the liquid has a low wetting angle with the 250 μ m diameter wire. The wire is very close to its initial diameter, suggesting that very little melted.

The sample was imaged in a FEI Quanta operating at 20 keV using secondary electrons; EDS data was collected from the various microconstituents inside the bond. The results of these can be seen in Figure 89, Table 18, Figure 90 and Table 19. The microstructure of the bond has a significant phase fraction of a dark, faceted precipitate phase, which EDS data suggests could be an intermetallic based on Ti_2Ni . The phase fraction of Ti_2Ni could be lowered by etching the tungsten before bonding it to NiTi, thus lowering oxygen contamination.

Niobium and tungsten are known to be miscible from the binary phase diagram. (Massalski 1986) In the regions very close to the tungsten wire, the tungsten has changed the morphology of the Nb rich phase in the eutectic into a more pronounced rod shape. The Nb phase near the tungsten wire has higher concentrations of tungsten than the NiTi phase nearby. This suggests that most of the melted tungsten has solidified in the Nb phase.

The NiTi phase appears unchanged; EDS data confirms very low concentrations of solutionized tungsten. The concentration of tungsten in NiTi is consistent near the unmelted NiTi and near the tungsten wire, which suggests sufficient mixing of the eutectic liquid. The titanium concentration inside the proeutectic and eutectic NiTi is lower than the base metal by approximately 6%, which is roughly equal to the concentration of Nb in the phase; again suggesting that Nb is substituting for Ti. The addition of a small concentration of tungsten into the material does not change this substitution.

156



Figure 87: Microstructure of NiTi-W bond. (a) Unmelted NiTi base metal (b) Proeutectic NiTi phase coherent with unmelted NiTi (c) Proeutectic NiTi lamellae (d) Voids in the microstructure (e) Tungsten wire



Figure 88: LOM of sample 053007A. (a) Pseudoelastic NiTi bonded with (b) 254 μ m diameter tungsten wire and mounted in (c) Konductomet @ phenolic mount material. A small void is present in the bond between the NiTi and tungsten, as well as a eutectic microstructure and a proeutectic phase consisting of Nb and tungsten. Also, note the low wetting angle between the wire and eutectic liquid.


 Figure 89: NIT is ide of 053007A.
 (a) Unmelted NiTi, (b) procutectic coherent NiTi (c) eutectic solidified

 Nb phase.
 (d) Faceted precipitate.
 (e) Bright eutectic phase.

Spot	at. % Ni	at. % Ti	at. % Nb	at. % W
(a)	52.04	47.96	None Detected	None Detected
(b)	51.4	43.10	5.5	None Detected
(c)	18.07	22.42	58.76	0.75

Table 18: EDS	Data collecte	d from spots	shown	in Figure	89.



Figure 90: Microstructure of 053007A near tungsten wire. (a) 'Matrix' phase that is dark grey, (b) tungsten wire approximately 15 µm inside the wire, (c) dark precipitate phase, which could be based on Ti₂Ni, and (d) bright eutectic phase.

Spot	at. % Ni	at. % Ti	at. % Nb	at. % W	at. % O
(a)	50.66	42.68	6.05	0.62	N.D.
(b)	0	0	0	100	N.D.
(c)	33.14	47.36	12.46	0.55	6.48
(d)	18.82	31.27	34.44	3.80	11.68

Table 19: EDS data collected from spots in Figure 90.

5.10 304 Stainless Steel

5.10.1 Introduction

Stainless steel is an important engineering material due to high corrosion resistance in many environments. The corrosion resistance is partly due to the protective surface oxide formed by alloying additions of chromium and nickel. This nickel can cause problems when bonding NiTi to stainless steel. Methods of joining, such as pulsed laser welding, have met with limited success. (Wang 1997) (Schlossmacher, Hass et al. 1997)

5.10.2 Materials and Methods

An attempt was made to bond NiTi to 304 stainless steel received from ESPI Metals using 127 μ m thick Nb foil and 1.588 mm thick pseudoelastic NiTi plate material. The bond was made using a Centorr vacuum annealing furnace with a dwell time of two minutes and a temperature of 1185°C according to Appendix A.1.

5.10.3 Results and Discussion

The bond was extremely brittle and fractured easily. The sample was cross-sectioned and observed using a Hitachi S-2500C SEM operating at 10 keV and an Oxford Instruments X-ray detector. A micrograph of the bond can be seen in Figure 91, which appears to be comprised of at least three different microstructures. EDS semi-quantitative analyses were performed on X-ray scans taken at the labeled spots in Figure 92; results are listed

in Table 20. Contrary to literature reports of NiTi to stainless steel welds containing TiFe, no precipitates contain large amounts of iron. (Wang 1997)

The significant microstructural difference between the bond shown in Figure 92 and a NiTi to NiTi bond is the formation of a third phase, labeled B in the figure. EDS semiquantitative analysis suggests the phase is rich in nickel and titanium, with small amounts of Nb, Fe and O. The phase could be a result of nickel provided by the stainless steel during the brazing process. If the phase were based on the Ni-Ti-Nb ternary system, it could a non-terminal phase rich in nickel and niobium. Literature reports these non-terminal phases as the X_A and X_E phase, which are not currently reported on. It is likely that this phase could be avoided if the stainless steel were coated with a material like niobium, tantalum or tungsten, which have been shown to not significantly affect the microstructure of the bond.



Figure 91: Low magnification SEI of post-fracture bond between NiTi and stainless steel. Bond was formed using Nb foil.



Figure 92: Three distinct solidified microstructures in the bond between NiTi and 304 stainless steel.

Spot	Ti at%	Ni at%	Fe at%	O at%	Nb at%
A	45.66	44.10	0.699	0.729	8.799
В	36.06	56.15	0.558	Not Detected	7.15
С	46.09	52.03	0.623	Not Detected	1.25
D	48.31	51.38	Not Detected	Not Detected	Not Detected

Table 20:	EDS	semi-quar	titative ana	lysis (correspon	ding to	snots i	n Figure	92
1 4010 20.	220	Sonn quu	itituti ve unu		0011000000		, ,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,		~~~

6 Conclusions

The Ni-Ti-Nb ternary is a unique system that combines biocompatibility with high strength and ductility. Brazing NiTi with Nb produces a eutectic structure upon solidification, and is compatible with low and medium vacuum processing. Complex structures can be produced using this brazing process: honeycombs, corrugations and tube arrays. These structures have demonstrated pseudoelastic amplification, low density and high compliance.

Dissimilar formulations of NiTi can also be bonded together using this brazing technique; producing a eutectic structure upon cooling. In some cases, Ti₂Ni forms upon cooling instead of the eutectic because of oxygen contamination. Bonds between dissimilar NiTi sections could be used in applications such as complex biomedical devices that incorporate porous NiTi, wrought NiTi and chemical NiTi. Other devices, such as MEMS, could be built using lower cost chemical NiTi and thin film NiTi for pumps, motors, actuators and valves.

Thin films made on glass slides can be delaminated by carefully peeling them from glass slides after crystallization. These films, despite being amorphous during deposition, show good shape recovery and could be used for low hysteresis applications by taking advantage of the R-phase that is formed while cooling. Transformation temperatures for these films are above room temperature, which implies the films are very close to the ideal Ni:Ti ratio for shape memory. Thin films with alternating layers of Nb and NiTi can also be produced on glass slides. These films also show shape memory with high transformation temperatures. These films drastically increase the contact surface area between NiTi and Nb for brazing, which substantially increases the melting rate. Due to oxidation, higher phase fractions of Ti₂Ni are found in brazes with multilayers rather than with niobium foil.

The NiTi – Nb multilayer films can also be adjusted to have a specific ratio of nickel titanium to niobium. With this adjustment, the film can be altered to either selectively etch or deposit NiTi to the surfaces of braze joints.

Multilayers of NiTi and Nb thin films can also be used to join dissimilar materials with NiTi. Eutectic NiTi and Nb form in bonds with Al₂O₃, tantalum, niobium, tungsten and magnesium oxide. Combining NiTi multilayers and Nb coatings on dissimilar materials can eliminate undesired intermetallics from forming in Ti-6Al-4V bonds with NiTi.

Other materials bonded to NiTi that were investigated produced complex solidification products upon cooling. Bonds with Fe₂AlV, cobalt chrome, boron carbide and 304 stainless steel produce complex solidification products. Bonds with boron carbide and 304 stainless steel are weak. NiTi bonds with stainless steel are brittle because of a third, non-terminal phase containing a high concentration of Ni. Coating these materials with a thin film of niobium could reduce the phase fractions of these undesirable intermetallics.

The wetting angle between NiTi and the liquid changes when bonding Fe₂AlV with NiTi, and further understanding of this change could lead to discovery of a material that does not bond with the liquid. The thermal expansion mismatch between NiTi and boron carbide could help discover a material for fixturing NiTi in brazing furnaces.

DC spot welding has higher tensile strength than AC spot welding, in part due to shorter processing times and greater control of the waveform. Using multilayers to spot weld NiTi has proven unnecessary. Properly designed spot welds can be made without filler metals.

The niobium – nickel – titanium ternary system thus allows for a novel, robust brazing system capable of joining NiTi to many materials with strong bonds.

7 Future Work

Now that the NiTi-Nb brazing process has been shown to be robust and applicable to other materials, future research should be focused on industrial applications. Additionally, a material must be found that is not wetted by the eutectic liquid to help create manufactured devices. Bonds between Fe₂AlV and NiTi should be reexamined, focusing on the change in wetting angle between Fe₂AlV and NiTi.

While *in vivo* corrosion is not expected, a study should be conducted to determine if the galvanic potential between NiTi and Nb is large enough to corrode NiTi-Nb bonds.

A fatigue study of brazed NiTi structures should be conducted to determine the fatigue resistance in the bond. In particular, low strain tests should be conducted on the honeycombs, to test the long term behavior of these designs.

Cold rolling of thin films should be developed to produce working actuators. It should be possible to make a large scale model of the Johnson valve using a cold rolled thin film to open and close a valve should be possible to make and will serve as a proof of concept. This device could also be used for a fatigue study of NiTi thin films.

High resolution TEM (HRTEM) work should be conducted to determine if the quasibinary truly exists. Additionally, HRTEM should be capable of determining if Ti_2Ni forms inside bonds from oxygen stabilization or due to other reasons. Foils should be produced from arc-melted buttons of material, and the overall chemistry of the buttons should be verified by a method such as plasma flame spectroscopy. Some researchers have reported terminal phases in the Ni-rich half of the Ni-Ti-Nb ternary system that would slightly intersect the quasi-binary, and these results should be verified.

Bonds with monolithic, fully dense sections of MgO, hydroxyapatite and other important engineering ceramics should be investigated. If bonding NiTi to these materials using Nb foil proves to form undesirable intermetallics, diffusion barrier coatings on the ceramics should be investigated.

Appendices

A.1 Brazing using Centorr Annealing Furnace

A Centorr vacuum annealing furnace was used for many experiments in this thesis. It accommodates large samples and uses simple fixtures for positioning samples. The furnace is heated by helical tungsten filaments inside the vacuum chamber, which are controlled manually by a Honeywell Versa Pro UDC 3000 temperature controller.

The fixtures used for many experiments had considerable thermal mass and therefore limited the actual heating rate of the sample. By trial and error, it was determined that the sample should be heated to 1200°C in no less than 7 minutes. Heating rates around 100°C per minute were the standard throughout this thesis, following the heating curve shown in Figure 17, located in Section 2.3.3.

This Centorr vacuum furnace operated with base pressures between 1 μ Torr and 10 μ Torr, and working pressures between 5 μ Torr and 30 μ Torr, based on the exact condition of the heating chamber. Typically, the furnace was heated to a moderate temperature of approximately 200°C and allowed to reach a base pressure of < 5 μ Torr. Once this base pressure was reached, the sample was heated inside the chamber at a heating rate of approximately 50°C – 100°C per minute until the hold temperature, or dwell temperature, was established. The hold temperature was maintained for the desired time, or dwell time, then the power was shut off to allow the furnace to cool.

Once the temperature was below 100°C, the chamber was opened and the sample was retrieved. It should be noted that the samples could not be taken out at a higher temperature due to the brittle nature of the heating elements. Once the samples were retrieved, they were quenched in water for handling purposes.

A.2 Brazing using MILA ULVAC rapid thermal heating system

The MILA ULVAC rapid thermal processing furnace was used for small samples. While it is not capable of high vacuum, it heats and cools much faster than other, more conventional furnaces. The ULVAC furnace heats using reflective infrared heaters that are outside the chamber. The furnace also features a PID controller, which allows heating schedules to be very accurate and repeatable.

A CTI Cryogenics pump provided the medium vacuum source for the MILA ULVAC heater. While running standard tests, the samples were allowed to pump to a soft vacuum of 0.1 mTorr. When this vacuum was achieved, the sample was heated to the dwell temperature, typically 1185°C, in 40 seconds. The PID maintained this dwell temperature within 1 - 2°C for the prescribed dwell time, which typically varied between 5 seconds and 2 minutes. The maximum use temperature of the MILA ULVAC heater is 1200°C, so long brazing times cannot be run on this machine, as it will overheat. The sample was allowed to furnace cool, which was rapid because of the low thermal mass of the chamber. Heating elements do not add to the thermal mass because the heating is infrared from outside the chamber. Samples typically cool to below 800°C within the first 30 seconds.

171

A.3 Polyimide backed thin films

Polyimide films were included in this thesis because the previous work at Michigan State University on thin films has led to a greater understanding of the intricacies of DC magnetron sputtering thin films.

A.1.1 Introduction

Nitinol thin films have high work density compared with piezoelectrics and thermoelectrics. (Gill, Ho et al. 2002) Microelectro-mechanical systems can be made from Nitinol thin films and produce large amounts of work using very small films. The Johnson valve is capable of pumping one liter per minute of fluid through a small orifice using NiTi thin films. (Johnson, Gupta et al.) The device consisted of several Nitinol thin film ribbons released from single crystal silicon by etching. A silicon poppet was connected to one of the ligaments, which closed a small orifice below the silicon and that allowed fluid flow through the device. The entire device was placed into a pressure vessel and was connected to an electrical source. Pressure from a liquid deformed the thin film ligaments out of the plane, closing the valve. When electricity was applied to the valve, the ligaments heated and shortened, which brought them back into plane and opened the valve.

Other devices have been built using NiTi thin films on silicon. Krulevitch et al. built a micro-gripper from NiTi thin films deposited on silicon. This gripper developed 13 mN

of clamping force between the jaws, and was capable of clamping onto features as large as 110 μ m. (Lee, Ciarlo et al. 1996) Carman et al. created a microwrapper capable of gripping an object as large as 320 μ m in diameter. The wrapper is a single NiTi thin film on polyimide, both of which have been chemically milled. (Gill, D.T. et al. 2001)

The strain developed in these devices is based on the difference in thermal expansion coefficients between the substrate and the film. Only 1-2% strain can be developed in NiTi thin films with large thermal expansion mismatches between the substrate and film, which does not take full advantage of the complete thermal hysteresis of NiTi. To take full advantage of the thermal hysteresis available with NiTi, thin films should be strained to as much as 7% strain. This level of strain is not possible using thermal expansion mismatches. To mitigate this problem, cold rolling of thin films could introduce unidirectional strains in the substrate and thin film. While these unidirectional strains strains in the substrate and thin film. While these unidirectional strains strains could be somewhat elastically recovered in some substrates such as polyimide, other substrates like silicon are not compatible with the process.

Uniaxial deformation is a method for developing larger strains in NiTi thin films. Grummon et al. reported large reversible strains in upwards of 7% using thin films deposited on polyimide. However, these large strains were developed using uniaxial dead load experiments, which can be difficult using cut-out sections of a thin film. If a small defect, such as a crack or tear, is present at the edge of a thin film, the overall stress before failure of the film can be drastically reduced due to stress concentrations. (Grummon 1995)

173

Cold rolling NiTi films for actuators has been done by Miyazaki et al., with mild success. Thin plates of NiTi were cold rolled to thicknesses of approximately 100 μ m, and were further chemically milled as low as 25 μ m. (Miyazaki 2000) These thin plates showed shape memory and were suggested to work well in actuator applications. However, chemical milling is an expensive process that wastes large amounts of NiTi. Chemical milling was used by Miyazaki because cold rolling is limited by the maximum force the cold rolling mill can supply. As reported in literature, the minimum rolling thickness is dependent on materials constants as shown: (Hosford and Caddell 1993)

$$h_{\min} = \frac{C\mu R}{E'}(\sigma_o - \sigma_t)$$

Equation 2: Minimum height for cold rolling thin films.

Where E' is an effective Young's modulus, R is roller height, μ is the friction between the rollers and the film, σ_o is the flow stress of the film, σ_t is the unidirectional stress on the film if it was being pulled or pushed into the rolling mill and C is a geometric constant assumed to be 7, based on the literature. For typical values for NiTi thin films and cold rolling mills, the minimum thickness is near 20 μ m, which is 25 times larger than the film used for the microwrapper.

To cold roll thinner films, literature reports suggest sandwiching samples between thin plates of a material that is softer than the thin film. Assuming no slip between the layers, the strain observed in the soft material also transferred into the thin film. Therefore, much thinner films can be deformed uniaxially or even biaxially rolled using this process without relying on elaborate rolling mills or expensive chemical milling.

A.1.2 Materials and Methods

Based on work by predecessors at Michigan State University, depositions on 7.6 μ m thick Dupont Kapton[®] 30 HN polyimide were conducted at elevated temperatures using DC magnetron sputtering (Zhang 2006). The configuration of the deposition and annealing chamber can be seen in Figure 93.

The sputtering cathode composition used for all polyimide work was a $Ti_{53.5}$ -Ni_{46.5} composition, which produced thin films with austenite start temperatures around 57°C and finish temperatures around 93°C. Sputtering power during deposition was 200 W, maintained for 2 hours per film. After initial investigations to find the best temperature, depositions were conducted with a substrate topside temperature of 420°C using a 100 mm heater placed below the substrate. The substrates were at a distance of 51 mm from the surface of the sputtering target to yield thicker films per unit time than previous thin film work at MSU. It was discovered that if the substrate distance was lowered below 51 mm, the films grown would be brittle in nature. This resulted in an approximate sputtering rate of 4.5 µm per hour.

The polyimide substrates were held taunt in fixtures that made 75 mm diameter samples, the same diameter as the sputtering cathodes used. The base pressure of the high vacuum chamber before sputtering was always below 1 μ Torr. The working pressure during deposition was between 5.5 and 6 mTorr of 99.9995% purity argon gas, which was further purified by a Restek Thermal Gas Purifier, model 21662.

A post-deposition heat treatment was also performed before breaking high vacuum to ensure crystallization of the NiTi film and to reduce internal stresses. During annealing, the topside substrate temperature was held at 575°C for two hours, with a backside temperature of less than 450°C to protect the polyimide, which decomposes above 480°C in vacuum. This annealing occurred at the same time as the deposition of other films, to decrease processing time.

Following the post-deposition anneal, the thin films on polyimide were removed from the sample holders and were trimmed to remove the uncoated polyimide. This left the circles of polyimide coated with approximately 9 μ m of NiTi, shown in Figure 94.

The thin films were sandwiched between thin metal plates of aluminum, stainless steel or brass and cooled to 0°C to fully martensitize the films before being passed through a Fenn 152.4 mm cold rolling mill. The material used did not affect the cold rolling of the films. Successive passes increased strain in the film, in addition to curling the film, as shown in Figure 95. This curling effect was most likely due to differences in springback between the polyimide and the NiTi. To measure the strain, films were flattened and digitally scanned with a flatbed scanner at 1200 dots per inch before and after the cold rolling procedure.

176

Several thin films were rolled between 0% and 10% strain, by manual adjustments of the rolling mill. Films were limited to 6% strain after several films formed microcracks at 7% strain. To measure the recovered strain after heating, the films were scanned after a heat treatment in an air furnace at 150°C for 15 minutes to fully austenitize the film and compared with previous scans. An example of the as-rolled condition of a thin film is shown in Figure 94.



Figure 93: (a) DC Magnetron sputtering gun, (b) 75 mm heater for post deposition heat treatment and (c) the substrate holder showing thermocouple placement.



Figure 94: As-rolled thin film of $10 \ \mu m$ NiTi deposited on 7.6 μm thick polyimide. Puckering is present around the edges of the film from the deposition plastically deforming the polyimide. The film was coldrolled to approximately 5% strain.



Figure 95: Thin film (left) and aluminum plates after cold rolling (right).

A.1.3 Results and discussion

Thin films of NiTi are capable of strains up to approximately 6%, before developing cracks or other damage. It was observed that the films took on the surface features of the material they were sandwiched between, so adhesives were not used to adhere the film to the sandwich. Microcracking was observed in films that were inherently brittle from irregularities in the sputtering process, or were strained beyond 6%. An example of a microcrack from over-straining can be seen in Figure 97.

Thermally recovered strain was observed to increase linearly with rolling strain. A rolling strain of approximately 0.8% was observed to be thermally irrecoverable, as described in Figure 96. At the maximum limit of 6% rolling strain, it is possible to induce up to 3.5% reversible strain in a thin film. This represents approximately a 350% increase in the maximum strain compared with silicon based NiTi films.

The microstructure of the thin films was inspected using a Camscan SEM equipped with a backscattered electron detector. A thin film produced was cross-sectioned and imaged with backscattered electrons. The sample was etched to reveal grain boundaries, shown in Figure 98. The film contained equiaxed grains ranging from approximately 1 to 10 μ m in diameter. As previously reported, good mechanical properties are obtained from a thin film containing equiaxed grains rather than columnar grains. (Hou 1998) It is also interesting that the grain boundaries fade away near the polyimide layer, which could be a result of anisotropic etching or a transition to an amorphous NiTi layer.

DSC results, Table 21, obtained from the Composite Center at Michigan State University, suggest that the thin films created by this method are Ti-rich based on the transformation from B2 austenite to R-phase to B19' martensite. (Otsuka and Ren 2005)

 Table 21: Transformation temperatures for thin film 052307A. Obtained from DSC results displayed in Figure 99.

M _f	Ms	R _f	R _s	A _s	A _f	
7°C	22°C	48°C	58°C	62°C	76°C	



Figure 96: Collective results of cold rolling experiments. As rolling strain increases, the thermally recoverable strain also increases. 0.8% of the rolling strain is permanent. Cracking becomes present in thin films rolled beyond 6 to 7% strain, shown in Figure 97.



Figure 97: Microcrack developed after the sample was cold rolled beyond 6% strain. This SEI from a Phillips Sirion SEM equipped with a field emission gun operating at 25 keV. Bright area is charging on the underlying polyimide.



Figure 98: BEI of NiTi thin film on polyimide (bright stripe along bottom of film). The grain boundaries of the film appear to terminate roughly one µm away from the polyimide film, which could be an etching effect or transition to anorphous NiTi.



Figure 99: DSC results from sample 052307A, a 10 µm thin film on a 7.6 µm thick polyimide substrate.

A.4 Freestanding thin film creation

Freestanding thin films of NiTi are of great technical importance. Not only can freestanding thin films show shape memory, but they can also be used as a basis for nickel titanium multilayers.

Freestanding thin films are grown on glass microscope slides at ambient temperatures, then post-crystallized and later manually peeled from the glass slide surface. The adhesion between the glass slides and NiTi thin films must be engineered properly to allow the films to be peeled off. If the films are not sputtered correctly, adhesion will be either too weak or too strong. If the adhesion is too weak the film can delaminate during the deposition process, which distorts the surface finish and shape of the film.

Conventional glass microscope slides were purchased precleaned from MSU stores. Before putting the slides into the sputtering chamber, the slides were given a final cleaning in acetone to remove any fingerprints or other contaminants. Acetone was chosen because it leaves a faint residue on the surface of the glass slides, which helps film removal.

To deposit the thin film, the chamber was allowed to reach a base pressure of $< 3 \mu$ Torr. The sputtering conditions for creation of freestanding thin films will be discussed in detail in Appendix A.5, but are summarized in Table 22.

Base Pressure	Working distance	Working pressure	Sputter	Sputter Rate
			Power	
< 3 x 10 ⁻⁶ Torr	50 mm	Initial: 7.5 x 10 ⁻³ Torr, 0.1 hr	200 Watts	4.5 μm/hr
		Remaining: $< 5 \times 10^{-3}$ Torr		
Ambient	Post sputter anneal	Post sputter anneal time	Sputtering	
Temperature	temperature		Cathode	
20°C	575°C	1.5 hr	Ti53.1-Ni46.9	

Table 22: Sputtering conditions for freestanding NiTi thin films.

To ensure correct adhesion between the film and slide, the working pressure during the first five minutes of the deposition was maintained at 7.5 mTorr, which is significantly higher than throughout the rest of the deposition. After five minutes, the pressure was lowered from 7.5 mTorr to below 5 mTorr. The pressure is further lowered to 4 mTorr if the plasma can be sustained.

After the completion of deposition, the thin films are crystallized using a Centorr vacuum annealing furnace. The films are heated to a temperature of 575°C for 1.5 hours and are then furnace cooled. Once they have been annealed, one of the glass slides is placed in a Scintag 2000 XRD to check for full crystallinity of the film. If the film is fully crystalline and shows X-ray peaks corresponding to a martensite crystal structure, the films are detached from the glass slides. If the film does not show a martensite structure, however, the films are heated in the annealing furnace for another hour. The variation in annealing time stems from changes in fixturing and thermocouple placement in the vacuum annealing furnace.

To remove the thin films, a glass cutter is used to score the glass and break it in half. The thin film is then peeled slowly away from the surface of the glass at a 45° angle to the

glass. The film sometimes catches on the edges of the glass slide and begins to tear, forceps are used to scrape the thin film to release it from the glass slide.

Currently, this process creates cellular-type grain growth in the thin films. It is believed that by raising the temperature of the deposition, the grain shape could be altered. Depositing fully crystalline films is also a possibility using high temperature depositions, around 400°C, but has not been explored yet. If this technique works on glass slides, the important factor in allowing film removal will be a high working pressure for the first few minutes of the deposition.

A.5 Multilayer creation

Multilayers of nickel titanium and niobium were made using DC magnetron sputtering in an ultra high vacuum chamber at Michigan State University. The films were created with two sputtering guns, shown in Figure 93, which were equipped with an off-stoichiometric nickel titanium cathode and a 99.9995% pure niobium cathode. The working distance between each of the cathodes and the glass slide substrates was 51 mm during deposition. The sputtering took place simultaneously on both sputtering guns with two sets of substrates. The substrates were rotated from one sputtering gun to the other after each deposited layer.

Before sputtering, the pressure in the vacuum chamber was less than 3 μ Torr. To assist pumping, halogen bake-out lights were used to heat the chamber to an elevated temperature, which helped drive off water from surfaces inside the chamber. An inert atmosphere ultra-high purity argon was maintained at a pressure of less than 5 mTorr during deposition. The argon supply was 99.9995% pure, and was further purified with a Restek thermal purifier.

Niobium was chosen as the top layer of the multilayer to avoid readily forming NiTi oxides. The sputtering power of each sputtering gun was adjusted so that the sputtering rates matched the desired foil composition of 2.2 NiTi : 1 Nb. The power of the NiTi sputtering gun was limited to less than 250 W due, to concerns that compositional changes in the NiTi films could occur at high cathode powers.

The deposition was conducted at room temperature so that adhesion between the thin film and the substrate would be low. As adhesion is expected to decrease with increasing working pressure, the first layer of the multilayers were deposited at a working pressure of 7 mTorr. Following deposition, the samples were annealed inside a vacuum furnace for 1.5 hours at 575°C to crystallize the NiTi phase and reduce any residual stresses in the thin film. Multilayers are removed the same way as freestanding thin films.

A.6 Oxide Removal Etch

Throughout this work, steps have been taken to minimize substantial oxide formation from thermal exposure. Oxides were removed from samples before brazing. Low base pressures were observed during brazing, and heating and cooling times were minimized to reduce oxide formation. Brazing NiTi, as well as crystallizing thin films, both take place in hard vacuum.

186

Some of the material received from NDC had a thick black oxide coating on it, which had to be removed before brazing. If the oxide was not removed before thermal exposure, the metal became embrittled, most likely due to the diffusion of interstitials into the B2 crystal structure.

One etchant recipe, a combination of nitric and hydrofluoric acids, was used for all oxide removal. These acids were mixed with liberal amounts of water to control the rate of etching. After some initial experimentation, it was determined that a recipe of 10 HNO_3 : $10 \text{ H}_2\text{O}$: 1 HF removed the oxide layer from the nickel titanium quickly without significantly attacking the base metal. This is also safer than other recipes that use larger concentrations of hydrofluoric acid. (Chiu, Cheng et al. 2005) (Gill, Ho et al. 2002)

The oxide removal etch was used primarily on the NiTi strip material, which was received with an oxide layer approximately 0.025 mm thick. The material was etched before and after shape setting the material. It was observed that the oxide layer was more difficult to completely remove if the material was not etched before shape setting.

Typically, samples were left to etch for no more than 2 minutes, with some material needing as little as 10 to 20 seconds before the oxide was completely removed. Once removed, the pieces were washed in tap water. The etching rate and variation in the oxide thickness account for the wide range in etching time required. The etching rate is dependent on the temperature of the chemical bath, which increases with the total amount of metal that has already been etched and the amount currently being etched.

187

A.7 Metallurgical Etch

The standard metallurgical etchant used is 20 HNO_3 : $100 \text{ H}_2\text{O}$: 10 HF, which yielded the best etching effect.

Etching time, as discussed in Appendix A.6, is dependent on many factors. Metallurgical samples were etched for 10 seconds to 120 seconds with good results. To ensure proper etching, the samples were etched, rinsed in tap water, and then viewed under an optical microscope. The etching was completed when the grains of the nickel titanium were distinguishable with a set of polarizing filters on an optical reflection microscope.

A.8 Tacking NiTi to Nb using AC spot welding

Using a low intensity pulse of AC power, Nb can be tacked to NiTi with enough strength to allow manual assembly of large NiTi arrays. An AC spot welder was homemade from a hand-wound transformer. The nominal output of the spot welder was 5 volts, and could supply up to 100 amps, based on the resistance of the pieces that were to be joined. The power output was limited to 0.10 seconds; with a square wave output centered around 0 volts.

The tacking process could only be used for thin gages of NiTi, such as strip NiTi, NiTi thin films, Nb wires and Nb foils. Thicker materials, like the plate NiTi, had a higher resistance and thermal mass, which limited the current in the joint enough to prevent

tacking. Using a higher power would have solved this, but this machine was only designed to tack thin gages of NiTi and Nb.

The joint was made by placing two or three pieces of NiTi and Nb together between two 14 gage copper wires. The wires were stiff enough to exert a small pressure onto the pieces and push them together. The electrical pulse was carried through the wires and into the sandwich of materials, where it made very small spot welds between the pieces. These spot welds were the basis for the research into true spot welding technology, which uses higher powers and much larger contact forces.

A.9 Post Braze Heat Treatment

To restore the pseudoelastic functionality of Ni-rich NiTi after brazing, a low temperature heat treatment was performed. During this heat treatment, the Ni₄Ti₃ metastable phase precipitates in finely dispersed particles, which raised the stresses required for dislocation motion in the NiTi B2 phase. Samples were heated in an air furnace to a temperature of 350°C for 1.5 hours and then quenched in water. This heat treatment was chosen by Ke Bin Low, working under Dr. Grummon at Michigan State University, and was borrowed for the production of NiTi arrays.

Bibliography

- Cheng, Y., W. Cai, et al. (2006). "Surface modification of NiTi alloy with tantalum to improve its biocompatibility and radiopacity." <u>Journal of Materials Science</u> 41: 4961-4964.
- Chiu, K. Y., F. T. Cheng, et al. (2005). "A preliminary study of cladding steel with NiTi by microwave-assisted brazing." <u>Materials Science & Engineering A</u> 407: 273-281.
- Cho, H., H. Y. Kim, et al. (2005). "Fabrication and characterization of Ti-Ni shape memory thin film using Ti/Ni multilayer technique." <u>Science and Technology of</u> <u>Advanced Materials</u> 6: 678-683.
- Chu, C. L., C. Y. Chung, et al. (2005). "Phase transformation behaviors in porous Ni-rich NiTi shape memory alloy fabricated by combustion synthesis." <u>Materials Science</u> <u>& Engineering A</u> 392: 106-111.
- Falvo, A., F. M. Furdiuele, et al. (2005). "Laser welding of a NiTi alloy: Mechanical and shape memory behaviour." <u>Materials Science & Engineering A</u> **412**: 235-240.
- Fernandes, F. M. B., R. Martins, et al. (2002). "Structural characterisation of NiTi thin film shape memory alloys." <u>Sensors and Actuators A Physical</u> **99**: 55-58.
- Foltz, J. W., D. S. Grummon, et al. (2006). "Plastic Deformation of Sputtered NiTi Thin Films on Polyimide Substrates by Co-Rolling." <u>Shape Memory and Superelastic Technologies Proceedings</u>: 1-7.
- Gale, W. F. and Y. Guan (1997). "Microstructural development in copper-interlayer transient liquid phase bonds between martensitic NiAl and NiTi." Journal of <u>Materials Science</u> 32: 357-364.
- Gaskell, D. R. (1995). Introduction to the Thermodynamics of Materials, Taylor & Francis.
- Gill, J. J., C. D.T., et al. (2001). "Manufacturing issues of thin film NiTi microwrapper." <u>Sensors and Actuators A: Physical</u> 93(2): 148-156.

- Gill, J. J., K. Ho, et al. (2002). "Three-Dimensional Thin-Film Shape Memory Alloy Microactuator with Two-Way Effect." <u>Journal of Microelectromechanical</u> <u>Systems</u> 11(1): 68-77.
- Greiner, O., Dunand (2005). "High Strength, low stiffness, porous NiTi with superelastic properties." <u>Acta Biomaterialia</u> 1(1): 705-716.
- Grummon, D. S. (1995). "Progress on Sputter-Deposited Thermotractive Titanium-Nickel Films." Journal de Physique IV(C8).
- Grummon, D. S., S. Nam, et al. (1992). "Effect of superelastically deforming NiTi surface microalloys on fatigue crack nucleation in copper." <u>Materials Research</u> <u>Society Symposium Proceedings</u> 246: 259-264.
- Grummon, D. S., J. A. Shaw, et al. (2003). "Low-density open-cell foams in the NiTi system." <u>Applied Physics Letters</u> 82(16): 2727-2729.
- Gupta, K. P. (1991). "Phase Diagrams of Ternary Nickel Alloys, Part 2, Section D.2, The Nb-Ni-Ti (Niobium-Nickel-Titanium) System." 98-112.
- Hall, P. C. (1997). <u>Methods of Promoting Solder Wetting on Nitinol</u>. SMST, Asilomar, Pacific Grove, CA, ASM International.
- He, X. M. and L. J. Rong (2004). "DSC analysis of reverse martensitic transformation in deformed Ti-Ni-Nb shape memory alloy." <u>Scripta Materialia</u> 51: 7-11.
- Hosford, W. F. and R. M. Caddell (1993). <u>Metal Forming: Mechanics and Metallurgy</u>. New Jersey, Prentice-Hall.
- Hou, L. (1998). Processing, Microstructure and Thermomechanical Behavior of Superelastic Nickel-Titanium thin films sputter-deposited at elevated temperatures. Michigan State University, Michigan State University.
- Johnson, Gupta, et al. "Silicon Oxide Diaphragm Valves and Pumps with TiNi Thin Film Actuation." <u>TiNi Alloy Company</u>.

- Karagoulis, M. (1991). Control of Materials Processing Variables in Production Resistance Spot Welding. <u>Metallurgy, Mechanics, and Materials Science</u>. East Lansing, MI, Michigan State University. **Doctor of Philosophy:** 10-15.
- Karagoulis, M. (1991). Control of Materials Processing Variables in Production Resistance Spot Welding. <u>Metallurgy, Mechanics, and Materials Science</u>. East Lansing, MI, Michigan State University. **Doctor of Philosophy:** 15-25.
- Lee, Ciarlo, et al. (1996). "A practical microgripper by fine alignment, eutectic bonding and SMA actuation." <u>Sensors and Actuators A Physical</u> 54.
- Li, B. Y., L. J. Rong, et al. (1998). "Porous NiTi alloy prepared from elemental powder sintering." Journal of Materials Research 13(10): 2847-2851.
- Li, M. G., D. Q. Sun, et al. (2006). "Effects of laser brazing parameters on microstructure and properties of TiNi shape memory alloy and stainless steel joint." <u>Materials</u> <u>Science & Engineering A</u> 424(1): 17-22.
- Low, K. B. (2006). Current Research, Michigan State University.
- Low, K. B. (2007). Current Research, Michigan State University.
- Lütjering, G. and J. C. Williams (2007). <u>Titanium</u>, Springer.
- MacDonald, W. D. and T. W. Eagar (1992). "Transient Liquid Phase Bonding Processes." <u>The Metal Science of Joining</u>.
- Massalski, T. B. (1986). <u>Binary Alloy Phase Diagrams</u>. Metals Park, American Society for Metals.
- Memry, C. (2006). "Nitinol FAQ." Retrieved 6/20, 2007, from <u>http://www.memry.com/nitinolfaq/nitinolfaq.html#solderedWeb</u>.
- Miyazaki, S. (2000). "Texture of Ti-Ni rolled thin plates and sputter-deposited thin films." Journal of Plasticity 16: 1135-1154.
- Otsuka, K. and X. Ren (2005). "Physical metallurgy of Ti-Ni-based shape memory alloys." <u>Progress in Materials Science</u> 50: 521.

- Piao, M., S. Miyazaki, et al. (1992). "Effects of Nb Addition on the Microstructure of Ti-Ni Alloys." <u>Materials Transactions</u> 33(4): 337 - 345.
- Porter, D. A. and K. E. Easterling (1989). <u>Phase Transformations in Metals and Alloys</u>. London, Van Nostrand Reinhold.
- Prima, S. B., L. A. Tret'yachenko, et al. (1995). "Phase Relationships In The Ti-TiNi-NbNi-Nb Region of the Ternary System Ti-Nb-Ni." <u>Powder Metallurgy and</u> <u>Metal Ceramics</u> 34(3,4): 155-160.

Saburi, T. "Ti₄₈Ni₅₂ Quench from 1000^OC." <u>Proc. Mat. Res. Soc.</u> 9: 78.

- Schlossmacher, P., T. Hass, et al. (1997). <u>Laser-Welding of a Ni-rick TiNi Shape</u> <u>Memory Alloy: Pseudoelastic Properties</u>. SMST, Asilomar, Pacific Grove, CA, ASM International.
- Sinha, A. K. (2003). Physical Metallurgy Handbook, McGraw-Hill Handbooks.
- Wang, G. (1997). <u>Welding of Nitinol to Stainless Steel</u>. SMST, Asilomar, Pacific Grove, CA, ASM International.
- Wert, C. and R. Thomson (1970). Physics of Solids, McGraw-Hill Book Company.
- William D. Callister, J. (2003). <u>Materials Science and Engineering: An Introduction</u>, John Wiley & Sons, Inc.
- Zhang, J. X., M. Sato, et al. (2005). "Deformation Mechanism of martensite in T-rich Ti-Ni shape memory alloy thin films." <u>Acta Materialia</u> 54: 1185-1198.
- Zhang, Y. (2006). NOVEL TRIBOLOGICAL SYSTEMS USING SHAPE-MEMORY ALLOYS AND THIN FILMS.

