Characterization of nickel-titanium based thin films crystallized by fast and ultra-fast annealing methods

Motemani Sharabiani, Yahya

2012

Motemani Sharabiani, Y. (2012). Characterization of nickel-titanium based thin films crystallized by fast and ultra-fast annealing methods. Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/48649>

<https://doi.org/10.32657/10356/48649>

NANYANG
TECHNOLOGICAL
UNIVERSITY

**CHARACTERIZATION OF NICKEL-TITANIUM BASED THIN
FILMS CRYSTALLIZED BY FAST AND ULTRA-FAST
ANNEALING METHODS**

YAHYA MOTEMANI SHARABIANI
SCHOOL OF MECHANICAL AND AEROSPACE ENGINEERING
2012

**CHARACTERIZATION OF NICKEL-TITANIUM BASED THIN
FILMS CRYSTALLIZED BY FAST AND ULTRA-FAST
ANNEALING METHODS**

YAHYA MOTEMANI SHARABIANI

School of Mechanical and Aerospace Engineering

A thesis submitted to the Nanyang Technological University
in partial fulfillment of the requirements for the degree of
Doctor of Philosophy

2012

To my lovely wife,

Sara

Acknowledgements

I would like to express my sincere gratitude to my adviser, Prof. Tan Ming Jen for his guidance, support, patience and encouragement. I am also grateful to my co-adviser Prof. Timothy John White for his support and fruitful discussions.

I would also like to extend my sincere gratitude to Prof. J.J. Vlassak for giving me the opportunity to visit Harvard University. I enjoyed working under his supervision and appreciate his constant guidance, encouragement and fruitful discussions. I am also grateful to Dr. Patrick McCluskey, who has continually and actively supported my efforts and experiments through the duration of my project at Harvard. The author is also especially indebted to Prof. Chunwang Zhao for his assistance and support in TEM analysis.

The author is also especially thankful to Dr. Banas Agnieszka from the Singapore Synchrotron Light Source (SSLS) for her support and help in EXAFS measurements. I am also grateful to Prof. Huang Wei Min and Prof. Christopher Shearwood for their fruitful discussions. Many thanks are due to the technicians of Materials Laboratories 1 and 2, and Micro-Machine Center, especially Mr. Pek Soo Siong and Ms. Yong Mei Yoke for their kind support. Special thanks go to Mr. Jia Wen and Ms. Shi Wen for their assistance and support.

I also would like to thank my friends, who created a friendly and pleasant working environment during this study.

I am deeply grateful to my kind mother, father and sister for their support, love and encouragement. Last but not least, I would like to express my sincere gratitude to my wife,

Sara, for her love, patience and encouragement. Her support and sacrifice throughout these years are the reasons for my achievements.

Publications

(a) Journal Papers

- (1) **Y. Motemani**, P.J. McCluskey, M.J. Tan, J.J. Vlassak, C. Zhao, Analysis of Ti-Ni-Hf shape memory alloys by combinatorial nano-Calorimetry, *Acta Materialia*, Vol. 59, pp. 7602-7614, 2011.
- (2) **Y. Motemani**, M.J. Tan, T.J. White, A. Banas, Evolution of structural, surfacial and mechanical properties of titanium-nickel-copper thin films during rapid thermal annealing, *Surface and Coatings Technology*, Vol. 205 (10), pp. 3147-3157, 2011.
- (3) **Y. Motemani**, M.J. Tan, T.J. White, W.M. Huang, Rapid thermal annealing of Ti-rich TiNi thin films: A new approach to fabricate patterned shape memory thin films, *Materials and Design*, Vol. 32, pp. 688-695, 2011.
- (4) **Y. Motemani**, M. Nili-Ahmadabadi, M.J. Tan, M. Bornapour, Sh. Raygan, Effect of cooling rate on phase transformation behavior and mechanical properties of Ni-rich NiTi shape memory alloys, *Journal of Alloys and Compounds*, Vol. 469, pp. 164-168, 2009.

(b) Conference Papers

- (1) **Y. Motemani**, M.J. Tan, T.J. White, Crystallization of nickel-titanium based shape memory thin films by rapid thermal annealing, *Material Science and Technology 2010 Conference and Exhibition*, October 17-21, Houston, United States, 2010.
- (2) P.J. McCluskey, C. Zhao, **Y. Motemani**, J.J. Vlassak, Structural analysis of nickel-titanium based shape memory alloys synthesized by combinatorial nano-Calorimetry, *ASME 2010 International Mechanical Engineering Congress & Exposition*, November 12-18, Vancouver, British Columbia, Canada, 2010.

- (3) **Y. Motemani**, M.J. Tan, T.J. White, A. Banas, Structural study of titanium-nickel-copper shape memory thin film after rapid and conventional thermal annealing, 3rd SSLS Synchrotron Radiation Workshop and Users' Meeting, November 20, Singapore, 2009,
- (4) **Y. Motemani**, M.J. Tan, T.J. White, W.M. Huang, C. Shearwood, Crystallization behavior of Ti-rich TiNi shape memory thin film: A new approach to fabricate combinatorial TiNi-based shape memory thin films, NTU-Tohoku Research Student Workshop on Materials Integration for Health, Energy and Better Environment, February 10-11, Sendai, Japan, 2009.
- (5) **Y. Motemani**, M.J. Tan, T.J. White, W.M. Huang, C. Shearwood, Crystallization of Ti-Ni-Cu shape memory alloys thin film by rapid thermal annealing (RTA), Third International Conference on Processing Materials for Properties (PMP III), December 7-10, Bangkok, Thailand, 2008.
- (6) **Y. Motemani**, M.J. Tan, T.J. White, C. Shearwood, W.M. Huang, Rapid thermal annealing (RTA) of Ti-rich TiNi thin films, Thin Film 2008, July 14-16, Singapore, 2008 .

Abstract

Titanium-nickel based thin films can be used as actuators in micro-electro-mechanical systems (MEMS) in such applications as valves, pumps, grippers and sensors. These films are typically prepared using magnetron sputtering. The resultant films are amorphous if deposited at room temperature and annealing is necessary as actuation occurs in the crystalline state by a martensitic phase transformation. Consequently, understanding the nature of the annealing process is critical for microstructural control and optimization of MEMS actuators.

The first part of the study is concerned with describing and correlating the evolution of structural, surfacial and nano-scale mechanical properties of amorphous Ti-Ni-Cu thin films crystallized by rapid thermal annealing (RTA), where the treatment takes place under a protected atmosphere by electromagnetic irradiation with fast heating rate ($< 100\text{ }^{\circ}\text{C/sec}$). Long range order of amorphous Ti-Ni-Cu thin films was achieved in a few seconds ($> 60\text{ sec}$), with the optimum crystallization temperature of 480°C . The fast crystallization process allows the precise control of microstructure in a lower thermal budget (product of processing temperature and time). With increasing the annealing time (up to 180 sec), roughness increased dramatically, and was far more prominent than in films prepared by conventional thermal annealing (CTA). Although RTA is energy efficient due to the shorter annealing time, the film roughness is less ideal than CTA, which may prove limiting in specific applications. Using X-ray absorption spectroscopy (XAS), it was found that the RTA (180 sec) and CTA (1 hr) films possessed the longest range order. The evolution of the nano-scale mechanical properties of the RTA films during annealing was also studied,

and demonstrated the suitability of nanoindentation as a simple and reliable tool to study crystalline domain formation in Ti-Ni-Cu thin films.

In the second part of this study, the martensitic transformation, crystallization and thermal cycling behavior of Ti-Ni-Hf thin films were analyzed as a function of composition using a high-throughput array of nanocalorimeters. Amorphous as-deposited thin-film samples were crystallized by local heating at a rate of approximately 1.6×10^4 °C/sec, resulting in an ultra-fine (18 ± 5 nm) grain structure. The (Ti,Hf)-rich Ti-Ni-Hf alloy compositions with Ni contents below ~ 49.3 at.% exhibited the martensite-austenite transformation. The transformation temperature increases linearly with increasing Hf content in the range 14-20 at.% at a rate comparable to that observed for bulk materials, but with reduced martensite-austenite transformation temperature. The decrease in transformation temperature is caused by the fine nano-scale structure in Ti-Ni-Hf thin samples.

The response of Ti-Ni-Hf thin films to high-temperature cycling ($22^\circ\text{C} < T < 850^\circ\text{C}$) changes with Ni concentration. For $\text{Ni} \leq 47$ at.%, the transformation temperature increases during high-temperature cycling due to precipitation of $(\text{Ti}_{1-x}\text{Hf}_x)_2\text{Ni}$ and the resulting enrichment of Hf in the surrounding matrix, while for $\text{Ni} \geq 47.7$ at.% the transformation is gradually suppressed due to the lack of undercooling as a result of a reduction in transformation temperature. Low-temperature cycling ($22^\circ\text{C} < T < 450^\circ\text{C}$) resulted in a decrease and stabilization of the transformation temperature. Relaxation of internal stresses by dislocations generated during thermal cycling is suggested as the active mechanism. Thermal cycling stability of the films was improved compared to previous studies on bulk Ti-Ni-Hf. This was attributed to the very small grain size (18 ± 5 nm) of the samples. Alloys with superior thermal cycling stability; i.e. $\text{Ti}_{39.6}\text{Ni}_{46.1}\text{Hf}_{14.3}$ and $\text{Ti}_{42.3}\text{Ni}_{42.5}\text{Hf}_{15.2}$ are

identified. The ability to control the transformation temperature through multiple thermal cycling has been demonstrated. A significantly improved level of time efficiency is achieved using an ultra-fast analysis of Ti-Ni-Hf sample library in a high-throughput manner.

Table of Content

Dedication	i
Acknowledgments	ii
Publications	iv
Abstract	vi
Table of Content	ix
List of Figures	xiii
List of Tables	xxi

Chapter 1

1. Introduction	1
1.1. Background and Problem Statement	1
1.2. Objectives and Scope	4
1.3. Organization of the Thesis	6

Chapter 2.....8

2. Literature Survey	8
2.1. Shape Memory Alloys.....	8
2.1.1. History	8
2.1.2. Shape Memory Alloys Compositions.....	9
2.2. TiNi-based Shape Memory Alloys.....	10
2.2.1. Thermoelastic Martensitic Transformation	10
2.2.2. Crystal Structures of TiNi-based Alloys	14
2.2.3. Functional Properties of TiNi-based Alloys.....	17
2.3. TiNi-based SMA Thin Films.....	19
2.3.1. Fabrication Techniques	20
2.3.2. Crystallization of TiNi-based Thin Films	22
2.3.3. TiNi binary SMA Thin Films	25

2.3.4. Ti-Ni-Cu SMA Thin Films	29
2.3.5. Ti-Ni-Hf SMA Thin Films	30
2.4. TiNi-based SMA Thin Film Applications.....	31
2.4.1. Micro Pumps and Micro Valves.....	32
2.4.2. Micro Wrappers.....	33
2.4.3. Micro Actuators in Microsurgery	34
2.5. Summary	35
Chapter 3.....	36
3. Fabrication, Processing and Characterization Techniques.....	36
3.1. Fabrication and Characterization of Ti-Ni-Cu thin films.....	37
3.1.1. Fabrication of Amorphous Ti-Ni-Cu Thin Films	37
3.1.2. Crystallization of Amorphous Ti-Ni-Cu Thin Films.....	39
3.1.3. Characterization Methods.....	41
3.2. Analysis of Ti-Ni-Hf Thin Films by PnSC	48
3.2.1. Physical Description of Parallel nano-Scanning Calorimeter	49
3.2.2. Device Fabrication	51
3.2.3. Ti-Ni-Hf Library Synthesis	54
3.2.4. Calorimetric Measurement	59
3.2.5. Structural Analysis Methods	66
3.3. Summary	67
Chapter 4.....	69
4. Characterization of Amorphous Ti-Ni-Cu Thin Films Crystallized by Rapid Thermal Annealing	69
4.1. Crystallization of Amorphous Ti-Ni-Cu Thin Films.....	69
4.2. Changes in Surface Morphology of Ti-Ni-Cu Film during RTA.....	72
4.3. Comparison of Surface Chemistry in RTA and CTA Films	77
4.4. Comparison of Local Atomic Structure in RTA and CTA Films	85
4.5. Evolution of Nanomechanical Properties due to RTA Crystallization	90

4.6. Challenges on Characterization of Transformation Temperatures and Functional Properties.....	94
4.7. Summary	98
Chapter 5	100
5. Phase Transformation Study of Ti-Ni-Hf Thin Films Using Parallel nano-Scanning Calorimetry.....	100
5.1. Crystallization of the Ti-Ni-Hf Sample Library	101
5.2. Martensite-Austenite Transformation in the Ti-Ni-Hf Sample Library	112
5.3. Summary	120
Chapter 6	122
6. Effect of Thermal Cycling on Transformation Behavior of Ti-Ni-Hf Thin Films.....	122
6.1. Low Temperature Cycling (LTC)	124
6.2. High Temperature Cycling (HTC)	129
6.3. Control of Transformation Temperature Aided by Multiple Thermal Cycling	137
6.4. Comparison between PnSC and Traditional Calorimetry: Time Assessment.....	138
6.5. Summary	139
Chapter 7	140
7. Conclusions	140
7.1. Characterization of Amorphous Ti-Ni-Cu Thin Film Crystallized by Rapid Thermal Annealing.....	140
7.2. Phase Transformation Study of Ti-Ni-Hf Thin Film Library Using Parallel nano-Scanning Calorimetry (PnSC)	142
7.3. Effect of Thermal Cycling on Transformation Behavior of Ti-Ni-Hf Thin Films...	143
Chapter 8	145

8. Suggestions for Future Work	145
8.1. Investigation of Crystallization Mechanism during RTA Treatment.....	145
8.2. Investigation of Shape Memory Effect and Superelasticity in Freestanding SMA Films Crystallized by RTA.....	146
8.3. Investigation of the Crystallization Kinetics in SMA Thin Films using PnSC.....	146
8.4. Development of a PnSC to Characterize SMA Thin Films with Low Transformation Temperatures (< Room Temperature)	147
References	148

List of Figures

Figure 2-1 DSC thermogram of a NiTi alloy [77].	11
Figure 2-2 M_s transformation temperature as a function of Ni content for binary Ti–Ni alloys. The solid line is from thermodynamic calculations [54, 79].	12
Figure 2-3 (a) austenite and (b) martensite crystal structures (The red and black balls indicate Ni and Ti atoms respectively [68].	15
Figure 2-4 A DSC curve for a Ni-rich TiNi SMA showing the R-phase transformation [67].	16
Figure 2-5 Schematic representation of the R-phase crystal structure [87].	16
Figure 2-6 Shape memory effect with respect to crystal structure, temperature and deformation [68].	18
Figure 2-7 Schematic representation of superelastic effect in shape memory alloys. The E_D represents the amount of dissipated strain energy, while the E_R is the amount of recoverable strain energy [77].	19
Figure 2-8 Schematic illustration of the sputtering configuration for preparing Ti–Ni–Cu thin films [13].	21
Figure 2-9 Schematic of the annealing techniques for crystallization of TiNi-based thin films; (a) conventional thermal annealing (CTA), (b) rapid thermal annealing (RTA) and (c) electrical thermal annealing (ETA).	26
Figure 2-10 Strain–temperature curves of Ti–Ni thin films under constant stresses: (a) near equiatomic composition, (b) Ni-rich composition. Films were crystallized by the heat-treatment at 500°C for 1 h. (a) shows one-stage transformation, while (b) shows two-stage transformation [111].	27
Figure 2-11 Ti–Ni binary phase diagram [112].	28

Figure 2-12 Micropump structure with SMA thin film actuator: (a) pressurization type; (b) evacuation type [6].	32
Figure 2-13 The micro-wrapper made of free-standing TiNi films [121].	33
Figure 2-14 Concept of actuation: (1) setting; (2) hold actuation; (3) pulse monitoring; (4) release actuation and (5) pull out [123].	35
Figure 3-1 Flow chart showing the experimental procedures and analyses methods.	38
Figure 3-2 The Coaxial MSS3A sputtering system.	39
Figure 3-3 a) Rapid thermal annealing; b) Conventional thermal annealing (vacuum tube furnace).	40
Figure 3-4 Schematic of the RTA processing.	41
Figure 3-5 The schematic of thermal profile during RTA treatment [124].	41
Figure 3-6 A typical indentation load-depth curve during nanoindentation [130].	46
Figure 3-7 (a) Photograph of the Parallel nano-Scanning Calorimeter; (b) Labeling of the calorimetric cells. The segment (a) has been drawn after Fig. 1 in Ref. [51].	50
Figure 3-8 Layout of the nano-calorimeter cell: (a) cross-section, and (b) plane-view schematic. Heater line-width is 0.8 mm and voltage probe line-width is 0.1 mm [51].	51
Figure 3-9 Cross section schematic of a nano-calorimeter cell during steps (a)-(g) in the PnSC fabrication process [51].	53
Figure 3-10 Sputter deposition schematic of Ni-Ti-Hf samples. The figure has been drawn after Fig. 4 in Ref. [51].	56
Figure 3-11 Photograph of the micro-machined shadow mask.	57
Figure 3-12 A Ti-Ni-Hf free-standing film.	58
Figure 3-14 Typical raw voltage recordings for a PnSC cell with Ni-Ti-Hf sample for an 86 mA current pulse lasting 25 ms.	60
Figure 3-15 Calibration fit of the temperature coefficient of resistance.	61

Figure 3-16 Vacuum chamber for the calorimetric measurement.....	62
Figure 4-1 XRD patterns of the Ti-Ni-Cu thin film in the as-sputtered condition and different crystallization temperatures for 180 sec.	70
Figure 4-2 XRD spectra of the as-sputtered and annealed films after rapid thermal annealing at 480°C for different duration times and conventional thermal annealing at 480°C for 1 hr.....	71
Figure 4-3 XRD indexed patterns of the RTA 180 sec and CTA 1 hr films.....	72
Figure 4-4 2D and 3D AFM images of the Si (100) substrate (a) and as-sputtered film (b) [124].	74
Figure 4-5 3D AFM images of the as-sputtered (a) RTA 10 sec (b) RTA 60 sec (c) RTA 120 sec (d) RTA 180 sec (e) and CTA 1 hr (f) films [124].....	75
Figure 4-6 Variation of roughness (determined by rms value) versus different crystallization condition.....	76
Figure 4-7 Schematic of the heating directions in rapid thermal annealing (RTA) and conventional thermal annealing (CTA) [124].	76
Figure 4-8 XPS survey profile of as-sputtered, crystallized film by RTA at 480°C for 120 sec and crystallized sample by CTA at 480°C for 1 hr [124].....	77
Figure 4-9 Typical Ni 2p spectra of the samples at surface and after Ar ⁺ sputtering for 5 and 10 min; (a) as-sputtered, (b) crystallized film by RTA at 480°C for 120 sec and (c) crystallized film by CTA at 480°C for 1 hr [124].	79
Figure 4-10 Typical Cu 2p spectra of the samples at surface and after Ar ⁺ sputtering for 5 and 10 min; (a) as-sputtered, (b) crystallized film by RTA at 480°C for 120 sec and (c) crystallized film by CTA at 480°C for 1 hr [124].	80

Figure 4-11 Typical Ti 2p spectra of the samples at surface and after Ar ⁺ sputtering for 5 and 10 min; (a) as-sputtered, (b) crystallized film by RTA at 480°C for 120 sec and (c) crystallized film by CTA at 480°C for 1 hr [124].	81
Figure 4-12 Typical Ti 2p spectra of the samples at surface; (a) as-sputtered, (b) crystallized film by RTA for 120 sec and (c) crystallized film by CTA for 1 hr. The empty triangles indicate the experimental spectra and the dash line shows fitted spectra. Standard peaks are shown with solid lines [124].	83
Figure 4-13 Typical Ti 2p spectra of the samples after Ar ⁺ sputtering for 10 min (subsurface); (a) as-sputtered, (b) crystallized film by RTA for 120 sec and (c) crystallized film by CTA for 1 hr. The empty triangles indicate the experimental spectra and the dash line shows fitted spectra. Standard peaks are shown with solid lines [124].	84
Figure 4-14 (a) XAFS spectra at Ni K-edges of the films, showing the differences due to changes of structural environment of the amorphous and annealed samples; (b) Fourier transforms of $k^3\chi(k)$ of Ni K-edge for as-sputtered and crystallized films by RTA and CTA (Phase shift was not corrected) [124].	86
Figure 4-15 Experimental and the fitting profiles of the first shell of Ni K-edge FT for RTA 60 sec by employing for Ni-Ti and Ni-Ni coordinations. The inelastic factor, S02 was fixed to 0.70 for Ni edge, while the same E ₀ was employed for the two coordination components [124].	88
Figure 4-16 The change of (a) Ni coordination environment, (b) Ni-Ti and Ni-Ni bond distances, and (c) individual Debye-Waller factors (σ^2) for Ti-Ni-Cu thin film with different annealing conditions [124].	89
Figure 4-17 Indenter load versus indentation depth curves at 2, 2.5 and 3 mN maximum loads for Ti-Ni-Cu films; (a) as-sputtered, (b) RTA 10 sec, (c) RTA 60 sec, (d) RTA 120	

sec, (e) RTA 180 sec, (f) CTA 1 hr. The square, circle and triangle represent the indentation at 2, 2.5 and 3 mN respectively [124].	91
Figure 4-18 Elastic modulus as a function of the maximum indentation load for as-sputtered, RTA 10 sec, RTA 60 sec, RTA 120 sec, RTA 180 sec and CTA 1 hr films. All data points are an average of 4 measurements and the error bars represent one standard deviation in the measured data [124].	92
Figure 4-19 Variation of the elastic modulus for as-sputtered, RTA 10 sec, RTA 60 sec, RTA 120 sec, RTA 180 sec and CTA 1 hr films (All data points are an average of 12 measurements and the error bar represent one standard deviation in the measured data [124].	93
Figure 4-20 Ti-Ni-Cu freestanding film after RTA treatment.	96
Figure 4-21 DSC thermogram of the Ti-Ni-Cu freestanding film.	96
Figure 4-22 Demonstration of two-way shape memory effect in Ti-Ni-Cu freestanding film after RTA treatment (480°C/180s).	98
Figure 5-1 XRD pattern of the as-sputtered Ti-Ni-Hf thin film. The reference sample was used for XRD analysis. The thickness of the film was 573 ± 18 nm.	101
Figure 5-2 (a) Temperature response of the as-deposited and crystallized sample to an 86 mA current pulse lasting 65 ms. (b) Variation of the heating rate versus time for as-deposited and crystallized sample. (c) Calorimetric signal of the as-deposited and crystallized sample plotted as a function of as-deposited sample temperature. (d) Variation of differential calorimetric signal versus temperature [166].	102
Figure 5-4 Glass transition as a function of composition; the circles (●) represent compositions of unmeasured samples. The glass transition was not observed in the samples with triangle sign (▼).	105

Figure 5-5 (a) Differential calorimetric signal as a function of temperature (crystallization curve) for cell G ($\text{Ti}_{36.1}\text{Ni}_{49.3}\text{Hf}_{14.6}$), (b) XRD pattern of the cell G after crystallization.	106
Figure 5-6 Crystallization peak temperature as a function of composition. The triangles ($\blacktriangle$) represent compositions of unmeasured samples.	107
Figure 5-7 (a) Comparison of crystallization process between PnSC and traditional DSC; (a) crystallization via PnSC (cell R: $\text{Ti}_{38.8}\text{Ni}_{43.6}\text{Hf}_{17.6}$), (b) crystallization via traditional DSC (freestanding film: $\text{Ti}_{39.7}\text{Ni}_{43.3}\text{Hf}_{17.0}$).	109
Figure 5-8 (a) TEM micrograph of the cell V ($\text{Ti}_{41.9}\text{Ni}_{41.9}\text{Hf}_{16.2}$); the inset shows a typical high-resolution image of twinned martensite, (b) TEM micrograph of the freestanding film [166].	110
Figure 5-9 (a) TEM micrograph of the freestanding film after crystallization, (b) HRTEM image of a selected $(\text{Ti,Hf})_2\text{Ni}$ precipitate and $(\text{Ti,Hf})\text{Ni}$ grain in segment a, (c) TEM micrograph of the $(\text{Ti,Hf})_2\text{Ni}$ precipitate with facet interfaces, (d) HRTEM image of the selected $(\text{Ti,Hf})_2\text{Ni}$ precipitate in segment c viewed along the $[1,-1,3]$ direction.	111
Figure 5-10 Temperature response of the as-deposited and crystallized sample to an 86 mA current pulse lasting 25 ms, with the crystallized sample transforming martensitically. (b) Variation of the heating rate versus time for the as-deposited and crystallized sample. (c) Calorimetric signal of the as-deposited and crystallized sample plotted as a function of as-deposited sample temperature. (d) Variation of differential calorimetric signal versus temperature [166].	113
Figure 5-11 Library of martensite-austenite transformation. The differential calorimetric signal (nJ/K) of the samples plotted as a function of temperature ($^{\circ}\text{C}$). The unmeasured cells were denoted by cross sign ($\times$) [166].	114

Figure 5-12 Martensite-austenit peak temperature (A_p) as a function of composition. The star shapes show compositions of non-transforming cell. The squares (■) represent compositions of unmeasured samples.	117
Figure 5-13 Martensite-austenite peak transformation temperature as a function of Hf content [166]. The bulk and thick film results of Abujudom et al. and Sanjabi et al. are also shown for comparison [32, 34].....	117
Figure 5-14 Comparison of martensite-austenite transformation in PnSC and traditional DSC; (a) M-A transformation in traditional calorimetry and (b) M-A transformation in PnSC [166].	120
Figure 6-1 Heating profiles applied to the cells for each cycle during thermal cycling; (a) low-temperature cycle and (b) high-temperature cycle.....	123
Figure 6-2 Martensite-austenite transformation peaks as a function of the number of low-temperature cycles; (a) cell L, (b) cell N, (c) cell Q, (d) cell R, (e) cell S, (f) cell V, (g) cell W and (h) cell X.	126
Figure 6-3 Variation in A_p transformation temperature as a function of the number of low-temperature cycles [166].	127
Figure 6-4 Martensite-austenite transformation peaks as a function of the number of high-temperature cycles; (a) cell L, (b) cell Q, (c) cell R, (d) cell S, (e) cell U, (f) cell V, (g) cell W and (h) cell X.	131
Figure 6-5 Variation in A_p transformation temperature as a function of the number of high-temperature cycles [166].	131
Figure 6-6 TEM micrograph and corresponding electron diffraction pattern of cell X (a and b) and cell N (c and d) after high-temperature thermal cycling [166].	133
Figure 6-7 Martensite-austenite transformation peaks as a function of the number of high-temperature cycles; (a) cell N and (b) cell O.....	134

Figure 6-8 Effect of high-temperature cycling on thermal cycling stability; (a) cell L, (b) cell P and (c) cell R.	136
Figure 6-9 Effect of high-temperature cycling on thermal cycling stability. Seven compositions from different locations of the library have been chosen for this analysis.	137
Figure 6-10 Multiple thermal cycling of the cell X ($\text{Ti}_{38.1}\text{Ni}_{43.3}\text{Hf}_{18.6}$). Step 1: high-temperature cycling; Step 2: low-temperature cycling; Step 3: high-temperature cycling; Step 4: low-temperature cycling [166].	138

List of Tables

Table 2-1 Shape memory alloy systems with their crystal structure in austenite state [65].	9
Table 2-2 M_s and A_s transformation temperatures in TiNi-based SMAs [53]. The compositions with $A_s > 100^\circ\text{C}$ is defined as high-temperature SMAs and the alloys with $A_s < 100^\circ\text{C}$ is considered as low-temperature SMAs [66].	13
Table 3-1 Sputtering conditions and composition of Ti-Ni-Cu thin films.	39
Table 3-2 Thickness of the Ti-Ni-Hf films after deposition (nm).	56
Table 3-3 Calorimetric cell labeling with corresponding sample chemical composition (atomic %). The Ti, Ni and Hf uncertainties were approximately 0.3, 0.4 and 0.1 at.% respectively.	58
Table 3-4 Current pulse amplitude and duration for calorimetric measurements.	67
Table 4-1 Surface and subsurface chemistry of as-sputtered and crystallized films by RTA and CTA [124].	78
Table 4-2 Atomic concentration of different oxidation states for as-sputtered and crystallized films by RTA and CTA [124].	85
Table 4-3 Structural parameters: N (coordination number), R (interatomic distance), σ (relative displacement of atoms) obtained from Ni K-edge spectra analyzed by the EXAFS technique of the as-sputtered and crystallized films by RTA and CTA [124].	87
Table 5-1 Martensite-austenite transformation results for compositions, demonstrating a transformation in the calorimetric signal [166].	116
Table 6-1 Thermal stability of Ti-Ni-Hf thin films over 100 low-temperature cycles as a function of composition.	128

Chapter 1

Introduction

1.1. Background and Problem Statement

In the early 1960s, Buehler and his co-workers at the U.S. Naval Ordnance Laboratory discovered the shape memory effect in an equiatomic alloy of nickel and titanium, which can be considered a breakthrough in the field of shape memory materials [1]. This alloy was named Nitinol (Nickel-Titanium Naval Ordnance Laboratory). Since then, intensive investigations have been made to elucidate the mechanism of its basic behavior. Titanium-nickel based shape memory alloys can restore their form through a thermoelastic martensitic transformation between cubic (austenite) and monoclinic (martensite) dimorphs that makes these materials suitable for biomedical and aerospace applications. As the miniaturization of modern device proceeds, shape memory thin films have become attractive because of their promising characteristics for micro-actuators that are key components of micro-electro-mechanical systems (MEMS). Since near equiatomic Ti-Ni alloys in the bulk form possess a pronounced shape memory effect and superelasticity, TiNi-based thin films become a natural candidate for the research and development of micro-actuation type materials. When fabricated as thin films, the alloys can be used as actuators in MEMS such as valves, pumps, grippers and pulsation sensors [2-9].

The addition of copper to Ti-Ni binary thin film increases the actuation response and reduces the sensitivity of the transformation temperature to the precise Ti and Ni composition, simplifying the synthesis and tailoring of functionality [10-12]. Ti-Ni-Cu

films are fabricated by magnetron co-sputtering of TiNi and Cu targets in a high pre-vacuum and argon atmosphere [13, 14]. The resultant films are amorphous, if deposited at room temperature, and annealing is necessary since the actuation properties appear in the crystalline phases during a martensitic transformation. Based on the heating source, two general techniques can be employed. In the first, conventional thermal annealing (CTA) is performed in an electric tube furnace ramped at $< 100^{\circ}\text{C}/\text{min}$ at high vacuum, while for the second, rapid thermal annealing (RTA) is driven by electromagnetic irradiation with ramping $< 100^{\circ}\text{C}/\text{sec}$ under a protected atmosphere. As the performance of Ti-Ni thin films are strongly modified by heat treatment, there has been extensive research to establish the optimal crystallization procedure and explore the CTA crystallization mechanism [15-21]. However, there are fewer studies of alternate approaches such as RTA. There are limited reports of laser annealing for the crystallization of amorphous Ti-Ni films [22-25]. Tong et al. investigated the crystallization of Ti-Ni-Cu ribbons modified by RTA, where the samples were annealed by irradiation of the photons from a halogen lamp and showed ability of RTA to crystallize the ribbons in a shorter dwell times allowing more precise control of microstructure and functionality [26, 27]. Many aspects of rapid thermal annealing of SMA thin films remain to be studied, and part of this research is concerned with describing and correlating the evolution of structural, surfacial and nano-scale mechanical properties of amorphous Ti-Ni-Cu thin films annealed in this manner.

TiNi binary thin films are used mainly in low-temperature applications because of their low transformation temperatures ($< 100^{\circ}\text{C}$) [28]. In order to use shape memory-based micro actuators at elevated temperatures, thin films with higher transformation temperatures need to be developed. Ti-Ni-Hf alloys are promising candidates for this purpose, as they demonstrate both high transformation temperatures ($> 100^{\circ}\text{C}$) and low cost compared to the

Ti-Ni-Pd and Ti-Ni-Pt systems [29-32]. A number of studies have been reported on the characterization of relatively thick Ti-Ni-Hf coatings prepared through magnetron sputtering and laser ablation [29, 33-35], but the number of studies on submicron films ($< 1\mu\text{m}$) is very limited [36].

Combinatorial materials synthesis and high-throughput screening accelerate materials discovery, development and optimization [37-40]. The combinatorial approach is now widely used to synthesize and explore various types of polymeric [41], inorganic [42] and hybrid materials [43]. This approach has been reported for Ti-Ni-Cu [44-46], Ti-Ni-Pd [47], Ni-Mn-Ga [39], Ni-Mn-Al [48, 49] and Ti-Ni-Zr [50-52] shape memory thin films. In these studies, composition spreads were characterized using high-throughput screening methods, resulting in the discovery of various shape memory materials with promising shape memory characteristics. In shape memory alloys (SMAs), exploring phase transformation characteristics such as transformation temperatures is important because they dictate the usable temperature range of the material [53-55]. Calorimetry is one of the most established methods to study phase transformations in SMAs. Using calorimetry, transformation temperatures, enthalpies and heat capacities can be measured over a wide range of temperatures [54-61]. Calorimetric techniques are typically employed for bulk samples where the sample mass is in the milligrams range; they are generally not sensitive enough to measure small quantities of materials in the range of micro or nano grams as required for thin films [62, 63]. Furthermore, analysis of SMA materials with a spread of compositions using conventional calorimetry takes a long time. In the second part of this study, the crystallization, martensitic transformation and thermal cycling behaviour of a Ti-Ni-Hf composition spread are explored through use of a parallel nano-scanning calorimeter (PnSC), a powerful device developed for calorimetric analysis of nano-scale to micro-scale

quantities of materials using a high-throughput methodology [51, 52, 64]. The PnSC is a silicon-based micromachined instrument that allows high-throughput measurement of enthalpy-related materials properties in thin-film samples. Besides the nanoJoule sensitivity, the main advantages of this device are its capability to characterize transformations in a range of compositions over a wide temperature range, its very fast measurement times, and the capability to heat treat and thermally cycle the samples in-situ [51].

1.2. Objectives and Scope

The objectives of this research are:

- (i) To establish a comprehensive understanding of the structural, surfacial and nano-scale mechanical properties evolution of Ti-Ni-Cu thin films prepared by magnetron co-sputtering at room temperature followed by rapid thermal annealing (RTA); and
- (ii) To study the crystallization, martensitic transformation and thermal cycling behavior of Ti-Ni-Hf high-temperature SMA thin films as a function of composition using parallel nano-scanning calorimeter (i.e. combinatorial nano-calorimetry).

To this end, the scope of this PhD includes:

- I. Study of rapid thermal annealing of Ti-Ni-Cu thin films through:
 - (i) Fabrication of amorphous Ti-Ni-Cu thin films by magnetron co-sputtering of TiNi and Cu targets;

- (ii) Crystallization of the films using RTA and CTA techniques;
- (iii) Structural analysis using X-ray diffraction (XRD) and extended X-ray absorption fine structure (EXAFS) spectroscopy;
- (iv) Study of surface chemistry and morphology using X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM); and
- (v) Investigation of nano-scale mechanical properties via nanoindentation.

II. Analysis of Ti-Ni-Hf shape memory alloys by parallel nano-scanning calorimetry is inclusive of:

- (i) Description of parallel nano-scanning calorimeter;
- (ii) Fabrication of amorphous Ti-Ni-Hf thin film library with a two-dimensional composition gradient using magnetron co-sputtering;
- (iii) Study of crystallization behavior of the Ti-Ni-Hf thin films as a function of composition;
- (iv) Investigation of martensitic transformation behavior of the Ti-Ni-Hf thin films as a function of composition;
- (v) Examination of thermal cycling behavior of the Ti-Ni-Hf thin films as a function of composition; and
- (vi) Control of the martensitic transformation temperature aided by multiple thermal cycling.

1.3. Organization of the Thesis

The Introduction (Chapter 1) provides a rationale for the research and establishes the goals and scope that are directed towards developing a deeper understanding of rapid thermal annealing and combinatorial nano-calorimetry in TiNi-based SMA thin films.

In Chapter 2, a literature survey of shape memory alloys (SMAs), TiNi-based SMAs, and TiNi-based SMA thin films with emphasis on fabrication methods and compositions, along with a brief review of applications are presented.

In Chapter 3, the experimental procedures and analysis methods are described. These include thin film fabrication, annealing methods and characterization techniques. The parallel nano-scanning calorimeter (PnSC) is described. The combinatorial capability of the PnSC device is demonstrated by synthesizing a sample library of Ti-Ni-Hf. Finally, the calorimetric measurement protocols to study the crystallization, martensitic transformation and thermal cycling in a Ti-Ni-Hf sample library are reported.

In Chapter 4, the evolution of structural, surfacial and nano-scale mechanical properties of amorphous Ti-Ni-Cu thin films crystallized by RTA and CTA treatments is investigated.

In Chapter 5, the crystallization and martensitic transformation behaviour of Ti-Ni-Hf thin films are investigated as a function of composition using PnSC. A systematic study is carried out to compare the PnSC and traditional calorimetry (DSC).

In Chapter 6, the PnSC is used to study the effect of thermal cycling on transformation behavior of Ti-Ni-Hf thin films. The ability of PnSC to control the transformation temperatures through multiple thermal cycling is also studied.

Finally, conclusions are given in Chapter 7, followed by suggestions for further work in Chapter 8.

Chapter 2

Literature Survey

2.1. Shape Memory Alloys

Shape memory alloys (SMAs) are a group of metallic materials which have the ability to remember their original shape after applying large deformations through either heating (shape memory effect / SME) or removal of the load (superelastic effect / SE) [57, 65]. These unique properties are due to a reversible martensitic transformation from a low symmetry (martensite) to a highly symmetric crystallographic structure (austenite) [54, 57, 66]. The SMAs can be utilized in a wide variety of applications in the aerospace, automotive, biomedical and oil exploration industries [67].

2.1.1. History

Although the discovery of the shape memory alloys can be traced to 1930s, when Olander found superelastic behavior in the Au-Cd alloys [68], the phenomenon of the shape memory effect was not described until 1951 by Chang & Read [69]. In the early 1960s, Buehler and his co-workers at the U.S. Naval Ordnance Laboratory conducted breakthrough experiments of the shape memory effect in a binary alloy of nickel and titanium [70], that was named Nitinol (Nickel-Titanium Naval Ordnance Laboratory).

2.1.2. Shape Memory Alloys Compositions

Up to now, numerous shape memory alloy systems have been discovered. Table 2-1 summarizes some of these systems with their crystal structures in austenite state (highly symmetric phase). Among the SMAs, TiNi-based (e.g. TiNi, Ti-Ni-Cu, and Ti-Ni-Hf), Cu-based (e.g. Cu-Zn-Al and Cu-Al-Ni), Fe-based (e.g. Fe-Mn-Si) and Ni-Mn-based (e.g. Ni-Mn-Ga) alloys are of commercial importance [65, 71, 72].

Table 2-1 Shape memory alloy systems with their crystal structure in austenite state [65].

Alloy	Austenite Structure
Au-Cd	B2
Cu-Zn	B2
In-Tl	FCC
Ni-Ti	B2
Cu-Zn-Al	B2 / DO3
Ti-Nb	BCC (disordered)
Cu-Zn-Sn	B2
Cu-Al-Ni	DO3
Cu-Sn	B2
Cu-Zn-Ga	B2
Ni-Al	B2 (disordered)
Fe-Pt	LI2
Fe-Mn-Si	FCC

2.2. TiNi-based Shape Memory Alloys

TiNi-based alloys are now the most widely used shape memory alloys due to the superior performance, including excellent mechanical properties, large recoverable strain, good corrosion resistance, stability, and biocompatibility [73, 74]. These properties make these alloys ideal for a numerous applications in biomedical and aerospace engineering [65]. TiNi-based alloys can be divided into TiNi binary and TiNiX (X=Cu, Cr, Fe, Hf, Zr, Pt, Pd, Au, Rh) ternary systems that operate over a wide range of temperatures [53, 75].

2.2.1. Thermoelastic Martensitic Transformation

The unique behaviors of TiNi alloys (SME and SE) are due to a temperature-dependent martensitic phase transformation from the austenite to martensite structure. This transformation is reversible and often called the thermoelastic martensitic transformation (TMT) [66]. The TMT is a diffusionless solid-state phase transformation accompanied by a small driving force and hysteresis [76]. TiNi alloys are able to transform from austenite to martensite through a TMT, either by reducing the temperature (Thermally Induced Martensite, TIM) or applying a mechanical stress (Stress Induced Martensite, SIM). The process is reversible and martensite is restored to austenite through either increasing temperature or removing the applied stress [57].

The transformation from austenite to martensite and vice versa is associated with the release and absorption of latent heat. The heat of transformation and the corresponding transformation temperatures are commonly determined using differential scanning calorimetry (DSC), as shown for TiNi alloy during cooling and heating (Fig. 2-1). When

austenite is cooled, the change to martensite is initiated through an exothermic transformation; the temperature at which this phenomenon starts is called martensite start temperature (M_s), while the temperature at which martensite is completely restored is called the martensite finish temperature (M_f). When martensite is heated, it transforms to austenite endothermally; with onset at the austenite start temperature (A_s), and the completion at the austenite finish temperature (A_f) [1, 65].

Figure 2-1 DSC thermogram of a NiTi alloy [77].

Transformation temperatures in TiNi-based alloys are of importance, since they dictate the low or high temperature applications [53]. These temperatures are profoundly affected by chemical composition [66]. In Ni-rich binary TiNi films, M_s is strongly dependent on Ni concentration (Fig. 2-2) where addition of 1 at.% Ni decreases the transformation temperature by as much as 100°C [54]. This is attributed to the composition dependence of

the elastic constants of these alloys [78]. Addition of various transition metals to TiNi binary alloy can either increase or decrease transformation temperatures [54]. Table 2-2 classifies TiNi-based alloys into two categories (i.e. low and high temperature SMAs) according to the transformation temperatures. This table shows that the effect of chemical composition on transformation temperature is considerable.

Figure 2-2 M_s transformation temperature as a function of Ni content for binary Ti-Ni alloys. The solid line is from thermodynamic calculations [54, 79].

Table 2-2 M_s and A_s transformation temperatures in TiNi-based SMAs [53]. The compositions with $A_s > 100^\circ\text{C}$ is defined as high-temperature SMAs and the alloys with $A_s < 100^\circ\text{C}$ is considered as low-temperature SMAs [66].

Low Temperature SMAs	Alloy	M_s ($^\circ\text{C}$)	A_s ($^\circ\text{C}$)
	$\text{Ni}_{47.6}\text{Ti}_{46.4}\text{Nb}_6$	-50	-29
	$\text{Ni}_{50}\text{Ti}_{48}\text{W}_2$	-37	-26
	$\text{Ni}_{42.5}\text{Ti}_{42.5}\text{Cu}_{15}$	-34	-30
	$\text{Ni}_{48.3}\text{Ti}_{51}\text{Mo}_{0.7}$	-13	20
	$\text{Ni}_{49}\text{Ti}_{50}\text{Mo}_1$	10	20
	$\text{Ni}_{50}\text{Ti}_{45}\text{Ta}_5$	44	76
	$\text{Ni}_{52}\text{Ti}_{46.74}\text{Re}_{1.26}$	37	87
	$\text{Ni}_{50}\text{Ti}_{45}\text{Ta}_5$	44	76
	$\text{Ni}_{48}\text{Ti}_{50}\text{W}_2$	55	70
	$\text{Ni}_{25}\text{Ti}_{50}\text{Cu}_{25}$	61	62
	$\text{Ti}_{50}\text{Ni}_{50}$	60	80
High Temperature SMAs	$\text{Ni}_{49.5}\text{Ti}_{45.5}\text{Zr}_5$	70	110
	$\text{Ni}_{40}\text{Ti}_{50}\text{Pt}_{10}$	90	100
	$\text{Ni}_{50}\text{Ti}_{40}\text{Hf}_{10}$	120	165
	$\text{Ni}_{49.5}\text{Ti}_{35.5}\text{Zr}_{15}$	190	235
	$\text{Ni}_{35}\text{Ti}_{50}\text{Hf}_{15}$	235	256
	$\text{Ni}_{30}\text{Ti}_{50}\text{Pt}_{20}$	266	271
	$\text{Ni}_{50}\text{Ti}_{30}\text{Hf}_{20}$	290	317
	$\text{Ni}_{25}\text{Ti}_{50}\text{Pt}_{25}$	430	450
	$\text{Ni}_{20}\text{Ti}_{50}\text{Pt}_{30}$	560	594
	$\text{Ni}_{15}\text{Ti}_{50}\text{Pt}_{35}$	680	750
	$\text{Ni}_{10}\text{Ti}_{50}\text{Pt}_{40}$	810	850
	$\text{Ni}_5\text{Ti}_{50}\text{Pt}_{45}$	900	950

The correlation of transformation temperatures in TiNi alloys with electronic structure was investigated by Zarinejad et al. [53, 66]. The valence electron density, c_v (a ratio of the number of valence electrons to the total number of electrons of the alloy) was introduced as an influencing factor on the transformation temperatures. It was postulated that increasing the valence electron concentration (c_v) of the as-quenched NiTi-based alloys caused the transformation temperature to decrease [53]. This effect was attributed to higher elastic constants of the crystal which increase the resistance against shear, and in consequence, reduce the martensitic transformation temperatures [53, 66]. Microstructural parameters such as grain size and precipitates have been also reported as influencing factors on the transformation temperatures [54, 80].

2.2.2. Crystal Structures of TiNi-based Alloys

As already introduced, TiNi shape memory alloys exist in two crystal structures (phases) called martensite (lower temperature) and austenite (higher temperature), whose physical and mechanical properties (i.e. Young modulus, electrical resistance, damping behavior, etc.) are notably different [54, 65]. Austenite is a cubic B2 (Pm-3m), with nickel at the body center of the lattice and titanium at the corner (Fig. 2-3a) [81]. Martensite is B19' monoclinic (P1m1) with lower symmetric, and its lattice distorted to a rhombus with respect to the B2 parent (Fig. 2-3b) [82].

Figure 2-3 (a) austenite and (b) martensite crystal structures (The red and black balls indicate Ni and Ti atoms respectively [68].

Besides austenite and martensite in TiNi-based systems, an intermediate phase with rhombohedral structure (R-phase, P3- [83]) may appear upon cooling, prior to the martensitic transformation (Fig. 2-4). The schematic illustration of this phase is shown in Fig. 2-5. The R-phase transformation significantly increases alloy electrical resistivity [84]. The B2–R–B19' transformation (two-stage phase transformation) has been reported in aged Ni-rich TiNi [85-87], cold-worked TiNi [88] and ternary Ti–Ni–X (X= Al, Fe and Co) alloys [89].

Figure 2-4 A DSC curve for a Ni-rich TiNi SMA showing the R-phase transformation [67].

Figure 2-5 Schematic representation of the R-phase crystal structure [87].

2.2.3. Functional Properties of TiNi-based Alloys

2.2.3.1. Shape Memory Effect (SME)

TiNi alloy demonstrates the shape memory effect (SME) when deformed in the martensitic phase (ductile phase) and then unloaded while the temperature is below M_f . If subsequently heated above A_f , the original shape is recovered by transforming back to the parent austenite phase (Fig. 2-6). If the austenite is cooled below the M_f temperature, the austenite changes into the self-accommodated martensite twins. By applying an external force in this state, the twinned martensite undergoes typical elastic deformation until the yield stress. Then the deformation proceeds through the twin boundary movement, in a process called de-twinning. At this stage, the specimen's shape changes and the material is called de-twinning martensite. Finally, the original shape can be recovered by heating above the A_f temperature. This cyclic behavior is called the shape memory effect (SME) [87].

The cooling of austenite produces a complex arrangement of several variants of twinned martensite, where self-accommodating growth ensures the average macroscopic transformation strain remains zero. The multiple interfaces (boundaries between the martensite variants and twinning interfaces) are very mobile, and this great mobility is at the heart of the SME; movement of these interfaces, accompanied by detwinning, takes place at stress levels lower than the plastic yield limit of martensite, but after unloading a large inelastic strain remains. The reverse transformation induced by heating recovers the inelastic strain. Since the martensite variants have been reoriented by stress, the reversion to austenite produces a large transformation strain having the same amplitude, but the opposite direction, and the SMA material returns to the shape of the original austenitic phase [68].

Figure 2-6 Shape memory effect with respect to crystal structure, temperature and deformation [68].

2.2.3.2. Superelastic Effect (SE)

The superelastic effect (SE) of NiTi alloys is associated with recovery of the deformation upon unloading (Fig. 2-7a). If the alloy is externally loaded at a temperature above A_f , the austenite changes into a de-twinned martensite (SIM, stress induced martensite), which is unstable over this range of temperature. Consequently, when the load is removed, the material transforms into austenite and the original shape is restored (Fig. 2-7b). The temperature window in which SE can occur is $A_f < T < M_d$, as beyond M_d , austenite cannot transform to de-twinned martensite by the application of stress [77]. The loading and unloading paths during this cycle are not coincident, with the later exhibiting a lower stress

plateau. The SE is also termed the pseudoelastic effect (PE) due to the non-linear response of the material upon unloading, as opposed to the conventional elastic materials [65, 77]. The area enclosed under the stress-strain diagram represents the energy dissipated during the transformation (Fig. 2-7a).

Figure 2-7 Schematic representation of superelastic effect in shape memory alloys. The E_D represents the amount of dissipated strain energy, while the E_R is the amount of recoverable strain energy [77].

2.3. TiNi-based SMA Thin Films

As the miniaturization of modern device proceeds, the thin SMA films become attractive because of their promising characteristics for micro-actuation, a key part of micro-electro-mechanical systems (MEMS). Inasmuch as TiNi alloys in bulk exhibit a pronounced shape memory effect and superelasticity, as well as excellent corrosion and biocompatibility, analogous thin films are candidates for research and development as micro-actuation materials [54].

2.3.1. Fabrication Techniques

TiNi-based films, the most frequently used SMA thin films materials, are typically prepared by sputtering technique [28, 34, 90-93]. Laser ablation, ion beam deposition, arc plasma ion plating, plasma spray and flash evaporation methods have been also reported, but each has certain disadvantages, including non-uniformity in film thickness and composition, low deposition rates, non-batch processing, and incompatibility with MEMS fabrication [28].

Magnetron sputtering is a well-developed means to produce TiNi-based thin films for MEMS applications [3, 91, 94], where energetic Ar^+ produced in a glow discharge, bombard the source material, ejecting the target atoms from the surface so they may deposit as a continuous thin film on a substrate. A schematic illustration of magnetron sputtering of the Ti-Ni-Cu thin films using TiNi and Cu targets is shown in Fig. 2-8. In this configuration, Ti-Ni-Cu film is deposited on a rotating Si substrate. Many factors affect the properties of sputtered SMA thin films, including Ar gas pressure, substrate temperature, substrate-target distance, and target power [28, 95].

Ar gas pressure dramatically impacts on the structure of the deposited TiNi films, as reported in 1999 by Miyazaki et al. [95]. Films prepared at low pressure exhibits a dense structure, while at a high Ar gas pressure, a porous columnar structure results, this supposedly is due to the restricted mobility of the deposited atoms on the surface of the growing film. At high Ar pressure, multiple collisions of the sputtered species decrease the surface diffusion. Additionally, at high pressure, adsorbed Ar atoms will also reduce the mobility of the deposited atoms [95].

Figure 2-8 Schematic illustration of the sputtering configuration for preparing Ti-Ni-Cu thin films [13].

Another influencing factor on the film fabrication is substrate temperature. In general, higher substrate temperature provides more thermal energy during deposition allowing the film to densify through diffusion [96]. When the films are deposited below 200°C, the deposited films are amorphous and post annealing is required for crystallization, while above 200°C, a crystalline film is directly produced [97].

Deviation of film composition from the targets is a challenging issue when sputtering TiNi-based films, as small changes in alloy chemistry can greatly change the martensitic transformation temperature [28]. The difference in sputtering yields of titanium and nickel at a given power density and the geometrical disposition of the target over the substrate, as well as wear, erosion and roughening of targets during sputtering lead to variations in composition and thickness [28]. These effects can be controlled in TiNi SMA thin films by co-sputtering of a near equiatomic TiNi target with another Ti target [98], using two

separate single element targets (Ni and Ti) [5, 99], or by adding titanium plates on the top of the TiNi target [95, 100].

In this study, magnetron co-sputtering of TiNi and Cu targets was employed to fabricate Ti-Ni-Cu thin films. We have also used Ti, Ni and Hf targets to produce Ti-Ni-Hf thin films with a compositional gradient.

2.3.2. Crystallization of TiNi-based Thin Films

TiNi-based thin films are usually prepared at ambient temperature, thus the as-deposited films are amorphous [28]. As actuation response is based on a crystallographic phase change during martensitic transformation, and occurs when the films are in crystalline state, post annealing is necessary to realize a transition to the crystalline state. There is a direct link between the martensitic transformation and the microstructures emerging during crystallization [92, 101, 102], so understanding the nature of the crystallization process is critical for microstructural control and optimization of MEMS actuators.

2.3.2.1. Crystallization Mechanisms and Influencing Factors

The crystallization of amorphous TiNi films has been characterized as polymorphic with continuous nucleation and growth through the crystallization process observed by transmission electron microscopy (TEM) [18, 103, 104]. In this mechanism, the amorphous phase crystallizes as single grains of identical composition that grow rapidly and isotropically into the amorphous matrix. As long distance diffusion is not required in this process, the growth rate shows linear relationship with time [76].

The effect of composition on the crystallization of TiNi binary films was studied by Ni et al. [105], who found that the process is strongly dependent on stoichiometry. Although equiatomic amorphous TiNi binary film crystallized by the polymorphic mechanism, Ti-rich films under the same heating conditions did not fully crystallize polymorphically due to a competing precipitation reaction [105]. Xu et al. found copper additions (~ 1.3 at.%) in binary films decreased crystal growth activation energy, while the activation energy for nucleation was increased due to a higher interfacial energy between the amorphous and crystalline phases [106, 107]. However, the overall activation energy and crystallization temperatures were found to be similar to the binary TiNi film [107]. Tong et al. showed that both crystallization temperature and activation energy increased with increasing the Hf concentration in Ti-Ni-Hf films, due to the difference in atomic sizes of the Ni and Hf constituents and creation of stronger chemical bonds between the elements [33].

The impact of thickness on crystallization kinetics of TiNi films sandwiched between two protective silicon nitride layers were investigated by Wang et al. [108]. In this case, the nucleation process takes place homogeneously inside the film with heterogeneous nucleation suppressed around the interfaces due to the small compositional shift. It was also found that in the films < 600 nm thick, the crystal growth rate decreased significantly with decreasing the film thickness, while the rate was invariant for thicker films [108]. The diffusion of hydrogen from the films interfaces was proposed as a possible mechanism for this phenomenon.

2.3.2.2. Annealing Techniques for Crystallization

Two techniques are usually employed for the crystallization of TiNi-based amorphous films. In the first, conventional thermal annealing (CTA) takes place in an electric tube furnace at high vacuum and ramped at $< 100^{\circ}\text{C}/\text{min}$, while for the second, rapid thermal annealing (RTA) is driven by electromagnetic irradiation with ramping of $< 100^{\circ}\text{C}/\text{sec}$ under a protected atmosphere (Fig. 2-9a and b). As the performance of TiNi thin films are strongly modified by heat treatment, there has been extensive research to establish the optimal crystallization procedure and explore the CTA [15-21], but fewer studies of alternate approaches such as RTA. Tong et al. investigated the crystallization of Ti-Ni-Cu ribbons modified by rapid thermal annealing (RTA) with photon irradiation from a halogen lamp (Fig. 2-9b) using shorter dwell times that allows more precise control of microstructure and functionality [26, 27]. Another technique is electrical thermal annealing (ETA) that generates ultra-fast heating by applying an electrical pulse current to a resistive heating element (e.g., Si, W and Pt) (Fig. 2-9c). In this method, the thin film of interest is deposited onto a resistive substrate that acts as both heating source and thermistor (i.e. resistance thermometer), and can measure the thin film temperature at ultra-fast heating rates of 10^3 - 10^6 $^{\circ}\text{C}/\text{sec}$ [109]. Recently, McCluskey et al. have investigated the crystallization behavior of Ti-Ni-Zr SMA thin films using ETA. In their study, the amorphous thin films have been crystallized by local heating in a process that lasted just tens of millisecond [51]. There also exist limited reports of laser annealing for the crystallization of amorphous TiNi-based thin films [22-25]. In this method, the light of laser can be focused on a small region of the material to provide sufficient heat for crystallization. Therefore, it has an ability to distribute shape memory properties spatially;

the part of material crystallized by laser irradiation demonstrates SMA properties, while the untransformed material does not show functional properties [23, 110].

In general, little information is available concerning amorphous TiNi-based films crystallized at fast and ultra-fast heating rates and many aspects of these methods require further explorations. Therefore, the characterization of the TiNi-based films crystallized by fast and ultra-fast annealing methods is the subject of this study.

2.3.3. TiNi binary SMA Thin Films

TiNi binary thin films exhibit desirable functional properties, including the shape memory effect and superelasticity which are comparable with the bulk counterparts [76]. They also demonstrate good mechanical properties, since the grain size is extremely fine [95]. The transformation behavior as a function of chemical composition is also very similar to the bulk counterparts, where near equiatomic TiNi film shows a single stage $B2 \rightarrow B19'$ transformation (Fig. 2-10a) and Ni-rich film exhibits a two-stage $B2 \rightarrow R \rightarrow B19'$ transformation (Fig. 2-10b). In Ni-rich film, the formation of Ti_3Ni_4 precipitates suppress the $B2 \rightarrow B19'$ transformation and promotes the $B2 \rightarrow R$ transformation, again similar to bulk materials [54].

Figure 2-9 Schematic of the annealing techniques for crystallization of TiNi-based thin films; (a) conventional thermal annealing (CTA), (b) rapid thermal annealing (RTA) and (c) electrical thermal annealing (ETA).

Figure 2-10 Strain–temperature curves of Ti–Ni thin films under constant stresses: (a) near equiatomic composition, (b) Ni-rich composition. Films were crystallized by the heat-treatment at 500°C for 1 h. (a) shows one-stage transformation, while (b) shows two-stage transformation [111].

Ti-rich thin films behaviors are distinct from Ni-rich films. Since the solubility limit on Ti-rich side of the binary Ti–Ni alloy is nearly vertical (Fig. 2-11), the Ti_2Ni precipitates only can form at grain boundaries in Ti-rich bulk alloy, that degrades the shape memory behavior through precipitation hardening. However, this may be avoided if the alloy are crystallized from the amorphous as-deposited thin films, as the precipitates are likely intergranular due to supersaturation of Ti in the matrix [54].

Figure 2-11 Ti-Ni binary phase diagram [112] .

Nakata et al. first reported that very thin precipitates plates uniformly form on the {100} B2 planes of as-sputtered Ti-48.2 at.% Ni films annealed at 500°C for 10 min [113]. Kajiwarra et al. also found *Guinier-Preston* (GP) zones precipitate on {100} B2 planes after annealing at the crystallization temperature (T_c) or $(T_c - 50)^\circ\text{C}$ with the shape memory behaviors improved significantly through precipitation hardening. When the heat treatment is carried out below T_c , the B2 structure with the equiatomic proportions will form from the amorphous region, since the bonding between Ti and Ni atoms is very strong at this low temperature. Consequently, excess Ti atoms accumulate in the amorphous region adjacent the crystalline-amorphous interface. After advancing some distance, migration of the crystal-amorphous interface ceases due to the increasing Ti concentration. To accommodate the excess Ti atoms in the amorphous region, a Ti-rich coherent plate precipitate with a body centered tetragonal (bct) structure is formed. Sequentially, a new B2 crystal is

nucleated near to this precipitate to preserve the coherency. This process is repeated and results in nanocrystals with identical orientations. On the other hand, if the heat treatment is performed at a higher temperature, near T_c , a B2 crystal with excess Ti atoms is formed at the time of crystallization from the amorphous region, and then Ti-rich precipitates are produced in this crystal to relieve the over saturation with those excess Ti atoms. However, as heat treatment temperature is low, diffusion of Ti is insufficient to form stable Ti_2Ni precipitates, and GP zone-type precipitates are produced [114, 115].

2.3.4. Ti-Ni-Cu SMA Thin Films

Ti-Ni-Cu thin films are suitable materials for applications requiring quick response, since they exhibit a narrow temperature hysteresis [10-12]. They divided into two groups; Ti-rich films in which the amount of Ti is > 50 at.% and (Ni,Cu)-rich films with (Ni, Cu) > 50 at.%. Among these, Ti-rich films are of interest, since they show a higher martensitic transformation temperature than (Ni, Cu)-rich thin films [4].

The addition of Cu decreases the transformation and pseudoelasticity hysteresis, as these are closely related to the ease of interface movement during transformation [57, 116]. The addition of 10 at.% Cu to the near equiatomic NiTi alloy can decrease the transformation hysteresis from 40 to 11°C, and the hysteresis of pseudoelasticity from 200 MPa to less than 100 MPa [57]. Copper also decreases the flow-stress, prevents the precipitation of the Ti_3Ni_4 phase, reduces the composition sensitivity of the transformation temperatures, and improves the thermal stability of SMA films [57, 65]. However, Cu introduced above 10 at.% embrittles the alloy and significantly reduces formability [57]. Films with < 9.5 at.%

Cu demonstrate a single-stage transformation from B2 to B19' (monoclinic martensite), while the films with more than 9.5 at.% Cu show a single stage transformation from B2 to B19 (orthorhombic martensite). For the films with 9.5 at.% Cu, a two-stage transformation, $B2 \rightarrow B19 \rightarrow B19'$ is observed [11].

2.3.5. Ti-Ni-Hf SMA Thin Films

TiNi binary and Ti-Ni-Cu thin films are used for applications requiring low transformation temperatures ($< 100^\circ\text{C}$) [28]. To deploy SMA-based micro actuators at high temperatures ($> 100^\circ\text{C}$), films with higher transformation temperatures are required, and Ti-Ni-Hf alloys are promising candidates for this purpose, and are of lower cost compared to Ti-Ni-Pd and Ti-Ni-Pt systems [30-32, 34]. Ti-Ni-Hf materials also show greater thermal stability during thermal cycling compared to the TiNi alloys [31].

Ti-Ni-Hf thin films were first fabricated using magnetron sputtering by Johnson et al. [117] with a Ti-Ni-Hf alloy target. It was found that the M_s temperature could be adjusted from 100 to 200°C by changing the Hf content of the target [117]. Due to the brittle nature of the as-cast Ti-Ni-Hf material, fabrication of the alloy target is difficult [118], and the high oxygen affinity of Hf increases the processing difficulties using powder metallurgical techniques [34]. Sanjabi et al. found the optimized conditions to fabricate $\text{Ni}_{50}\text{Ti}_{50-x}\text{Hf}_x$ films using simultaneous deposition from separate Ni, Ti and Hf targets, where the films compositions were easily controlled by adjusting the ratio of the DC power supplied to each target [29, 34]. Again, the transformation temperatures are dependent to the Hf

concentration, where addition of Hf increased the martensite-austenite transformation peak-temperature (A_p) up to 414°C at 24.4 at.% Hf.

Tong et al. investigated the crystallization and martensitic transformation of Ti-Ni-Hf films prepared by magnetron sputtering at room temperature, and found crystallization temperature and activation energy increased with Hf content. The transformation temperature also increased with annealing temperature. This is attributed to the grain size effect, where the smaller grain size suppresses the martensitic transformation [33]. The optimized conditions to fabricate $\text{NiTi}_{1-x}\text{Hf}_x$ thin films using laser ablation method were reported by Gu et al. [35] who found the R-phase transformation in a $\text{Ni}_{50.04}\text{Ti}_{36.63}\text{Hf}_{13.33}$ thin film, but not be in the bulk counterpart [33, 35]. All investigations to date have focused on Ti-Ni-Hf films $> 2 \mu\text{m}$ thick and further work is required to explore Ti-Ni-Hf thin films at submicron levels ($< 1 \mu\text{m}$) for use in high temperature micro-actuators.

2.4. TiNi-based SMA Thin Film Applications

Thin film shape memory alloys are promising materials for MEMS applications [28, 54, 119, 120]. In particular, TiNi films can provide large forces and displacements for actuation in MEMS. They are usually employed in micro-actuators including micro pumps, micro valves, micro grippers, micro wrappers, micro sensors, micro switches and micro petitioners [28].

2.4.1. Micro Pumps and Micro Valves

TiNi thin films used for the fabrication of micro valves and pumps are attractive for implantable drug delivery, chemical analysis and analytical instrumentation. In these applications, the films form membranes or diaphragms for actuation [28]. Fig. 2-12 shows diaphragm-based micro pumps for pressurization and evacuation [6]. These devices consist of two major components, the SMA actuator and check valve, where the SMA actuator comprises a TiNi thin film diaphragm with a flat memorized shape, and a glass cap which forms a chamber between them (Fig. 2-12). When an external force is applied to the chamber at room temperature, the diaphragm deforms. By heating the diaphragm with electric current or other techniques, the original shape of the SMA diaphragm (flat shape) is recovered. In the pressurization pump, the diaphragm deforms the chamber and pushes the liquid out by application of an external force (Fig. 2-12a). When the diaphragm is heated, the flat shape recovers and the pump draws in liquid [6].

Figure 2-12 Micropump structure with SMA thin film actuator: (a) pressurization type; (b) evacuation type [6].

2.4.2. Micro Wrappers

Grabbing and manipulating small objects (micro or nano-scale) is required for the assembly in micro systems, endoscopes for microsurgery, and micro manipulators for drug injection into cells [28]. The actuation mechanism of a TiNi thin film micro-wrapper [121] in plan-view is illustrated in Fig. 2-13a. The bonding pad, current path and central parts of the arms are attached to the substrate, while the other parts are free to move and are either curled-up or flat shape (Fig. 2-13b). Due to the residual stress, the arms form a cage-like structure after releasing from the substrate, but when the actuator is heated, the arms flatten due to the SME. The heat for actuation is provided by passing an electric current from one bonding pad to the others [121].

Figure 2-13 The micro-wrapper made of free-standing TiNi films [121].

2.4.3. Micro Actuators in Microsurgery

Free tissue transfer has been applied to important organ graft operations such as liver transplantation. Thrombus formation near an anastomotic site of a blood vessel is an important problem and tissue failure usually takes place in 5–10 % of patients 24 hrs after the operation due to poor blood circulation. A reliable monitoring technique for thrombus formation is required and various techniques have been employed for measuring microvascular blood flow and have been used in clinical trials [122].

Using a SMA thin film actuator to hold a fine blood vessel appears promising. The actuator attaches a blood stream sensor to the outer wall of a blood vessel (Fig. 2-14) [123]. The arms and a base part of the actuator are made up of a Ti-Ni-Cu SMA film which is flash-evaporated on a flat substrate. The Ti-Ni-Cu film is annealed to memorize a flat shape, and the outer arm bent by a gentle force using forceps, so that the blood vessel is caught between the outer and inner arms (Step 1). When micro-heater A is turned on for a short time, the outer arm closes downward and holds the blood vessel securely (Step 2). The strain gauge on the inner arm transfers the periodical variation of diameter of the vessel by arterial pulsation into a voltage waveform (Step 3). The results are transferred to a computer for display on a monitor. When the micro-heater B is turned on, the outer arm opens to release the blood vessel safely (Step 4). The heaters reach to $\sim 65^{\circ}\text{C}$, which is equal to the deformation temperature of the Ti-Ni-Cu SMA film. The resistive heating lasts for a few seconds and does not produce any biological damage [123].

Figure 2-14 Concept of actuation: (1) setting; (2) hold actuation; (3) pulse monitoring; (4) release actuation and (5) pull out [123].

2.5. Summary

The characteristics of TiNi-based shape memory alloys including their thermoelastic martensitic transformation, transformation temperatures and crystal structures were described. Recent progress on TiNi-based thin films including the fabrication methods, crystallization mechanisms and techniques was reviewed. Fast and ultra-fast annealing methods were described as potential candidates for crystallization of TiNi-based amorphous thin films. TiNi binary, Ti-Ni-Cu and Ti-Ni-Hf thin films were studied as promising materials for MEMS applications. Finally, several applications of TiNi-based thin films were reported.

Chapter 3

Fabrication, Processing and Characterization Techniques

In Chapter 3, the experimental procedures and analysis methods are described. These include thin films fabrication, annealing methods and characterization techniques. This chapter is organized as follows:

1) Fabrication and characterization of Ti-Ni-Cu thin films

In this section, amorphous Ti-Ni-Cu thin films were fabricated by sputtering technique. The resultant films were crystallized by rapid thermal annealing (RTA) and conventional thermal annealing (CTA). Finally, the characterization methods to explore the structural, surfacial and nano-scale mechanical properties of the amorphous, partially crystalline and crystalline films are described.

2) Analysis of Ti-Ni-Hf thin film library by PnSC

In the second part, the PnSC [51] was employed to study the crystallization, martensitic transformation and thermal cycling behavior of Ti-Ni-Hf thin films as a function of composition. A Ti-Ni-Hf sample library was synthesized using magnetron co-sputtering. The principle of calorimetric measurement using PnSC is explained. Finally, the characterization methods for structural analysis are described.

3.1. Fabrication and Characterization of Ti-Ni-Cu thin films

The experimental procedures and characterization methods of this part are illustrated in the chart of Fig. 3-1. The description of the methods and procedures are given in this section.

3.1.1. Fabrication of Amorphous Ti-Ni-Cu Thin Films

Ti-Ni-Cu thin films were deposited on rotating (4 rpm) 4 inch (100)-type silicon substrates at room temperature by magnetron co-sputtering of Ti-Ni (99.99% purity) and Cu (99.99 % purity) targets ($\varnothing$ 50.8 mm) at a base pressure $< 1.5 \times 10^{-6}$ Torr and a substrate-to-target separation of 100 mm under an argon pressure of ~ 1.5 mTorr. The depositions were performed in a Coaxial MSS3A/LL sputter deposition system (Fig. 3-2). Before deposition, all the Si substrates were soaked at 120°C in H₂SO₄ solution for 20 minutes and cleaned by DI water followed by curing at 120°C for 15 min. After deposition, the thickness of the films was determined using a Dektak3ST surface profilometer (Veeco Instruments Inc.). The target powers (DC / RF) as well as the films thicknesses are listed in Table 3-1. Chemical compositions of the samples were determined semi-quantitatively by standardless energy dispersive X-ray microanalysis (EDS) in association with a JEOL JSM-5600LN scanning electron microscope (SEM) (Table 3-1). For each sample, the composition was measured from five areas and averaged.

Figure 3-1 Flow chart showing the experimental procedures and analyses methods.

Figure 3-2 The Coaxial MSS3A sputtering system.

Table 3-1 Sputtering conditions and composition of Ti-Ni-Cu thin films.

Sample	Target Power		Deposition Time (hr)	Thickness (nm)	Chemical Composition		
	TiNi (at.%), RF (W)	Cu DC (W)			Ti (at.%)	Ni (at.%)	Cu (at.%)
Ti-Ni-Cu (Thin film)	Ti55Ni45, 400	2	1	544 ± 13	49.3 (± 0.5)	47.4 (± 0.3)	3.3 (± 0.3)
Ti-Ni-Cu (Thick film)	Ti50Ni50, 400	2	6	1810 ± 10	43.1 (± 0.3)	52.8 (± 0.2)	4.1 (± 0.2)

3.1.2. Crystallization of Amorphous Ti-Ni-Cu Thin Films

As-deposited samples were annealed in a Jipelec Jetfirst 100 rapid thermal processor (Fig. 3-3 a) in an argon atmosphere while resting on a dummy silicon wafer. The schematic of the RTA treatment is shown in Fig. 3-4, where the film of interest was heated through a series of tungsten-halogen lamps located at top of the film. The temperature was measured by a K-type thermocouple attached to the Si dummy wafer from the backside. The schematic of thermal profile during RTA is shown in Fig. 3-5. Successive Ar purging and

evacuation were employed for 35 min to minimize the oxygen content of the RTA chamber before annealing (stage 1). The samples heated to the annealing temperature (450-500°C) in two steps (stages 2 and 3), held isothermally (2-180 s) (stage 4), then cooled in two ramps (stages 5 and 6) (Fig. 3-5). Alternatively, the sputtered films were annealed in a Lenton vacuum tube furnace (CTA) under vacuum of the 10^{-5} mbar at 480°C using a ramp of $5^{\circ}\text{C min}^{-1}$ and maintained for 1 h (Fig. 3-3 b).

Figure 3-3 a) Rapid thermal annealing; b) Conventional thermal annealing (vacuum tube furnace).

Figure 3-4 Schematic of the RTA processing.

Figure 3-5 The schematic of thermal profile during RTA treatment [124].

3.1.3. Characterization Methods

3.1.3.1. Surface Analysis

3.1.3.1.1. Surface Morphology

A Digital Instruments S-3000 atomic force microscope (AFM) operating in tapping mode, with Si_3N_4 tip cantilevers of 7 nm nominal curvatures and a resonance frequency of 325 kHz was used to determine surface morphology and the roughness of the films. The

roughness was represented as a root mean square (rms) value (defined by the standard deviation of the height distribution) determined over an area of $5 \times 5 \mu\text{m}^2$.

3.1.3.1.2. Surface Chemistry

To study the surface chemistry of the films, X-ray photoelectron spectroscopy (XPS) was conducted with a Kratos Axis Ultra system at a chamber pressure of 10^{-9} Torr and monochromatic Al K α X-ray (1486.7 eV) as the incident radiation. Survey spectra were recorded at pass energy of 160 eV, and the high resolution analysis was conducted at 40 eV. The sub-surface chemistry of the films was analyzed after 5 and 10 min Ar⁺ ion sputtering.

3.1.3.2. Structural Analysis

3.1.3.2.1. Crystal Structure

The crystal structure of the films was examined by glancing incidence X-ray diffraction (GI-XRD) using a Rigaku diffractometer with Cu K α radiation over the 2θ range $10-100^\circ$ with a step size of 0.02° , a glancing angle of 1.0° and a count time of 1.5 hrs. In order to obtain enough intensity for phase identification of the phases in the fully-crystallized films, the XRD were performed at the longer count time (12 hrs).

3.1.3.2.2. Local Atomic Structure

X-ray absorption spectroscopy (XAS) of the as-sputtered and annealed films was conducted at the Singapore Synchrotron Light Source (SSLS) [125], using the X-ray Demonstration and Development (XDD) beam line, that provides focused irradiation at the end station of about 2×4 mm in size at a photon flux of $\sim 10^9$ photon/s. The spectral range was selected with a Si (111) channel-cut crystal monochromator. Since the measurement of nanometer thick films is challenging for hard X-rays, due to the comparably large penetration depth (the order of several micrometers), and the dominant background scattering from the substrate, an in-house X-ray detector (filled with high purity argon gas at ambient pressure and temperature) was used. Thin films were placed in the sample cell at grazing incidence angles of 2° with the sample plane parallel to the electric field vector of the incident X-rays. The vertical exit slit was 0.5 mm wide but the horizontal dimension was not confined. For each experiment, the films were mounted on a two-dimensional translation stage and the whole assembly scanned vertically and horizontally, with a step around 0.3 mm. A rough scan around the absorption edge (-20 eV $\sim$ $+40$ eV, relative to E_0 in a step of 1 or 2 eV) was carried out to find the highest absorption jump for the K-edge of the analyte.

The X-ray absorption spectra were recorded by measuring the fluorescence signal from the thin films. To minimize the elastic scattering contribution, four separate segments of anode plates were used to collect the radiation in a solid angle centered on the direction of the incoming X-ray polarization vector. K-edges of Ti, Ni and Cu were analyzed with collection of the absorption spectra from -150 to 900 eV (for Ti) and -150 to 600 eV (for Ni and Cu) relative to the metal K-edges of the respective elements. The high noise for Ti and

Cu K-edge spectra was due to co-existing titanium oxide and low copper concentration respectively.

Data analysis followed a standard procedure using WinXAS [126]. The spectra were background corrected using 1-degree and 3-degree polynomial fitting to the pre-edge and post-edge regions respectively, followed by the spectral normalization. Subsequent processing included: a) transformation from energy to momentum (k) space based on the photoelectrons energy ejected from the sample spectra (E_0) obtained from the first and second derivatives; b) a 7-segment spline fit to the post-edge region; and c) Fourier transformation (FT) from k to real R space. In the FT, EXAFS in the range of 22.5-105 nm⁻¹ in k space was extracted, k^3 weighted, and a Bessel window function employed. The data fit was performed in R space (by filtering out the first peak in FT spectra) using the theoretical phase shift and backscattering amplitude extracted from the nickel-titanium austenite model [127]. The amplitudes and phases for the scattering paths of photoelectrons were calculated for this model using FEFF 8.2 software [128].

3.1.3.3. Nano Mechanical Properties

Nanoindentation is a simple and accurate technique to extract elastic modulus and hardness where a hard indenter is pressed into the film and the indentation load (P) and indentation depth (h) are continuously measured (Fig. 3-6). As the indenter is pressed into the sample, the material response is both elastic and plastic resulting in an impression, conforming the shape of the indenter. During the unloading process only the elastic portion of the deformation is recovered allowing the use of elastic solution to explain the process. Fig. 3-6 illustrates a typical load-displacement curve obtained from a nanoindentation experiment.

In this graph, some important parameters such as maximum load (P_{max}), maximum depth (h_{max} or h_t), the permanent depth of penetration after unloading (h_p) are labeled. The elastic unloading stiffness defined as the slope of the unloading curve during the initial stages of unloading ($S=dP/dh$). As shown in this figure, the elastic deflection of the surface of the sample can be determined by extrapolating the tangent of the initial portion of unload curve to zero load. Following the Oliver and Pharr model [129] the contact depth (h_c) can be calculated as:

$$h_c = h_t - (0.75 \times P_{max} \times S^{-1}) \quad (3-1)$$

The contact area can hence be calculated using the contact depth through an empirically determined function. The polynomial expressing the area function of the tip (A) as a function of indentation depth (h) can be expressed by:

$$A(h) = C_1 h^2 + C_2 h + C_3 h^{1/2} + C_4 h^{1/4} + C_5 h^{1/8} \quad (3-2)$$

The area function coefficients values of the Berkovic diamond indenter used in this study (C_1 - C_5) were considered in the measurements by the nanoindenter software.

Figure 3-6 A typical indentation load-depth curve during nanoindentation [130].

The contact stiffness corresponding to the initial unloading curve can be related to the young's modulus (E) and the projected contact area (A_c) using the following equation:

$$S = \frac{2}{\sqrt{\pi}} \frac{E}{1-\nu^2} \sqrt{A_c} \quad (3-3)$$

where ν is Poisson's ratio. Equation (3-3) is only valid under the assumption that the indenter is ideally rigid. If the behavior of the indenter and specimen is assumed as a series set of springs, the elastic deformation of both can be characterized by E_r (reduced modulus) described as:

$$\frac{1}{E_r} = \frac{1-\nu_i^2}{E_i} + \frac{1-\nu_s^2}{E_s} \quad (3-4)$$

where ν_i , E_i , ν_s and E_s are Young's modulus and Poisson's ratio of indenter and specimen respectively. For the diamond indenter used in this work $E_i=1141$ GPa and $\nu_i=0.07$ were considered. The corrected equation for stiffness taking into account E_r is as follows:

$$S = \frac{2}{\sqrt{\pi}} \cdot E_r \cdot \sqrt{A_c} . \quad (3-5)$$

In this study, nanoindentation was employed to understand the mechanical properties evolution due to the crystallization of Ti-Ni-Cu films. The elastic modulus of the films was determined using a CSM Nanoindentation system with a diamond Berkovich tip. As explained earlier, the elastic moduli of the films were extracted from the load-depth curves using the Oliver-Pharr method [129]. Indentation was performed for 2, 2.5 and 3 mN loads at room temperature, and loading and unloading rates of 4 mN min^{-1} . In order to avoid the so-called substrate effect, the experiments were conducted at contact depth of less than 10-20 % of the total film thickness [131]. In each test, upon reaching the maximum load, there was a 5 sec holding period before unloading at the same rate as loading.

3.1.3.4. Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) (Q200, TA instrument) was employed to study the transformation behavior of Ti-Ni-Cu freestanding film (i.e. peeled off from the Si substrate after RTA treatment). The DSC was performed under N₂ atmosphere (50 ml.min^{-1}) at heating and cooling rates of 5°C.min^{-1} . The film were cut into the small pieces and packed into an aluminum pan. The mass of the sample was 1.2 mg and an empty aluminum pan was used as a reference. The DSC sample was heated to 300°C and held isothermally for 1

min to establish thermal equilibrium. The sample was cooled to - 80°C, held isothermally for 1 min, followed by heating to 300°C (transformation cycle). The transformation temperatures were determined using slope line extension method.

3.2. Analysis of Ti-Ni-Hf Thin Films by PnSC

As discussed in Chapters 1 and 2, the best established method to investigate the phase transformation characteristics in SMAs is differential scanning calorimetry (DSC), where the transformation temperatures, enthalpies and heat capacities can be analysed over a large range of temperatures [54-61]. However, DSC is typically employed for bulk samples in which the mass of sample is in the range of milligram and is not sensitive enough to measure the small quantity of material in the range of micro or nanograms, since the amount of heat exchanged during the transformation is too small and the heat capacity of the calorimeter is too large [62, 63]. Therefore, a new tool is required to study the phase transformation characteristics in SMA thin films. Nano-calorimetry is a technique to probe the thermal properties of small samples at nanometer-scale. By utilizing thin film fabrication and advanced micro-machining, the addendum of calorimeter reduced significantly for ultra-sensitive calorimetric measurements [63, 132-134]. Allen's group in 1995 developed this technique for thin films using a membrane-based micro-device as a heating pulse calorimeter [135, 136]. This method has been used to study polymer thin films [137, 138], Ti/Si and Ni/Si bilayers [109, 139], Sn and Ge ultrathin films [132, 135, 136], nano particles of In, Sn, Al and Bi [51, 133, 136, 140-142]. Therefore, advances in nano-calorimetric analysis of materials can be employed to characterize the phase transformation characteristics in SMA thin films. Furthermore, analysis of SMA materials with a spread of compositions using traditional calorimetry (DSC) takes a long time.

Combinatorial synthesis technologies and high-throughput screening methods can be a solution for this issue. These methods have been proven to accelerate materials discovery, development and optimization [37-40], and is now widely used to explore polymeric [41], inorganic [42] and hybrid materials [43]. This approach has been applied to Ti-Ni-Cu [44-46], Ti-Ni-Pd [47], Ni-Mn-Ga [39], Ni-Mn-Al [48, 49] and Ti-Ni-Zr [51] SMA thin films.

In the second part of this study, the crystallization, martensitic transformation and thermal cycling behaviour of a Ti-Ni-Hf composition spread were explored using the PnSC, a powerful device developed for calorimetric measurement of nano-scale to micro-scale materials in a high-throughput methodology [51, 52, 64]. The PnSC is a silicon-based micromachined instrument that allows high-throughput measurement of enthalpy-related materials properties in thin-film samples. The main advantages of this device are its capability to characterize transformations in a range of compositions, over a wide temperature range, its very fast measurement time, and the capability to heat treat and thermally cycle the samples in-situ [51].

In this section, first, a description of the PnSC device is provided; the synthesis of the Ti-Ni-Hf sample library is described and the calorimetric measurement technique is explained. Finally, the structural analysis methods to characterize Ti-Ni-Hf thin films are described.

3.2.1. Physical Description of Parallel nano-Scanning Calorimeter

The PnSC device consisted of a 5×5 array of micromachined calorimetric cells supported by a square Si frame and edge dimension of 55 mm (Fig. 3-7a) [51]. Each calorimetric cell consisted of a thin-film resistance thermometer sandwiched between two electrically

insulating silicon nitride layers that form a membrane (Fig. 3-8a). The membrane had a thickness of 200 nm and in-plane dimensions of $2.5\text{ mm} \times 5\text{ mm}$. The resistance thermometer consisted of tungsten strip approximately $800\text{ }\mu\text{m}$ wide and 125 nm thick patterned for a four-point measurement scheme. The resistance thermometer was also used as a resistive heater during the experiments (Fig. 3-8b). The horizontal metal lines at the extremes of the heater in Fig. 3-7a were the voltage probes. The segment of the heating element between the voltage probes was the resistance thermometer and constituted the sensing area of the cell. Each cell had four electrical leads that were connected to the contact pads at the edges of the Si substrate through a $\sim 1\text{ }\mu\text{m}$ patterned copper film (Fig. 3-7a). The calorimetric cells were labeled alphabetically, as depicted in Fig. 3-7b.

(a)

(b)

Figure 3-7 (a) Photograph of the Parallel nano-Scanning Calorimeter; (b) Labeling of the calorimetric cells. The segment (a) has been drawn after Fig. 1 in Ref. [51].

Figure 3-8 Layout of the nano-calorimeter cell: (a) cross-section, and (b) plane-view schematic. Heater line-width is 0.8 mm and voltage probe line-width is 0.1 mm [51].

3.2.2. Device Fabrication

The PnSC device was fabricated by a standard microfabrication technology developed at Harvard University [51]. One-side polished, (100) oriented silicon wafers, and 200 mm in diameter was used for the fabrication process. The both sides of the wafers were coated with a layer of ~ 80 nm amorphous Si₃N₄ using a low-pressure chemical vapor deposition process (Fig. 3-9a). A 55 mm x 55 mm square substrate was cleaved from the Si wafer. The Si₃N₄ on the polished side of the wafer will eventually serve as a support membrane for the resistance thermometers, while the nitride on the backside will serve as a hard mask in the fabrication process. First 125 nm of tungsten then 1.2 μ m of copper were deposited on the polished side of the square substrate using DC magnetron sputtering (Fig. 3-9b).

Both sides of substrate were spin-coated with a Shipley 1805 photoresist (S1805), followed by baking at 150°C for 5 min. The front side of the substrate was exposed to UV light through a mask with the metallization artwork, and the backside was exposed through a mask with the cavity window artwork. Both sides of the substrate were developed simultaneously in a Microposit CD-30 for 1 minute (Fig. 3-9c).

The Si_3N_4 on the backside of the wafer was etched away by reactive ion etching (RIE) using CF_4 to create rectangular openings in the silicon nitride layer. Copper was etched in an aqueous solution of phosphoric, nitric, and acetic acid at 50°C, followed by etching of the underlying tungsten in 30% H_2O_2 at 50°C (Fig. 3-9d). Next the remaining resist was exposed and removed. After removing the resist, a S1805 photoresist was applied to the metallization side and patterned with the rectangular cavity artwork (Fig. 3-9e). The remaining copper on tungsten metallization was then etched from the membrane area, leaving only tungsten within the area that will form the membrane.

Figure 3-9 Cross section schematic of a nano-calorimeter cell during steps (a)-(g) in the PnSC fabrication process [51].

After creation of metallization pattern, the device was coated with ~ 100 nm of silicon nitride (SiN_x) by plasma-enhanced chemical vapor deposition (PECVD) (Fig. 3-9f). According to the described photolithography and etching process, the nitride layer was removed from the Cu contact pad area. At this point the device was annealed at 450°C for 8 hours in a vacuum tube furnace with a base pressure of 10^{-7} Torr to stabilize the SiN_x and

tungsten resistance thermometer. Finally, freestanding membranes were fabricated by anisotropically etching the Si in a solution of 15 g KOH in 50 ml H₂O at 85°C for approximately 9 hours (Fig. 3-9g). In this etching process, the patterned Si₃N₄ coating on the backside of the substrate served as a hard mask. The created metallization pattern on the front side was protected by a sample holder that exposes only the backside of the device to the KOH solution [51].

3.2.3. Ti-Ni-Hf Library Synthesis

Ti-Ni-Hf films were deposited onto the PnSC through a micro-machined shadow mask via DC magnetron co-sputtering of pure Ni, Ti and Hf at room temperature (Fig. 3-10). The depositions were performed in an ATC 1800 AJA International sputtering system. The system was equipped with three confocal sputter guns with adjustable inclination. The sputtering guns were tilted toward the concentric point so that the chimneys were close to touching (Fig. 3-10). This positioned the guns directly under the device and reduced the possibility of any secondary shadowing from the openings of the shadow mask. By this same reasoning, the working distance was set to the maximum for the sputtering system, i.e. approximately 120 mm. The shadow mask is used to restrict the deposition only to the area of the Si₃N₄ membrane measured by the resistance thermometer (Fig. 3-11), where the extrusions in the shadow mask fit into the recesses of the PnSC (Fig. 3-10).

The deposition was performed at an Ar working gas pressure of 3 mTorr in a vacuum chamber with a base pressure in the 10⁻⁸ Torr range. The DC powers applied to Ni, Ti and Hf targets (Ø 50.8 mm) were 70, 180 and 30 W, respectively. The deposition lasted 30 minutes and resulted in a uniform sample thickness of approximately 300 nm. The PnSC

device and attached shadow mask were held stationary to produce a composition gradient across the array of nano-calorimeters (Fig. 3-10). Finally, the samples were capped with approximately 30 nm of SiN_x using a plasma-enhanced chemical vapor deposition process (PECVD, Surface Technology Systems).

The areas of the openings in the shadow mask were measured by optical transmission microscopy using a Nikon Eclipse ME600L microscope equipped with a CCD camera. The volumes of the Ti-Ni-Hf films were determined by depositing reference samples on a dummy substrate immediately prior to depositing the calorimetry samples and by measuring the reference sample thickness with a Veeco Detek 6M profilometer (Table 3-2). The thicknesses of the samples can be found in Table 3-2.

Figure 3-10 Sputter deposition schematic of Ni-Ti-Hf samples. The figure has been drawn after Fig. 4 in Ref. [51].

Table 3-2 Thickness of the Ti-Ni-Hf films after deposition (nm).

A 292 ± 4	B 292 ± 6	C 292 ± 8	D 293 ± 6	E 294 ± 4
F 293 ± 1	G 295 ± 4	H 297 ± 6	I 295 ± 4	J 291 ± 3
K 293 ± 2	L 298 ± 2	M 303 ± 3	N 297 ± 3	O 291 ± 3
P 288 ± 1	Q 288 ± 2	R 300 ± 2	S 297 ± 3	T 293 ± 4
U 282 ± 6	V 289 ± 1	W 298 ± 2	X 297 ± 4	Y 295 ± 5

Figure 3-11 Photograph of the micro-machined shadow mask.

The chemical compositions of the samples were determined quantitatively by wavelength dispersive X-ray spectroscopy in a JEOL JXA 8200 scanning electron microscope using the standard spectra of pure nickel, titanium and hafnium. The array of chemical compositions based on the cells' location is shown in Table 3-3.

A 4800 nm film of a specific Ti-Ni-Hf alloy was also deposited on a rotating (3 rpm) Si_3Ni_4 -coated Si substrate using the same sputtering conditions. The as-deposited film was peeled off (freestanding film) and used for traditional DSC measurements (Fig. 3-12). The composition of the film was approximately similar to the cell R of PnSC device (Table 3-3).

Figure 3-12 A Ti-Ni-Hf free-standing film.

Table 3-3 Calorimetric cell labeling with corresponding sample chemical composition (atomic %). The Ti, Ni and Hf uncertainties were approximately 0.3, 0.4 and 0.1 at.% respectively.

A $\text{Ti}_{35.7}\text{Ni}_{50.9}\text{Hf}_{13.4}$	B $\text{Ti}_{34.4}\text{Ni}_{51.4}\text{Hf}_{14.2}$	C $\text{Ti}_{32.9}\text{Ni}_{51.9}\text{Hf}_{15.2}$	D $\text{Ti}_{31.9}\text{Ni}_{52.4}\text{Hf}_{15.7}$	E $\text{Ti}_{30.6}\text{Ni}_{52.2}\text{Hf}_{17.2}$
F $\text{Ti}_{37.7}\text{Ni}_{48.7}\text{Hf}_{13.6}$	G $\text{Ti}_{36.1}\text{Ni}_{49.3}\text{Hf}_{14.6}$	H $\text{Ti}_{34.7}\text{Ni}_{49.8}\text{Hf}_{15.5}$	I $\text{Ti}_{33.3}\text{Ni}_{50.0}\text{Hf}_{16.7}$	J $\text{Ti}_{32.1}\text{Ni}_{50.2}\text{Hf}_{17.7}$
K $\text{Ti}_{39.6}\text{Ni}_{46.1}\text{Hf}_{14.3}$	L $\text{Ti}_{38.1}\text{Ni}_{47.0}\text{Hf}_{14.9}$	M $\text{Ti}_{36.5}\text{Ni}_{47.5}\text{Hf}_{16.0}$	N $\text{Ti}_{35.1}\text{Ni}_{47.7}\text{Hf}_{17.2}$	O $\text{Ti}_{33.5}\text{Ni}_{47.9}\text{Hf}_{18.6}$
P $\text{Ti}_{42.3}\text{Ni}_{42.5}\text{Hf}_{15.2}$	Q $\text{Ti}_{40.6}\text{Ni}_{43.1}\text{Hf}_{16.3}$	R $\text{Ti}_{38.8}\text{Ni}_{43.6}\text{Hf}_{17.6}$	S $\text{Ti}_{36.7}\text{Ni}_{45.4}\text{Hf}_{17.9}$	T $\text{Ti}_{34.8}\text{Ni}_{46.0}\text{Hf}_{19.2}$
U $\text{Ti}_{43.3}\text{Ni}_{41.5}\text{Hf}_{15.2}$	V $\text{Ti}_{41.9}\text{Ni}_{41.9}\text{Hf}_{16.2}$	W $\text{Ti}_{39.9}\text{Ni}_{42.7}\text{Hf}_{17.4}$	X $\text{Ti}_{38.1}\text{Ni}_{43.3}\text{Hf}_{18.6}$	Y $\text{Ti}_{36.7}\text{Ni}_{43.4}\text{Hf}_{19.9}$

3.2.4. Calorimetric Measurement

The scanning calorimetry measurement was performed by applying a DC pulse current (I_S) to the W heater, thus increasing the temperature of the system by Joule heating (Fig. 3-13). The current was determined from the voltage drop V_{IS} across a 100 Ω precision resistor (R_{IS}), while the voltage across the heating element (V_S) was measured via two sense probes. The I_S and V_S values were monitored using a National Instruments PCI-6221 data acquisition card (DAQ), followed by recording the data through a personal computer. Schematic of the measurement is shown in Fig. 3-13 and a typical result is demonstrated in Fig. 3-14. Therefore, the heater resistance (R_S) and power dissipated in the resistance thermometer ($P = V_S I_S$) can be obtained. The temperature of the system was determined by measuring the changes in resistance ($R = V_S / I_S$) of the W strip heater.

Figure 3-13 Schematic of the nano-calorimetry measurement.

Figure 3-14 Typical raw voltage recordings for a PnSC cell with Ni-Ti-Hf sample for an 86 mA current pulse lasting 25 ms.

The $R(t)$ function was employed to calculate the temperature $T(t)$ of the sensor. To do this, the resistance was calibrated against the temperature in an oven. A small pulse current (1 mA) (i.e. produces a negligible heat) was applied to the W heater, while the temperature of the oven was gradually increased and monitored with a K-type thermocouple. By measuring the voltage drop across the heater, the resistance and corresponding temperature function were obtained using the following equations:

$$R(T) = R(T_0) [1 + \alpha \cdot (T - T_0)] \quad (3-6), \text{ Ref. [51]}$$

$$T(R) = \frac{\left(\frac{R}{R(T_0)} - 1 \right)}{\alpha} + T_0 \quad (3-7)$$

where $R(T_0)$ and α were resistance of each cell at ambient temperature (T_0) and temperature coefficient of resistance (TCR) respectively. The value of TCR was determined

from a linear least squares fit of the resistance data as a function of temperature (Fig. 3-15). The TCR and T_0 were $1.56 \times 10^{-3} \text{ K}^{-1}$ and 22°C respectively. The sampling rate for the calorimetry measurement was 100 KHz, which corresponds to a temperature resolution of $\sim 0.1^\circ\text{C}/\text{sample}$ at a heating rate of $10^4^\circ\text{C}/\text{sec}$. All the measurements were performed inside the load lock of a sputter deposition system at a pressure of 10^{-5} Torr (Fig. 3-16) to eliminate convection losses and oxidation.

Figure 3-15 Calibration fit of the temperature coefficient of resistance.

Figure 3-16 Vacuum chamber for the calorimetric measurement.

The power dissipated in the resistance thermometer can be parsed into stored power and power lost to the surroundings. At a constant pressure, the stored power results in a change of the enthalpy of the sample and calorimeter addendum. If we define a control volume (CV) that comprises the sample and the calorimeter addendum, then

$$P = \frac{dH}{dt} + Q \quad (3-8), \text{ Ref. [51]}$$

where P is the total power dissipated in the resistance thermometer, dH/dt is the time rate of change of the enthalpy within the CV, and Q is the heat loss through the boundaries of the CV. The rate of change of the enthalpy can be written as,

$$\frac{dH}{dt} = \frac{dH}{dT} \cdot \frac{dT}{dt} \quad (3-9)$$

where T is the temperature of the resistance thermometer. Substituting equation 3-9 into equation 3-8 and rearranging results in,

$$\frac{P}{\frac{dT}{dt}} = \frac{dH}{dT} + \frac{Q}{\frac{dT}{dt}} \quad (3-10), \text{ Ref. [51]}$$

where dT/dt is the heating rate of the resistance thermometer. The left hand side of equation 3-10 can be directly calculated from measured quantities and is defined as the calorimetric signal from the sensor. If Q is known or if its contribution to equation 3-10 is negligible (e.g., in case of very large heating rates), the change in enthalpy with temperature, dH/dT , can be determined directly from the calorimetric signal. If no phase transformations or reactions take place, dH/dT is equal to the heat capacity C_P of the control volume; during a phase transformation this term also includes the latent heat of transformation H_L . The heating rate is derived from the following equations:

$$T(R) = \frac{R}{\alpha \cdot R(T_0)} - \frac{1}{\alpha} + T_0 \quad (3-11)$$

Substituting $R = \frac{V_S \cdot R_{IS}}{V_{IS}}$ into equation 3-11 results in,

$$T(R) = \frac{R_{IS}}{\alpha \cdot R(T_0)} \times \frac{V_S}{V_{IS}} - \frac{1}{\alpha} + T_0 \quad (3-12)$$

Taking the derivative of equation 3-12 with respect to the time gives:

$$\frac{dT}{dt} = \frac{R_{IS}}{\alpha \cdot R(T_0)} \times \left[\frac{\frac{dV_S}{dt} \times V_{IS} - \frac{dV_{IS}}{dt} \times V_S}{V_{IS}^2} \right] \quad (3-13)$$

Using the formula $R_{IS} = \frac{R \cdot V_{IS}}{V_S}$ and equation 3-13, the $\frac{dT}{dt}$ can be expressed as:

$$\frac{dT}{dt} = \frac{R(T)}{\alpha \cdot R(T_0)} \times \left(\frac{1}{V_S} \cdot \frac{dV_S}{dt} - \frac{1}{V_{IS}} \cdot \frac{dV_{IS}}{dt} \right) \quad (3-14)$$

where $\frac{dV_S}{dt}$ and $\frac{dV_{IS}}{dt}$ are the voltage rates calculated from a linear least squares fit to the respective data history. The calorimetric signal can be expressed in terms of measurable quantities as,

$$\frac{P}{\frac{dT}{dt}} = \alpha \cdot R(T_0) \cdot I^2 \times \left(\frac{1}{V_S} \cdot \frac{dV_S}{dt} - \frac{1}{V_{IS}} \cdot \frac{dV_{IS}}{dt} \right)^{-1} \quad (3-15)$$

To reduce the effect of the calorimeter addendum and/or heat loss on the measurement, it is often convenient to perform a reference measurement. Equation 3-10 can then be rewritten to define the differential calorimetric signal as,

$$\Delta \frac{P}{\frac{dT}{dt}} = \Delta \frac{dH}{dT} + \Delta \frac{Q}{\frac{dT}{dt}} \quad (3-16), \text{Ref. [51]}$$

where Δ represents the difference between a sensor with a sample and a sensor that is either empty or that contains a reference sample. The differential calorimetric signal is the quantity that is analyzed to determine transformation temperatures and latent heats throughout this study. The heat loss is typically small because of the near-adiabatic conditions of the measurements. Its contribution can be eliminated from the signal by comparing measurements on a sample and on a reference performed at the same heating rate.

In this study, both the sample and the reference measurements were made using the same sensor in a scheme where calorimetric measurements on non-transforming phases were used as reference measurements for transforming phases. Specifically, the as-deposited amorphous samples were fully crystallized in one heating cycle to approximately 850°C, resulting from a current pulse of 86 mA lasting 65 ms. Subsequent cycles to 850°C showed no indication of further crystallization; two of these cycles were used to ensure that the microstructure was stable before performing low-temperature cycles. The average of ten additional high-temperature cycles then served as a reference measurement for the crystallization process. Low-temperature cycling to 450°C was used to investigate the martensite-austenite phase transformation. One hundred of these low-temperature cycles were performed before and after the ten additional high-temperature cycles. The reference for low-temperature measurements was established by averaging 100 low-temperature cycles of each as-deposited amorphous sample. This reference measurement approach very nearly eliminated the contributions to the calorimetric signals from both heat loss and calorimeter addendum. An advantage of using a sensor plus sample as its own reference, as opposed to a bare reference sensor, is that its mass is exactly the same. Consequently, any deviation between calorimetric signals must be related to a change in the enthalpy of the

sample. The difference in calorimetric signals between sample and reference, i.e., the differential calorimetric signal, was used to calculate transformation temperatures and latent heats throughout this study. The details of nano-calorimetric experiments for each measurement (i.e. applied current amplitudes and durations) are reported in Table 3-4. The raw data were analyzed by Wolfram Mathematica (version 9) and Origin (version 8.5) software using the previously explained equations.

Alternatively, traditional differential scanning calorimetry (DSC) using a TA Q200 instrument was employed to study the transformation behavior of a Ti-Ni-Hf freestanding film. The DSC was performed under N₂ atmosphere (50 ml.min⁻¹) at heating and cooling rates of 10 °C /min. The mass of the sample was 7.4 mg and an empty aluminum pan was used as a reference. The as-deposited film was first crystallized by heating the sample to 540°C, followed by cooling to -10°C before equilibrating at room temperature. To analyze the martensitic transformation, the crystallized sample was heated to 540°C, followed by cooling to -10°C; this cycle was repeated twice.

3.2.5. Structural Analysis Methods

The crystal structure of the samples was examined by X-ray diffraction (XRD) using a Brucker D8 system with Cu K α radiation and a Vantec2000 2D area detector. Transmission electron microscopy (TEM) operating in high-resolution mode was conducted using a JEOL 2010 FEG-TEM instrument at an accelerating voltage of 200 kV. To prepare the TEM samples, a calorimetric cell including Ti-Ni-Hf thin film and W heater were glued to the small pieces of Si (100) wafers from the W part. The samples were cut to the pieces

smaller than a 3 mm diameter and were glued to the copper support grids from the film side. The substrate sides of the samples (Si wafer) were ground away until the total thickness was approximately 10 μm . Finally, the samples were thinned to electron transparency by argon ion beam milling. TEM micrographs were recorded using a Gatan 1k $\times$ 1k slow-scan CCD camera, and were processed using a Gatan Digital Micrograph software.

Table 3-4 Current pulse amplitude and duration for calorimetric measurements.

Treatment	Amplitude (mA)	Duration (ms)	Number of Cycles
$R(T_0)$ measurement	1	20	10
Martensite-austenite transformation baseline	86	25	100
Crystallization of the as-deposited samples	86	65	1
Stabilization of the microstructure after crystallization	86	65	2
Martensite-austenite transformation / Thermal cycling	86	25	100
Amorphous-crystalline baseline	86	75	10
Martensite-austenite transformation / Thermal cycling	86	25	100

3.3. Summary

In summary, the experimental procedures and analysis methods to study the effect of rapid thermal annealing (RTA) and conventional thermal annealing (CTA) on the evolution of structural, surfacial and nano-scale mechanical properties of Ti-Ni-Cu thin films were described. The amorphous Ti-Ni-Cu thin films (~500 nm) were synthesized by magnetron co-sputtering at room temperature. The resultant films were crystallized by RTA and CTA treatments. The crystallinity, surface morphology and chemistry, local atomic structure and

mechanical properties of the films were probed quantitatively by X-ray diffraction, atomic force microscopy, X-ray photoelectron spectroscopy, X-ray absorption spectroscopy and nanoindentation.

The PnSC device was described in details. This device combined a combinatorial synthesis method and nano-calorimetry to create a powerful tool for fast calorimetric analysis of thin film materials. The combinatorial capability of the device was demonstrated by synthesizing a sample library of Ti-Ni-Hf thin films (~ 300 nm). The principles of scanning calorimetry measurement through PnSC were reported. The calorimetric measurement protocols to study the crystallization, martensitic transformation and thermal cycling in Ti-Ni-Hf sample library were described.

Chapter 4

Characterization of Amorphous Ti-Ni-Cu Thin Films Crystallized by Rapid Thermal Annealing

In this chapter, the structural, surfacial and nano-scale mechanical properties evolution of Ti-Ni-Cu thin films, prepared by the co-sputtering of TiNi and Cu targets during rapid thermal annealing (RTA) are investigated. The crystallinity, surface morphology and chemistry, local atomic structure and mechanical properties of the films are probed by X-ray diffraction, atomic force microscopy, X-ray photoelectron spectroscopy, X-ray absorption spectroscopy and nanoindentation.

4.1. Crystallization of Amorphous Ti-Ni-Cu Thin Films

Crystallization of Ti-Ni-Cu films were studied at 450, 480 and 500°C for 180 sec. Fig. 4-1 shows the XRD patterns of these samples. A broad peak is clearly seen in the as-sputtered sample. The annealed film at 450°C remains largely amorphous, but some low intense Bragg diffraction is observed in the pattern. The films annealed at 480 and 500°C show similar XRD patterns with clear and sharp peaks. Therefore, these temperatures are suitable for crystallization of the Ti-Ni-Cu films by rapid thermal annealing.

Figure 4-1 XRD patterns of the Ti-Ni-Cu thin film in the as-sputtered condition and different crystallization temperatures for 180 sec.

Fig. 4-2 shows the X-ray diffraction patterns of the as-sputtered film and after RTA at 480°C for different holding times (10 to 180 sec) and for CTA at (480°C / 1 hr). The broad X-ray diffraction feature confirms the deposited film is substantially amorphous. After RTA for 10 sec, the film is primarily aperiodic, but higher angle intensity is indicative of the onset of crystal nucleation. Longer times (up to 180 sec) yielded intense Bragg reflections. Similarly, pronounced X-ray diffraction was evident after CTA, but in detail is distinct from RTA films. Nevertheless, the CTA sample can be used as a benchmark for comparison with short annealed RTA films. The XRD shows the 60, 120 and 180 sec RTA samples are similar to CTA for 1 hr, thus verifying the ability of rapid thermal annealing to crystallize Ti-Ni-Cu films in a few seconds. In order to identify the phases in the crystallized films (RTA 180 sec and CTA 1 hr), long XRD scan (12 hrs) were performed,

and showed both RTA and CTA films contain austenite (B2), martensite (B19') and Ti_2Ni phases (Fig. 4-3).

Figure 4-2 XRD spectra of the as-sputtered and annealed films after rapid thermal annealing at 480°C for different duration times and conventional thermal annealing at 480°C for 1 hr.

The kinetics of RTA crystallization is evidently different from CTA [26, 143]. In the former, a light source of incoherent photons (tungsten halogen lamp) is shone on infinite regions of the sample surface, and particularly in thin films, the crystallization temperature is rapidly reached. In addition, during RTA photonic absorption in visible, ultraviolet (UV) and vacuum ultraviolet (VUV) regions may promote high activation energy reactions [144]. Furthermore, interactions of the irradiated photons with surface atoms (photo-effect) may enhance atomic diffusion [145]. On the other hand, it is the likely presence of a thermal

gradient between the attached thermocouple placed on the bottom of the dummy silicon wafer ($\sim 300 \mu\text{m}$ thick) and the thin film surface; consequently, higher temperature is expected near the exposed areas. Taken together, these effects greatly accelerate crystallization, and consequently, grain growth is limited, microstructures more easily controlled, and the thermal budget (product of processing temperature and time) optimized.

Figure 4-3 XRD indexed patterns of the RTA 180 sec and CTA 1 hr films.

4.2. Changes in Surface Morphology of Ti-Ni-Cu Film during RTA

Thin film surfaces are of key importance and determine the technological impact of the solid surface interaction with its surroundings. It is well known that surface chemistry and

morphology dictate properties such as wear, corrosion resistance and biocompatibility which are of particular significance for TiNi thin films. A few studies have investigated the surface morphology and chemistry of TiNi films after conventional thermal annealing [146, 147], but there are no comparable experiments where crystallization was driven by irradiation (RTA).

Fig. 4-4 shows the atomic force microscopy (AFM) 2D and 3D images of the Si (100) substrate and the as-sputtered film. Parallel features (texture) in the substrate (Fig. 4-4a) remain visible after sputtering with atoms deposited as uniform islands on the Si (Fig. 4-4b). The roughness (rms value) of the Si substrate and as-sputtered film were 0.9 and 1.2 nm respectively. The surface morphologies of the RTA films at (480°C for 10-180 sec) and CTA at (480°C for 1 hr) are compared in Fig. 4-5. The size and distribution of the surface islands varied significantly during RTA, and for longer treatments (up to 180 sec), became large and irregular; in contrast to the CTA product, where the distribution was more homogeneous and variation in height was far less. For all samples, the variation of the surface roughness was obtained from 5 μ m $\times$ 5 μ m AFM images of the samples. The roughness increased greatly in the RTA films up to 180 sec (Fig. 4-6), while for the CTA film, it was little changed by heat treatment. The structural evolution of the amorphous islands formed during sputtering can be driven by crystallization, or possibly, oxidation. The distinct surface morphologies of the films crystallized by RTA and CTA are attributed to the heating process (Fig. 4-7). In RTA, a series of parallel halogen lamps are shone on the films in argon with heating primarily perpendicular to the film (Fig. 4-7), whereas during CTA, heating in the vacuum tube furnace is uniform (Fig. 4-7). Therefore, RTA promotes growth perpendicular to the substrate leading to greater roughness. Additionally, the irregular crystal growth induced by the higher temperature gradients in the film-

substrate surface of the RTA sample may also cause the higher roughness values. Although RTA is energy efficient, the films are less uniform than those produced by CTA if roughness was critical for a specific application.

Figure 4-4 2D and 3D AFM images of the Si (100) substrate (a) and as-sputtered film (b)

[124].

Figure 4-5 3D AFM images of the as-sputtered (a) RTA 10 sec (b) RTA 60 sec (c) RTA 120 sec (d) RTA 180 sec (e) and CTA 1 hr (f) films [124].

Figure 4-6 Variation of roughness (determined by rms value) versus different crystallization condition.

Figure 4-7 Schematic of the heating directions in rapid thermal annealing (RTA) and conventional thermal annealing (CTA) [124].

4.3. Comparison of Surface Chemistry in RTA and CTA Films

XPS of as-sputtered, RTA (480°C / 120 sec) and CTA (480°C / 1 hr) films are essentially identical and contain Ti, O and C and Auger O KLL peaks, but no distinct Cu and Ni signatures (Fig. 4-8).

Figure 4-8 XPS survey profile of as-sputtered, crystallized film by RTA at 480°C for 120 sec and crystallized sample by CTA at 480°C for 1 hr [124].

High resolution spectra of Ti 2p, Ni 2p, Cu 2p, O 1s, C 1s and Ar 2p of the surface and subsurface were obtained. The standard C 1s and Ar 2p binding energies are used for energy calibration [148] with the chemical composition data summarized in Table 4-1.

Table 4-1 Surface and subsurface chemistry of as-sputtered and crystallized films by RTA and CTA [124].

Samples	Atomic Concentration					
	As-sputtered		RTA 120 sec		CTA 1 hr	
	Surface (at. %)	Subsurface (at. %)	Surface (at. %)	Subsurface (at. %)	Surface (at. %)	Subsurface (at. %)
Ti	25.3	20.8	22.2	39.0	21.6	36.5
Ni	1.3	61.4	0.0	0.0	0.0	0.0
Cu	0.5	1.4	0.0	0.7	0.0	0.0
O	72.9	16.4	77.8	60.3	78.4	63.5

The nickel high resolution profiles of the films are shown in Fig. 4-9. The main Ni 2p 3/2, Ni 2p 1/2 and satellite peaks are evident after ion etching of the as-sputtered film, while only an indistinct Ni 2p 3/2 signature was observed at the surface. There are no distinct Ni photoelectron peaks at the surface (monolayer) or subsurface of both crystallized films by RTA and CTA. Similarly, Cu is observed on the surface of the as-sputtered sample, but the Cu 2p 3/2 and Cu 2p 1/2 B.E.'s are clearly evident after etching (Fig. 4-10). For the RTA film, 10 min Ar⁺ sputtering was required to expose the Cu-enriched subsurface. Fig 4-11 shows Ti 2p spectra indicative of mixed chemical states in both as-sputtered and crystallized films.

Figure 4-9 Typical Ni 2p spectra of the samples at surface and after Ar⁺ sputtering for 5 and 10 min; (a) as-sputtered, (b) crystallized film by RTA at 480°C for 120 sec and (c) crystallized film by CTA at 480°C for 1 hr [124].

Figure 4-10 Typical Cu 2p spectra of the samples at surface and after Ar⁺ sputtering for 5 and 10 min; (a) as-sputtered, (b) crystallized film by RTA at 480°C for 120 sec and (c) crystallized film by CTA at 480°C for 1 hr [124].

Figure 4-11 Typical Ti 2p spectra of the samples at surface and after Ar^+ sputtering for 5 and 10 min; (a) as-sputtered, (b) crystallized film by RTA at 480°C for 120 sec and (c) crystallized film by CTA at 480°C for 1 hr [124].

At the surface, the Ti 2p spectra could be fitted to three chemical states, namely, Ti^0 (TiNi), Ti^{3+} (Ti_2O_3) and Ti^{4+} (TiO_2) in the as-sputtered film [146, 148, 149], whereas there is no metallic Ti^0 (TiNi) for RTA and CTA films (Fig. 4-12), and the dominant oxide phase is TiO_2 for all the samples (Table 4-2). It is likely that oxide formation on the surface of the as-sputtered film is due to the high reactivity of Ti with air, even at low temperature. The change in color of the crystallized films is believed to be related to the oxidation state of titanium, and Ti^{4+} is more abundant after CTA compared to RTA (Table 4-2).

The chemical states of Ti in the subsurface (~ 30 nm depth) for the as-sputtered and the crystallized films by RTA and CTA are shown in Fig. 4-13. Two chemical states of Ti, namely, Ti^0 (TiNi) and Ti^{2+} (TiO) were observed for the as-sputtered film with higher concentration of the Ti^0 (TiNi) state compared to the Ti^{2+} (TiO) state (Table 4-2). The XPS profile of the crystallized RTA film is similar to the CTA sample. In the subsurface, four chemical states of Ti, namely, Ti^0 (TiNi), Ti^{2+} (TiO), Ti^{3+} (Ti_2O_3) and Ti^{4+} (TiO_2) are observed (Fig. 4-13) for RTA and CTA samples that are compositionally similar (Table 4-2).

Figure 4-12 Typical Ti 2p spectra of the samples at surface; (a) as-sputtered, (b) crystallized film by RTA for 120 sec and (c) crystallized film by CTA for 1 hr. The empty triangles indicate the experimental spectra and the dash line shows fitted spectra. Standard peaks are shown with solid lines [124].

Figure 4-13 Typical Ti 2p spectra of the samples after Ar^+ sputtering for 10 min (subsurface); (a) as-sputtered, (b) crystallized film by RTA for 120 sec and (c) crystallized film by CTA for 1 hr. The empty triangles indicate the experimental spectra and the dash line shows fitted spectra. Standard peaks are shown with solid lines [124].

Table 4-2 Atomic concentration of different oxidation states for as-sputtered and crystallized films by RTA and CTA [124].

Samples	Atomic Concentration					
	As-sputtered		RTA 120 sec		CTA 1 hr	
	Surface (at.%)	Subsurface (at.%)	Surface (at.%)	Subsurface (at.%)	Surface (at.%)	Subsurface (at.%)
Ti ⁰ (TiNi)	3.3	55.8	-	26.5	-	25.0
Ti ²⁺ (TiO)	-	44.2	-	25.8	-	28.0
Ti ³⁺ (Ti ₂ O ₃)	2.6	-	19.6	28.9	6.4	25.7
Ti ⁴⁺ (TiO ₂)	94.1	-	80.4	18.8	93.6	21.3

4.4. Comparison of Local Atomic Structure in RTA and CTA Films

X-ray absorption spectroscopy (XAS) is a powerful technique to examine near-neighbor atomic pairs and assess order-disorder phenomena [150, 151]. However, there is no information on the evolution of co-ordination shells of TiNi-based thin films during the aperiodic-crystalline transition. Therefore, to obtain a deeper understanding of crystallization during annealing, local atomic environments were probed by extended X-ray absorption fine structure (EXAFS) spectroscopy.

Changes in metal co-ordination number accompanying the crystallization of Ti-Ni-Cu films were investigated using XAFS. The Ni K-edge spectra for as-sputtered, RTA and CTA products are shown in Fig. 4-14a, where the amplitude of the crystalline materials is more pronounced than the amorphous film. The degree of atomic ordering is best seen in the radial distribution functions (RDF) of the EXAFS spectra (Fig. 4-14a) over the wavenumber (k) range of 2.25-10.5 Å⁻¹ (Fig. 4-14b). It is evident that all the films have

similar first coordination spheres. Fig. 4-15 depicts the fitting results in the R space employing two scattering paths for Ni-Ti and Ni-Ni (Table 4-3).

Figure 4-14 (a) XAFS spectra at Ni K-edges of the films, showing the differences due to changes of structural environment of the amorphous and annealed samples; (b) Fourier transforms of $k^3\chi(k)$ of Ni K-edge for as-sputtered and crystallized films by RTA and CTA (Phase shift was not corrected) [124].

Table 4-3 Structural parameters: N (coordination number), R (interatomic distance), σ (relative displacement of atoms) obtained from Ni K-edge spectra analyzed by the EXAFS technique of the as-sputtered and crystallized films by RTA and CTA [124].

Sample	N (± 1)		R [$\text{\AA}$]		$\sigma^2 (\text{\AA}^2)$	
	Ni-Ti	Ni-Ni	Ni-Ti	Ni-Ni	Ni-Ti	Ni-Ni
As-sputtered	6.9	4.2	2.455 $\pm$ 0.012	2.907 $\pm$ 0.018	0.0127 $\pm$ 0.0001	0.0200 $\pm$ 0.0010
RTA 10 s	7.8	4.1	2.458 $\pm$ 0.011	2.939 $\pm$ 0.009	0.0089 $\pm$ 0.0002	0.0095 $\pm$ 0.0004
RTA 60 s	7.6	4.5	2.456 $\pm$ 0.016	2.899 $\pm$ 0.021	0.0075 $\pm$ 0.0003	0.0079 $\pm$ 0.0001
RTA 180 s	8.1	4.3	2.513 $\pm$ 0.009	3.023 $\pm$ 0.012	0.0068 $\pm$ 0.0004	0.0072 $\pm$ 0.0003
CTA 1 hr	9.2	3.4	2.526 $\pm$ 0.008	3.005 $\pm$ 0.009	0.0046 $\pm$ 0.0003	0.0057 $\pm$ 0.0004

The change of Ni coordination environment, Ni-Ti and Ni-Ni bond distances, and individual Debye-Waller factors (σ^2) for the as-sputtered and crystallized films show that the number of Ti atoms around each individual Ni increased during rapid and conventional thermal annealing with the highest value for the CTA film (Fig. 4-16). The Ni-Ti and Ni-Ni bond distances after rapid thermal annealing (10 and 60 sec) are near those for the as-sputtered samples and with further annealing up to 180 sec increased to the atomic distances of the CTA crystallized film. The Debye-Walter factor (σ^2) is reflective of order correlation, and as expected, the as-sputtered film showed highest disorder indicative of aperiodic structure formation after deposition at ambient temperature (Fig. 4-16c). With longer holding times, σ^2 is reduced with the longest range order for RTA (180 sec) and CTA (1 hr) samples (Fig. 4-16c).

Figure 4-15 Experimental and the fitting profiles of the first shell of Ni K-edge FT for RTA 60 sec by employing for Ni-Ti and Ni-Ni coordinations. The inelastic factor, $S02$ was fixed to 0.70 for Ni edge, while the same E_0 was employed for the two coordination components

[124].

Figure 4-16 The change of (a) Ni coordination environment, (b) Ni-Ti and Ni-Ni bond distances, and (c) individual Debye-Waller factors (σ^2) for Ti-Ni-Cu thin film with different annealing conditions [124].

4.5. Evolution of Nanomechanical Properties due to RTA Crystallization

Nanoindentation is a simple and accurate technique to extract the elastic modulus and hardness of the films. Previous studies have revealed the mechanisms behind the superelastic and shape memory behavior of TiNi-based thin films during nanoindentation [152-155], but the evolution of nano-scale mechanical properties during crystallization of shape memory thin films is not available. In this study, the RTA crystallization of the Ti-Ni-Cu films was examined by nanoindentation to establish the correlation of mechanical properties as a function of crystallization conditions. The fully-crystallized CTA (480°C for 1 hr) film was used as the reference sample. Nanoindentation performed at 2, 2.5 and 3 mN loads for the as-sputtered, crystallized by RTA (480°C / 10, 60, 120 and 180 sec) and the reference films are compared in Fig. 4-17. The load-depth curves are derived from an average of 4 measurements, and show elasto-plastic behavior typical of brittle materials where the unloading path is less linear [156]. To further quantify the effect of crystallization on nanomechanical properties, the elastic modulus of the films were extracted from the load-depth curves using the Oliver-Pharr method [129]. Variation of elastic modulus with load was averaged for all indentation forces (i.e. 12 indents for each sample) (Fig. 4-18). The error bar in Fig. 4-19 represents one standard deviation in the data as calculated using 12 measurements for each particular annealing. The as-sputtered sample has a lowest elastic modulus of ~125 GPa that increased with annealing time to the highest value (~168 GPa) after RTA for 120 sec; a small reduction was observed after 180 sec.

Figure 4-17 Indenter load versus indentation depth curves at 2, 2.5 and 3 mN maximum loads for Ti-Ni-Cu films; (a) as-sputtered, (b) RTA 10 sec, (c) RTA 60 sec, (d) RTA 120 sec, (e) RTA 180 sec, (f) CTA 1 hr. The square, circle and triangle represent the indentation at 2, 2.5 and 3 mN respectively [124].

Figure 4-18 Elastic modulus as a function of the maximum indentation load for as-sputtered, RTA 10 sec, RTA 60 sec, RTA 120 sec, RTA 180 sec and CTA 1 hr films. All data points are an average of 4 measurements and the error bars represent one standard deviation in the measured data [124].

The films can be divided into two groups with respect to the elastic modulus of the CTA reference sample ($E_{\text{Ref}} \sim 158$ GPa): a) The as-sputtered and RTA 10 sec films have elastic moduli significantly lower than the reference sample ($E \ll E_{\text{Ref}}$), and show a large error bar. This large deviation in the as-sputtered film is attributed to domains with short range order encapsulated in an amorphous matrix. Alternatively, in the RTA 10 sec film, the greater volumetric proportion of crystalline regions in the non-crystalline matrix causes large local variance in elastic modulus. b) The films after RTA for 60, 120 and 180 sec possess elastic moduli close to the CTA crystallized film ($E \approx E_{\text{Ref}}$) and display a smaller deviation from the average value, indicative of homogenized crystallized phase formation. These results demonstrate the suitability of nanoindentation as a simple and reliable tool to study crystalline domain formation in Ti-Ni-Cu thin films. The high elastic moduli of the

crystallized films (i.e. RTA 60 sec, RTA 120 sec, RTA 180 sec and CTA 1hr films) compared to the reported values for TiNi-based thin films [157, 158] can be attributed to the formation of precipitates in these samples. The formation of Ti_2Ni precipitates inside austenite-martensite matrix has been previously demonstrated in XRD spectra of RTA 180 sec and CTA 1hr films (Fig. 4-3). Therefore, according to the rule of mixture, $E_{\text{film}} = V_{\text{Matrix}} \cdot E_{\text{Matrix}} + V_{\text{Precipitate}} \cdot E_{\text{Precipitate}}$, where V is the volume fraction; the high elastic moduli of the crystallized films can be explained. The increase of elastic moduli in Ti-Ni-Cu thin films due to the formation of precipitates has been also reported by Borgia et al. [46]. The films oxidation during crystallization can be also an influencing factor for high elastic moduli of the films.

Figure 4-19 Variation of the elastic modulus for as-sputtered, RTA 10 sec, RTA 60 sec, RTA 120 sec, RTA 180 sec and CTA 1 hr films (All data points are an average of 12 measurements and the error bar represent one standard deviation in the measured data [124]).

4.6. Challenges on Characterization of Transformation Temperatures and Functional Properties

As introduced in Chapters 1 and 2, exploring the martensitic transformation characteristics in SMA materials including transformation temperatures is of importance. This study included several attempts to investigate these characteristics; but, some complications during analyses were observed. One of the most common techniques is to load the film and measure the strain changes upon heating and cooling [76]. However, this approach requires testing of freestanding films, which is increasingly difficult with decreasing film thickness [73]. The Ti-Ni-Cu (~550 nm) films of this study were deposited on Si substrate and removing the films from the substrate was challenging.

Substrate curvature measurement during thermal cycling can overcome this limitation and allow analysis of the films supported by substrate in the nano-scale range [73]. The established apparatus for curvature measurement usually requires a whole circular wafer (3 or 4 inch in diameter), but in RTA process, the temperature distribution across the wafer during treatment is not uniform, due to greater heat loss at the wafer edge [159]. To combat this problem, smaller pieces of the films (~1.5 cm × 1.5 cm) were used and this prevented curvature technique measurements.

Nanoindentation as a function of temperatures is another method for exploring the functionality of SMA thin films. High temperature nanoindentation was attempted in this study by building a heater and using the conventional Oliver-Pharr technique [129]. In order to conduct this test accurately, the transducer and the indenter load cell should be isolated from the heating components with a water cooled shield; also the thermal stability

of the heater should be monitored via a feedback loop. In order to control the thermal drift, rigorous analysis of the nanoindentation method is required [160, 161]. Unfortunately, the facilities at hand did not allow such investigations, since the instrument was a conventional room temperature indenter. Thermal drift and creep of the sample could not be distinguished, preventing reliable and reportable analysis.

Differential scanning calorimetry (DSC) is also a well-established method to explore phase transformation characteristics in SMA materials [54-61]. However, as explained in Chapter 3, the DSC technique is typically employed in bulk samples, where the sample mass is in the range of milligrams, and is insufficiently to measure micro or nano grams, since the amount of heat exchanged during the transformation is too small, and the heat capacity of the calorimeter too large [62, 63]. In the case of thin films deposited on a substrate, these issues are more severe. In this study, to characterize the phase transformation temperatures after RTA treatment, a thick layer of Ti-Ni-Cu ($\sim 1.8 \mu\text{m}$) was deposited on a Si wafer, followed by RTA at 480°C for 180 sec. The crystalline film was peeled off from the substrate, as shown in Fig. 4-20. By cutting the film to the small pieces and stacking the resultant layers, ~ 1.2 milligram mass was obtained for DSC measurement. Fig. 4-21 demonstrates the DSC curve of the sample. The double peaks can be clearly observed in both heating and cooling profiles. On cooling, the first transformation is B2 (austenite /cubic) to B19 (martensite /orthorhombic), while the second transformation occurs from B19 to B19' (martenite, monoclinic). The transformation temperatures of the sample can be found in Fig. 4-21. The similar transformations features have been also reported by Miyazaki et al. [12]. The sample shows the small hysteresis of approximately 3°C (i.e. the difference between the peak temperatures on cooling and heating), which is in a good agreement with reported values for Ti-Ni-Cu system [11, 12, 27, 44, 162].

Figure 4-20 Ti-Ni-Cu freestanding film after RTA treatment.

Figure 4-21 DSC thermogram of the Ti-Ni-Cu freestanding film.

The quantification of shape recovery of the free-standing films in this study using the available micro-tensile tester was challenging, because of the difficulties in clamping of the films with the grips. Instead, the shape memory effect is demonstrated qualitatively. The film is heated to $\sim 250^{\circ}\text{C}$, followed by cooling to room temperature (Fig. 4-22). The two-

way shape memory effect can be clearly observed from the photos taken during the heating and cooling of the sample. The film shows a round shape at low temperatures, which is due to the residual stress after sputtering (Fig. 4-22). The rolled film is gradually unrolled by increasing the film temperature. Finally, with cooling of the sample, its original shape is recovered (Fig. 4-22). This type of two-way shape memory effect has been also reported by Fu et al. [163].

Electrical resistivity measurement as a function of temperature is also a promising method to explore phase transformation temperatures in SMA thin films deposited on a substrate [162, 164, 165], which is based on a change in crystal structure with temperature. However, the resistivity method is unable to measure the enthalpy of transformation in the SMA thin film materials. As described in Chapter 3, the parallel nano-scanning calorimeter (PnSC) has been recently developed as a powerful device for calorimetric measurement of nano-scale to micro-scale materials in a high-throughput methodology [51, 52, 64]. More specifically, the PnSC allows high-throughput measurement of enthalpy-related materials properties in thin-film samples. The evaluation of transformations in a range of compositions over a wide temperature range, fast measurement analysis and ability to heat treatment and thermal cycling of thin films are advantages of this device [51]. Therefore, in the next chapters (i.e. 5 and 6), the PnSC will be employed to explore the crystallization; martensitic transformation and thermal cycling behaviour of SMA thin films.

Figure 4-22 Demonstration of two-way shape memory effect in Ti-Ni-Cu freestanding film after RTA treatment (480°C/180s).

4.7. Summary

The structural, surfacial and nano-scale mechanical properties evolution of Ti-Ni-Cu thin films, prepared by the co-sputtering of TiNi and Cu targets during rapid thermal annealing (RTA) were investigated. Crystallization took place in a few seconds at 480°C. With longer annealing time (up to 180 sec), roughness increased dramatically, and was far more prominent than in films crystallized by conventional thermal annealing (CTA). Although RTA is energy efficient due to the shorter heat treatment, the film roughness is less ideal than CTA, which may prove limiting in specific applications. The surface and subsurface

chemical states of Ti, Ni and Cu were compared for RTA and CTA processed materials. Using X-ray absorption spectroscopy (XAS), it was found that the RTA (180 sec) and CTA (1 hr) films possessed the longest range order. The evolution of nano-scale mechanical properties of the RTA films during rapid thermal annealing was also studied. The results demonstrated the suitability of nanoindentation as a simple and reliable tool to study crystalline domain formation in Ti-Ni-Cu thin films. The challenges to characterize the phase transformation characteristics in Ti-Ni-Cu thin films crystallized by RTA were also addressed.

Chapter 5

Phase Transformation Study of Ti-Ni-Hf Thin Films Using Parallel nano-Scanning Calorimetry

TiNi binary and Ti-Ni-Cu thin films are mainly used in low-temperature applications because of their low transformation temperatures ($< 100^{\circ}\text{C}$) [14, 28]. In order to use shape memory-based micro actuators at elevated temperatures, thin films with higher transformation temperatures need to be developed. Ti-Ni-Hf alloys are promising candidates for this purpose, as they demonstrate both high transformation temperatures ($> 100^{\circ}\text{C}$) and low cost compared to the Ti-Ni-Pd and Ti-Ni-Pt systems [29-32]. A number of studies have been reported on the characterization of relatively thick Ti-Ni-Hf coatings prepared through magnetron sputtering and laser ablation [29, 33-35], but there are only few studies on submicron films ($< 1\ \mu\text{m}$) [36]. In this chapter, the transformation behaviour of a Ti-Ni-Hf composition spread is characterized through use of the parallel nano-scanning calorimeter (PnSC), a powerful device developed for calorimetric analysis of nano-scale to micro-scale quantities of materials using a high-throughput methodology [51, 52, 64]. In Chapter 3, the PnSC device and its operation principles are described. In this chapter, the dependence of the crystallization and martensitic transformation characteristics of Ti-Ni-Hf thin films on the composition is explored. A systematic study is also carried out to compare the PnSC and bulk calorimetry results.

5.1. Crystallization of the Ti-Ni-Hf Sample Library

The as-deposited Ti-Ni-Hf samples were confirmed as amorphous by X-ray diffraction (XRD) (Fig. 5-1). The heating profiles of a calorimetric cell with a sample in the as-deposited state and of the cell with sample in the crystalline state are shown in Fig. 5-2a. A step in the temperature response of the as-deposited film is due to the exothermic crystallization, which creates a sharp rise in the heating rate of the sample between 35 and 45 msec (Fig. 5-2b). The corresponding crystallization peak is readily observed in the calorimetric signal for the as-deposited sample (Fig. 5-2c) and is clearly absent in the curve for the crystallized sample (reference sample).

Figure 5-1 XRD pattern of the as-sputtered Ti-Ni-Hf thin film. The reference sample was used for XRD analysis. The thickness of the film was 573 ± 18 nm.

Figure 5-2 (a) Temperature response of the as-deposited and crystallized sample to an 86 mA current pulse lasting 65 ms. (b) Variation of the heating rate versus time for as-deposited and crystallized sample. (c) Calorimetric signal of the as-deposited and crystallized sample plotted as a function of as-deposited sample temperature. (d) Variation of differential calorimetric signal versus temperature [166].

Fig. 5-2c also shows that radiation losses become significant at high temperatures causing a decrease in the overall heating rate. This heat loss is eliminated by taking the difference of the sample and reference signals, although a small radiation correction is needed to completely eliminate it as explained in reference [50]. Fig. 5-2d shows the differential

calorimetric signal as a function of temperature; the exothermic crystallization peak and a glass transition right before crystallization are clearly visible.

The differential calorimetric signal as a function of temperature (crystallization curve) is plotted for all the cells in Fig. 5-3, producing a crystallization library for the as-deposited Ti-Ni-Hf thin films. The glass transition was detected in all the samples except for three: Cell D ($\text{Ti}_{31.9}\text{Ni}_{52.4}\text{Hf}_{15.7}$), Cell E ($\text{Ti}_{30.6}\text{Ni}_{52.2}\text{Hf}_{17.2}$) and Cell J ($\text{Ti}_{32.1}\text{Ni}_{50.2}\text{Hf}_{17.7}$). The glass transition temperature (T_g) is measured for all the samples using the ASTM standard method [167] and the results are mapped in a ternary diagram (Fig. 5-4). The T_g values do not show any correlation with chemical composition. In majority of the samples, the small exothermic peak is evident preceding the larger exothermic peaks (Fig. 5-3J). This peak is attributed to the surface crystallization due to the heterogeneous nucleation from the surface [50]. The samples with Ni content ≥ 50.2 at.% (cells D, E and J) show the strong surface crystallization peaks, which results in a weak glass transition trace in these samples. The barrier energy of nucleation on the surface for these samples is probably lower than the other cells. As the temperature increases, the samples crystallize in the volume of the sample with formation of multi-peaks calorimetric traces (Fig. 5-3).

Figure 5-3 Library of crystallization. The differential calorimetric signal ($\mu\text{J/K}$) of the samples plotted as a function of temperature ($^{\circ}\text{C}$). The unmeasured cells were denoted by cross sign ($\times$).

Figure 5-4 Glass transition as a function of composition; the circles (●) represent compositions of unmeasured samples. The glass transition was not observed in the samples with triangle sign (▼).

A typical example of the crystallization behavior in the library is shown in Fig. 5-5a. A primary crystallization peak, a secondary peak as appeared in the shoulder and an additional high-temperature peak are observed during the crystallization process. Fig. 5-5b shows the XRD pattern of the sample after crystallization. The crystallization process results in formation of Ni(Ti,Hf) austenite phase, (Ti,Hf)₂Ni and (Ti,Hf)₃Ni₄ intermetallic precipitates. The primary crystallization peak is attributed to the formation of Ni(Ti,Hf) austenite, while the second and third peaks are due to the formation of (Ti,Hf)₂Ni and (Ti,Hf)₃Ni₄ phases (Fig. 5-5b). The multi-peaks during crystallization and glass transition have been also reported in the Ti-Ni-Zr thin films grown under the same condition and studied by PnSC [50].

Figure 5-5 (a) Differential calorimetric signal as a function of temperature (crystallization curve) for cell G (Ti_{36.1}Ni_{49.3}Hf_{14.6}), (b) XRD pattern of the cell G after crystallization.

Fig. 5-6 shows the map of crystallization peak temperature (T_c) as a function of composition. The T_c values do not show any correlation with composition and can be described by a mean value and standard deviation of $T_c = 691 \pm 27^\circ\text{C}$. The minimum temperature recorded for the crystallization peak ($\sim 646^\circ\text{C}$) is significantly higher than the previously reported values for Ti-Ni-Hf films in micro-scale thickness ($505 \pm 11^\circ\text{C}$) [34]. This temperature shift is caused by the different heating rates in the studies and the kinetics of the crystallization reaction. In this study, the heating rate is nominally 1.6×10^4 °C/sec while Sanjabi *et al.* used a heating rate of approximately 0.17 °C/sec [34]. It has been also

reported that for TiNi films thinner than 600 nm, the crystal growth rate decreases rapidly with reduction of film thickness, whereas the activation energy increases [108]. Thus, the lower thickness in this study (~ 300 nm) could be also an influencing factor for higher crystallization temperature.

Figure 5-6 Crystallization peak temperature as a function of composition. The triangles (▲) represent compositions of unmeasured samples.

To compare the PnSC crystallization results with bulk calorimetry, a 4.8 μm Ti-Ni-Hf freestanding film in the as-deposited state was crystallized using traditional DSC. The typical heating rate in PnSC, 1.6×10^4 $^{\circ}\text{C}/\text{sec}$, is five orders of magnitude faster than traditional DSC, 0.17 $^{\circ}\text{C}/\text{sec}$. The film composition was approximately similar to the cell R of the PnSC (Table 3-3). Fig. 5-7 shows the differential calorimetric signals as a function of temperature for both techniques. In contrast to traditional DSC, the glass transition is evident immediately before crystallization of the sample by PnSC. Instead, a wide

exothermic peak is clearly observed in traditional DSC, which is a typical feature for structural relaxation in amorphous materials. The high cooling rate during the sputtering process of both samples produces the aperiodic structure (glassy) with significant amounts of free-volume. In traditional DSC, the glassy material is gradually relaxed structurally during slow heating process (Fig. 5-7b). This relaxation is usually occurred in amorphous systems due to the annihilation of free volumes and is accompanied with a heat generation [168-170]. However, in PnSC sample, the structural relaxation is suppressed due to the ultra-fast heating rate (Fig. 5-7a). The crystallization enthalpy in PnSC (~ 55 J/g) is significantly larger than traditional DSC (~ 22 J/g). This disparity could be due to the suppression of structural relaxation during heating and overlapping of multiple peaks during crystallization process.

Fig. 5-8a shows a typical TEM micrograph of a sample crystallized using the PnSC. The crystallization process results in a very small (18 ± 5 nm) grain size. The inset in Fig. 5-8a shows the fine twin structure of the martensite that is observed in some of the grains. The grain size in this sample is much smaller than for the freestanding film crystallized using traditional calorimetry (197 ± 32 nm) (Fig. 5-8b). The small grains formed at grain boundaries of the freestanding film are $(\text{Ti}_{1-x},\text{Hf}_x)_2\text{Ni}$ precipitates, which have the Ti_2Ni base structure [171]. The high-resolution TEM images of these precipitates at different orientations are demonstrated in Fig. 5-9. The low-magnification TEM micrograph of the freestanding film after crystallization can be found in Fig. 5-9a, where $(\text{Ti}_{1-x},\text{Hf}_x)_2\text{Ni}$ precipitates have formed along grain boundaries of $(\text{Ti},\text{Hf})\text{Ni}$ austenite. The HRTEM micrograph of the selected precipitate and $(\text{Ti},\text{Hf})\text{Ni}$ grain have been shown in Fig. 5-9b. The $(0,0,1)$ and $(1,-1,0)$ atomic planes of austenite are clearly observed along $[110]$ zone axis. According to the measured d-spacing values, the lattice constant of $(\text{Ti},\text{Hf})\text{Ni}$ austenite

is 0.2982 ± 0.0028 nm. TEM micrograph of a $(\text{Ti}_{1-x}\text{Hf}_x)_2\text{Ni}$ precipitate ,with a facet interface with respect to the matrix, is shown in Fig. 5-9c. Fig. 5-9d depicts the HRTEM image of the selected $(\text{Ti}_{1-x}\text{Hf}_x)_2\text{Ni}$ precipitate along the $[1,-1,3]$ zone axis. The $(4,-2,-2)$ and $(-2,-2, 0)$ crystallographic planes are observed in this micrograph with the lattice constant of 1.1295 ± 0.0738 nm for $(\text{Ti}_{1-x}\text{Hf}_x)_2\text{Ni}$ precipitate.

Figure 5-7 (a) Comparison of crystallization process between PnSC and traditional DSC;

(a) crystallization via PnSC (cell R: $\text{Ti}_{38.8}\text{Ni}_{43.6}\text{Hf}_{17.6}$), (b) crystallization via traditional

DSC (freestanding film: $\text{Ti}_{39.7}\text{Ni}_{43.3}\text{Hf}_{17.0}$).

Figure 5-8 (a) TEM micrograph of the cell V ($\text{Ti}_{41.9}\text{Ni}_{41.9}\text{Hf}_{16.2}$); the inset shows a typical high-resolution image of twinned martensite, (b) TEM micrograph of the freestanding film [166].

Figure 5-9 (a) TEM micrograph of the freestanding film after crystallization, (b) HRTEM image of a selected $(\text{Ti,Hf})_2\text{Ni}$ precipitate and $(\text{Ti,Hf})\text{Ni}$ grain in segment a, (c) TEM micrograph of the $(\text{Ti,Hf})_2\text{Ni}$ precipitate with facet interfaces, (d) HRTEM image of the selected $(\text{Ti,Hf})_2\text{Ni}$ precipitate in segment c viewed along the $[1,-1,3]$ direction.

5.2. Martensite-Austenite Transformation in the Ti-Ni-Hf Sample Library

Typical low-temperature responses of a cell with a sample in the crystalline state, and that of the same cell with the sample in the amorphous state (reference sample) are shown in Fig. 5-10a. The martensite-austenite (M-A) transformation is not immediately obvious in the temperature history of the crystalline sample, but can be clearly observed in the heating rate trace and the calorimetric signal (Fig. 5-10b and c). The calorimetric signal of the amorphous sample increases faster than that of the crystalline film at temperatures above the M-A transformation (Fig. 5-10c), demonstrating that the specific heat capacity of the amorphous samples increases faster with temperature than that of the crystalline sample. The differential calorimetric signal is shown in Fig. 5-10d.

The enthalpy of transformation (H_{M-A}) is obtained as the area between the transformation peak and a linear baseline fitted to the differential calorimetric signal outside the transformation region. The peak transformation temperature, A_p , is the temperature at which the differential calorimetric signal during the transformation is farthest from the baseline. The differential calorimetric signal is plotted versus temperature for all the cells resulting in a transformation library (Fig. 5-11). A majority of the cells show a M-A transformation except for a few samples in the Ni-rich region of the library.

Figure 5-10 Temperature response of the as-deposited and crystallized sample to an 86 mA current pulse lasting 25 ms, with the crystallized sample transforming martensitically. (b) Variation of the heating rate versus time for the as-deposited and crystallized sample. (c) Calorimetric signal of the as-deposited and crystallized sample plotted as a function of as-deposited sample temperature. (d) Variation of differential calorimetric signal versus temperature [166].

Figure 5-11 Library of martensite-austenite transformation. The differential calorimetric signal (nJ/K) of the samples plotted as a function of temperature ($^{\circ}\text{C}$). The unmeasured cells were denoted by cross sign (X) [166].

The specific enthalpy of transformation ($h_{\text{M-A}}$) is calculated by normalizing $H_{\text{M-A}}$ with respect to sample mass. Assuming that the transforming samples have the martensite structure (B19') at room temperature, the mass of each sample is given by the following expression,

$$m_s = 4V_s \left(\frac{f_{Ni}M_{Ni} + f_{Ti}M_{Ti} + f_{Hf}M_{Hf}}{N_A V_{UC}} \right), \quad (5-1)$$

considering that the martensite unit cell contains four atoms [172]. In this expression, V_s is the measured sample volume, f represents the atomic fractions of Ni, Ti, or Hf obtained from the measured chemical composition, M denotes the molar mass, and N_A is Avogadro's number. V_{UC} is the volume of the martensite unit cell for each sample estimated from the crystal structure information for the $Ni_{50}Hf_xTi_{50-x}$ and $Ni_{(100-x)/2}Ti_{(100-x)/2}Hf_x$ systems [172]. The values of h_{M-A} calculated using this method are reported in Table 5-1 along with the measured A_p values. Fig. 5-12 shows the A_p temperature of the samples in a ternary diagram.

The dependence of A_p on Hf content at different Ni concentrations can be found in Fig. 5-13. A_p increases with increasing the Hf content, reproducing the trend previously reported for *bulk* samples by Abujudom and Sanjabi [32, 34] (Fig. 5-13). The Ni content, by contrast, does not seem to affect the transformation temperature (Fig. 5-13), which has also been observed for bulk samples [32]. It is, however, evident from the figure that the A_p values of the 300 nm thin films are lower than those for 2 μ m films [34] or bulk samples [32]. This size effect is attributed to the microstructure of the samples, i.e., the fine grain structure and even finer twin structure (Fig. 5-8a). For TiNi, it was shown that the excess twin-boundary energy associated with a fine twin structure decreases the stability of the martensite and lowers the transformation temperature [80]. This effect was also observed for Ni-Ti-Zr samples crystallized by PnSC [51]. It is clear that the decrease in transformation temperature observed in the Ni-Ti-Hf samples crystallized by PnSC is caused by the fine nano-scale structure in these samples.

Table 5-1 Martensite-austenite transformation results for compositions, demonstrating a transformation in the calorimetric signal [166].

Cell	Composition (Atomic %)	A_P ($^{\circ}\text{C}$)	$h_{\text{M-A}}$ (J/g)
F	Ti _{37.7} Ni _{48.7} Hf _{13.6}	126.7 ± 0.6	3.4 ± 0.3
G	Ti _{36.1} Ni _{49.3} Hf _{14.6}	107.6 ± 3	0.4 ± 0.1
K	Ti _{39.6} Ni _{46.1} Hf _{14.3}	92.3 ± 0.6	4.8 ± 0.2
L	Ti _{38.1} Ni ₄₇ Hf _{14.9}	131.2 ± 0.5	8.8 ± 0.4
N	Ti _{35.1} Ni _{47.7} Hf _{17.2}	166.9 ± 0.5	5.7 ± 0.4
O	Ti _{33.5} Ni _{47.9} Hf _{18.6}	159.5 ± 1	4.5 ± 0.5
P	Ti _{42.3} Ni _{42.5} Hf _{15.2}	126.7 ± 0.6	4.3 ± 0.3
Q	Ti _{40.6} Ni _{43.1} Hf _{16.3}	137.2 ± 0.4	5.3 ± 0.4
R	Ti _{38.8} Ni _{43.6} Hf _{17.6}	150.2 ± 0.9	9.1 ± 0.7
S	Ti _{36.7} Ni _{45.4} Hf _{17.9}	148.2 ± 0.9	15.4 ± 0.5
U	Ti _{43.3} Ni _{41.5} Hf _{15.2}	153.0 ± 0.6	5.8 ± 0.4
V	Ti _{41.9} Ni _{41.9} Hf _{16.2}	157.9 ± 0.9	8.2 ± 0.3
W	Ti _{39.9} Ni _{42.7} Hf _{17.4}	173.3 ± 0.3	9.5 ± 0.6
X	Ti _{38.1} Ni _{43.3} Hf _{18.6}	207 ± 0.6	8.6 ± 0.5

The transition between transforming and non-transforming samples takes place at a Ni concentration between 49.3 and 49.8 at.%. This transition is likely related to the dependence of the transformation temperature on Ni content reported for binary Ti-Ni alloys [173]. Once the Ni content exceeds 50 at.% in a binary Ti-Ni alloy, an increase of the Ni content by 1 at.% Ni decreases the transformation temperature by as much as 100 $^{\circ}\text{C}$ [54]. This behavior is also observed in Hf₁₀Ti_{90-x}Ni_x alloys, where A_P is significantly reduced by the addition of Ni above 50 at.% [32], suggesting that at least some of the Ni-rich cells (Cells B-E and H-J) may demonstrate a M-A transformation below ambient temperature.

Figure 5-12 Martensite-austenite peak temperature (A_p) as a function of composition. The star shapes show compositions of non-transforming cell. The squares ($\blacksquare$) represent compositions of unmeasured samples.

Figure 5-13 Martensite-austenite peak transformation temperature as a function of Hf content [166]. The bulk and thick film results of Abujudom et al. and Sanjabi et al. are also shown for comparison [32, 34].

In contrast to the transformation temperature, the h_{M-A} values do not show any obvious correlation with chemical composition (Table 5-1). The majority of samples transform with a specific enthalpy ranging from 3.8–15.4 J/g, which is less than the reported bulk value of 25.3 J/g [174]. A comparable range of h_{M-A} (4.9-14.9 J/g) has been also reported for Ti-Ni-Hf films with micro-scale thickness [34, 35]. Cell G ($\text{Ti}_{36.1}\text{Ni}_{49.3}\text{Hf}_{14.6}$) demonstrates a reduced specific enthalpy of transformation, which is most likely due to the formation of the R-phase instead of the B19' martensite phase. The R-phase has a reduced lattice distortion relative to the austenite phase, which decreases the entropy of transformation, and hence the latent heat [89]. It is also possible that the martensite volume fraction in this sample is reduced because of the low transformation temperature and insufficient undercooling. The maximum value of h_{M-A} (15.4 ± 0.5 J/g) belongs to cell S ($\text{Ti}_{36.7}\text{Ni}_{45.4}\text{Hf}_{17.9}$), where the martensite phase transforms to austenite in a two-stage process. The first stage is attributed to the martensite $\rightarrow$ R-phase and the second one is for the R-phase $\rightarrow$ austenite transformation. In binary NiTi, the R-phase has been shown to stabilize with reduced length scale [175] and increased Ni content [176]. The R-phase transformation has been reported in $\text{Ni}_{50}\text{Ti}_{50-x}\text{Hf}_x$ thin films, where the Hf content is less than 16 at.% [34]. A second report observed the R-phase at Hf compositions of less than 3 at.% in the $\text{Ti}_{51-x}\text{Ni}_{49}\text{Hf}_x$ and $\text{Ti}_{52.5-x}\text{Ni}_{47.5}\text{Hf}_x$ systems [36]. These reports combined with the results of this work show that the R-phase can be observed over a wide range of Hf compositions (1-16 at.%), depending on processing conditions.

Fig. 5-14 compares the martensite-austenite transformation curves of samples crystallized by fast scanning on the PnSC device or slow heating in a conventional DSC. The transformation peak is significantly wider for the PnSC measurement. This observation is not caused by temperature non-uniformity in the PnSC device. Indeed, thermal modeling

and calibration experiments show that the temperature distribution along the W sensor is uniform in the temperature range of 22 to 450°C [51, 64], indicating that the broadening of the peak is a real material effect. We attribute the broadening of the transformation peak to the small grain size and the heterogeneous microstructure of the PnSC samples. As mentioned earlier, the grain sizes of PnSC samples are significantly smaller than for samples crystallized using traditional means. The relative widths of the grain size distributions (i.e. the standard deviation divided by the average value) of PnSC samples (~28 %) are also larger than for traditional samples (~16%). It has been reported that the energy barrier to form martensite in TiNi increases significantly when the grain size decreases below 50 nm, due to grain boundary constraints and the interfacial energy of the refined twin variants [80]. Given that the PnSC samples have a wide distribution of very small grains and that these grains transform at different temperatures, it is not surprising that the transformation peak is much broader than for samples with larger grains.

Figure 5-14 Comparison of martensite-austenite transformation in PnSC and traditional DSC; (a) M-A transformation in traditional calorimetry and (b) M-A transformation in PnSC [166].

5.3. Summary

In summary, the PnSC was employed to study the crystallization and martensitic transformation of Ti-Ni-Hf thin-films as a function of composition. The amorphous Ti-Ni-Hf thin films (~ 300 nm) were crystallized by local heating in a process that lasted only tens of milliseconds, resulting in ultra-fine (18 ± 5 nm) grains structure. The glass transition and

crystallization behavior of the thin film sample library were explored. The crystallization occurred as a multi-stage process, initiating with surface crystallization followed by volume crystallization of (Ti,Hf)Ni austenite phase. The calorimetric traces of equilibrium precipitates were observed after crystallization. The (Ti,Hf)-rich Ti-Ni-Hf alloy compositions with Ni contents below ~ 49.3 at.% exhibited the martensite-austenite transformation. The transformation temperature increased linearly with increase of Hf content in the range 14-20 at.% at a rate comparable to that observed for bulk materials, but with reduced A_p temperature. The decrease in transformation temperature is caused by the fine nano-scale structure in Ti-Ni-Hf thin samples. The marteniste–austenite transformation peak in the PnSC was significantly broader than that observed in bulk calorimetry. The peak broadening was attributed to the ultra-fine grain structure in PnSC sample and also its large relative grain size distribution compared to the bulk calorimetry sample.

Chapter 6

Effect of Thermal Cycling on Transformation Behavior of Ti-Ni-Hf Thin Films

Understanding the thermal stability of SMA materials is of importance, since in many applications they are subjected to many thermal cycles [177-179]. Typically, Shape memory phases are intermetallic compounds that exist over a restricted composition range in a materials system with many intermetallic phases. During cycling, the SMA component is heated to a temperature above austenite formation and cooled to a temperature in the martensitic state. At higher temperatures in the austenite phase, it is possible formation of new phases which may affect the thermal cycling behavior of material. Precipitation of secondary phases will alter the composition and the stress state of the shape memory phase; both affect the shape memory characteristics. SMA can exhibit another thermal instability associated with the martensite phase transformation, where repeated cycling through the martensite-austenite phase transformation results in reduced transformation temperatures, enthalpies and useable work capacity [177, 180, 181]. This fatigue is a dislocation-mediated phenomenon [177]; therefore its importance can become significant in high- temperature SMA where the dislocation activity can be increased due to the higher transformation temperatures.

In this chapter, the PnSC was used to study the effect of thermal cycling on the transformation behavior of the Ti-Ni-Hf alloy. Two types of thermal cycles were applied to the samples: In the first type, samples were heated to 450°C and then cooled to ambient

temperature (low-temperature or LT cycling) (Fig. 6-1a). In the second type, samples were heated to 850°C before cooling (high-temperature or HT cycling) (Fig. 6-1b).

Figure 6-1 Heating profiles applied to the cells for each cycle during thermal cycling; (a) low-temperature cycle and (b) high-temperature cycle.

6.1. Low Temperature Cycling (LTC)

Fig. 6-2 shows the variation of the differential calorimetric signal as a function of the number of low-temperature thermal cycles for cells L, N, Q, R, S, V, W and X. In the figure, the transformation peak shifts toward lower temperatures with increasing number of cycles. This behavior is observed for all transforming samples as illustrated in Fig. 6-3. The value of A_P decreases fast initially, but then stabilizes after a certain number of cycles.

The reduction in A_P is attributed to plastic deformation caused by the crystallographic incompatibility between the austenite and martensite phases at the phase boundary [177, 182]. This mismatch results in large stresses that lead to the formation of dislocations. These dislocations, in turn, can relax residual stresses caused by crystallization and precipitation. Since the residual stresses can be relaxed more easily by the self-accommodating twin structure of the martensite, and the elimination of these stresses removes this bias, the net result is to make the austenite relatively more stable, thus reducing the transformation temperature. It is difficult to discern a clear correlation between the change in A_P temperature and the composition of the samples (Table 6-1). The average reduction in transformation temperature of Ti-Ni-Hf thin films in this study ($7.9 \pm 4.0^\circ\text{C}$ for 100 cycles) (Table 6-1) is significantly less than the reported bulk values ($28 \pm 13^\circ\text{C}$) [30, 118, 183].

Chapter 6 Effect of Thermal Cycling on Transformation Behavior of Ti-Ni-Hf Thin Films

Caption in the next page ...

Figure 6-2 Martensite-austenite transformation peaks as a function of the number of low-temperature cycles; (a) cell L, (b) cell N, (c) cell Q, (d) cell R, (e) cell S, (f) cell V, (g) cell W and (h) cell X.

Thermal fatigue is undesirable from a practical standpoint. It has been shown that thermal cycling stability can be improved by various methods. Reducing the lattice mismatch, and hence the driving force to generate dislocations, can improve thermal cycling stability [165, 184]. Limiting the activity of dislocations by creating barriers within the crystal structure, for example grain boundaries or precipitates, will also improve stability [185]. Finally, a fine grain structure and martensite twin structure will reduce the volume of material exposed to the large elastic stresses caused by the lattice mismatch. This decreases the elastic energy available to create dislocations, thus reducing the likelihood of dislocation formation. The improved thermal cycling stability of the samples in this study compared to previous results for *bulk* materials can be attributed to their nano-scale grain structure, which reduces the elastic energy available to nucleate dislocations and creates boundaries to dislocation motion. This finding is supported by recent reports that demonstrate improved thermal cycling stability in Ni-Ti-Hf thin films due to Laves phase precipitates

acting as barriers to dislocation motion [36], and improved thermal cycling stability in nanocrystalline Ni-Ti-Zr [181].

Figure 6-3 Variation in A_P transformation temperature as a function of the number of low-temperature cycles [166].

Table 6-1 Thermal stability of Ti-Ni-Hf thin films over 100 low-temperature cycles as a function of composition.

No.	Composition	$\Delta T(^{\circ}\text{C})$ $T_{\text{cycle 1}} - T_{\text{cycle 100}}$
1	Ti _{36.1} Ni _{49.3} Hf _{14.6}	3
2	Ti _{39.6} Ni _{46.1} Hf _{14.3}	2
3	Ti _{38.1} Ni ₄₇ Hf _{14.9}	10
4	Ti _{35.1} Ni _{47.7} Hf _{17.2}	16
5	Ti _{33.5} Ni _{47.9} Hf _{18.6}	7
6	Ti _{42.3} Ni _{42.5} Hf _{15.2}	2
7	Ti _{40.6} Ni _{43.1} Hf _{16.3}	9
8	Ti _{38.8} Ni _{43.6} Hf _{17.6}	10
9	Ti _{36.7} Ni _{45.4} Hf _{17.9}	5
10	Ti _{43.3} Ni _{41.5} Hf _{15.2}	10
11	Ti _{41.9} Ni _{41.9} Hf _{16.2}	9
12	Ti _{39.9} Ni _{42.7} Hf _{17.4}	11
13	Ti _{38.1} Ni _{43.3} Hf _{18.6}	9

Among the samples in this study, the Ti_{39.6}Ni_{46.1}Hf_{14.3}, Ti_{42.3}Ni_{42.5}Hf_{15.2} and Ti_{36.1}Ni_{49.3}Hf_{14.6} alloys demonstrate superior thermal cycling stability— approximately 2°C for 100 cycles (Table 6-1). This extraordinary stability suggests a high degree of crystallographic compatibility between the austenitic and martensitic phases for these samples [165, 184], although the nano-scale grain size and multiple phases make it difficult to confirm this by X-ray diffraction because of broad and overlapping diffraction peaks.

For Ti-Ni-Hf thin films, the martensite twin structure has been observed in grain sizes ranging from 9 to 27 nm (e.g. Fig. 5-8a, Chapter 5). Previous observations of nanocrystalline TiNi binary systems have reported martensite only in grains larger than 50 nm [80, 175]. These observations suggest that the Ti-Ni-Hf system is an attractive materials system for control of thermal cycling stability by grain refinement, since martensite can be formed at smaller grain sizes than in the Ti-Ni system. For example, Kockar et al. have reported improved thermal cycling stability of Ti-Ni-Hf bulk material after severe plastic deformation (SPD) due to grain refinement [186].

6.2. High Temperature Cycling (HTC)

A total of twelve HT cycles were applied to each transforming cell. Depending on the Ni concentration, two distinct trends were observed during cycling:

(a) For $\text{Ni} \leq 47 \text{ at.}\%$, the M-A transformation peak shifts toward higher temperatures with increasing number of cycles (Fig. 6-4). The evolution of A_P with cycle number is illustrated in Fig. 6-5 for all samples demonstrating this behavior. It is evident from the figure that A_P increases by 30-51°C over twelve cycles. TEM analysis of cell X ($\text{Ti}_{38.1}\text{Ni}_{43.3}\text{Hf}_{18.6}$) shows that the microstructure consists of finely twinned martensite grains and $(\text{Ti}_{1-x}\text{Hf}_x)_2\text{Ni}$ precipitates with a Ti_2Ni base structure [171] (Fig. 6-6a and b). Precipitation of $(\text{Ti}_{1-x}\text{Hf}_x)_2\text{Ni}$ with HT cycling increases the Hf content of the matrix and leads to a higher transformation temperature. A similar mechanism has also been observed in Ni-Ti-Zr thin films [181].

Chapter 6 Effect of Thermal Cycling on Transformation Behavior of Ti-Ni-Hf Thin Films

Caption in the next page ...

Figure 6-4 Martensite-austenite transformation peaks as a function of the number of high-temperature cycles; (a) cell L, (b) cell Q, (c) cell R, (d) cell S, (e) cell U, (f) cell V, (g) cell W and (h) cell X.

Figure 6-5 Variation in A_p transformation temperature as a function of the number of high-temperature cycles [166].

(b) For $\text{Ni} \geq 47.7$ at%, the behavior with HT cycling is significantly different. Fig. 6-7 demonstrates the transformation curve of cell N ($\text{Ti}_{35.1}\text{Ni}_{47.7}\text{Hf}_{17.2}$) and cell O ($\text{Ti}_{33.5}\text{Ni}_{47.9}\text{Hf}_{18.6}$) as a function of the number of HT cycles. In this case, the martensite-austenite transformation is gradually suppressed with thermal cycling. Initially a single-stage transformation is observed. As thermal cycling continues, two peaks develop, indicative of a two-stage phase transformation. With further cycling, the transformation disappears altogether. Cells F and G also demonstrate this behavior when subjected to HT cycles.

TEM analysis of cell N after the calorimetric measurements shows that this cell consists of austenite (B2), $(\text{Ti}_{1-x}\text{Hf}_x)_2\text{Ni}$ precipitates, and some R-phase (Fig. 6-6c and d). Evidently, precipitation of $(\text{Ti}_{1-x}\text{Hf}_x)_2\text{Ni}$ with HT cycling enriches the austenite in Ni. Consequently, the sample starts to behave more like the Ni-rich samples of Ti-Ni-Hf transformation library (non-transforming samples) (Fig. 5-11, Chapter 5). This evolution is indeed observed: the transformation temperature shifts down and the martensitic transformation is suppressed due to the lack of sufficient undercooling.

Figure 6-6 TEM micrograph and corresponding electron diffraction pattern of cell X (a and b) and cell N (c and d) after high-temperature thermal cycling [166].

Figure 6-7 Martensite-austenite transformation peaks as a function of the number of high-temperature cycles; (a) cell N and (b) cell O.

The effect of HT cycling on the thermal stability of Ti-Ni-Hf thin films is explored. For this purpose, seven cells were subjected to 100 low-temperature cycles after the HT heat treatments. All the cells show a similar trend, which is illustrated in Fig. 6-8 using cells L, P and R as representative examples. Evidently HT cycling reduces the thermal stability of Ti-Ni-Hf thin films. The average A_P reduction after high-temperature cycling (15.3°C for 100 cycles) is significantly larger than before HT cycling (7.8°C for 100 cycles) (Fig. 6-9). We attribute this increase in thermal fatigue to the continued precipitation of $(\text{Ti}_{1-x},\text{Hf}_x)_2\text{Ni}$ during the HT heat treatments. Precipitation of $(\text{Ti}_{1-x},\text{Hf}_x)_2\text{Ni}$ has several effects. Precipitation of $(\text{Ti}_{1-x},\text{Hf}_x)_2\text{Ni}$ enriches the matrix in Hf, which apart from a rise in transformation temperature also leads to a decrease of the compatibility between the austenite and martensite phases. As mentioned earlier, such a decrease makes the alloy more sensitive to thermal fatigue. It has indeed been reported in the literature that increasing the Hf content in Ti-Ni-Hf materials increases the thermal hysteresis, and increasing the hysteresis degrades the thermal cycling stability [36]. Precipitation also enhances the internal stresses in the austenite, which in turn leads to greater dissipation during transformation and to more pronounced thermal fatigue [181]. Finally, precipitation can create obstacles to dislocation motion, which would reduce thermal fatigue. This last effect is not significant in this case, presumably because the grain size is so small that the additional obstacles created by precipitation have little effect on dislocation motion.

Figure 6-8 Effect of high-temperature cycling on thermal cycling stability; (a) cell L, (b) cell P and (c) cell R.

Figure 6-9 Effect of high-temperature cycling on thermal cycling stability. Seven compositions from different locations of the library have been chosen for this analysis.

6.3. Control of Transformation Temperature Aided by Multiple Thermal Cycling

The transformation temperatures are important characteristics of a shape memory alloy, since they dictate the specific applications of the alloy [53, 54]. Adjusting the chemical composition is one method to control these temperatures. Transformation temperatures are, however, sensitive to slight changes in chemical composition and this makes reliable temperature control difficult [54]. An alternative method for controlling the transformation temperatures consists of a thermal treatment such as aging in which the transformation temperatures vary due to the formation of second phases as described previously. The results obtained from LT and HT cycling experiments demonstrate the capability to change A_P using a combination of these two treatments. Figure 6-10 shows a possible treatment

that includes two series of LT heat treatments and two series of HT heat treatments. The results show that A_P of this sample can be precisely controlled between 207 and 260°C through the application of appropriate heat treatments protocols.

Figure 6-10 Multiple thermal cycling of the cell X ($\text{Ti}_{38.1}\text{Ni}_{43.3}\text{Hf}_{18.6}$). Step 1: high-temperature cycling; Step 2: low-temperature cycling; Step 3: high-temperature cycling; Step 4: low-temperature cycling [166].

6.4. Comparison between PnSC and Traditional Calorimetry: Time Assessment

In this study, 323 calorimetric measurements were carried out for each sample of the library using PnSC (Table 3-4). Totally, 6460 calorimetric measurements were carried out for 20

samples of library. All the measurements lasted approximately 2 days. In traditional calorimetry, a typical heating rate of approximately 10 °C/min is usually employed for calorimetric analysis. Therefore, a similar study would take approximately 363 days of continuous measurement time. Consequently, a significantly improved level of time efficiency is achieved using PnSC.

6.5. Summary

In summary, the effect of thermal cycling on the martensitic transformation behavior of Ti-Ni-Hf combinatorial thin films was explored. The response of thin films to high temperature cycling ($22^{\circ}\text{C} < T < 850^{\circ}\text{C}$) was dependent on the Ni concentration. For Ni < 47 at.%, the transformation temperature increased significantly during cycling. The precipitation of $(\text{Ti}_{1-x}\text{Hf}_x)_2\text{Ni}$ with thermal cycling caused formation of a Hf enriched matrix with an elevated transformation temperature. In contrast, for Ni > 47.7 at.% , the transformation was gradually suppressed with cycling. The Ni enrichment of the matrix due to $(\text{Ti}_{1-x}\text{Hf}_x)_2\text{Ni}$ precipitation was proposed as a governing mechanism. Applying low temperature cycles ($22^{\circ}\text{C} < T < 450^{\circ}\text{C}$) reduces and stabilizes the transformation temperature. The relaxation of the residual and precipitate stresses with dislocations generated via cycling was suggested as the dominant mechanism. The ability of PnSC to control the transformation temperature through multiple thermal cycling was investigated.

Chapter 7

Conclusions

7.1. Characterization of Amorphous Ti-Ni-Cu Thin Film Crystallized by Rapid Thermal Annealing

Amorphous Ti-Ni-Cu thin films were synthesized by magnetron sputtering at room temperature. The resultant films were crystallized by either rapid thermal annealing (RTA) or conventional thermal annealing (CTA). A systematic study was carried out to explore the evolution of structural, surfacial and nano-scale mechanical properties of amorphous thin films crystallized by RTA treatment. The experimental results provide the following novel outcomes:

1. The optimum crystallization temperature and holding time were obtained for Ti-Ni-Cu amorphous thin films using RTA method. Long range order of amorphous Ti-Ni-Cu thin film was achieved in a few seconds (> 60 sec) with the optimum crystallization temperature of 480°C . The fast crystallization process allows the precise control of microstructure in a lower thermal budget (product of processing temperature and time).
2. The size and distribution of the surface islands of Ti-Ni-Cu film changed with RTA holding time (up to 180 sec) and showed significantly increased roughness, while conventional thermal annealing (CTA), produced a smoother surface. Although RTA is energy efficient due to the shorter annealing time, the coarse film morphology may

prove less suitable than more homogeneous CTA products for some applications. The RTA process promotes growth perpendicular to the substrate leading to greater roughness.

3. The evolution of local atomic structure during RTA crystallization was established using X-ray absorption spectroscopy. The Ni-Ti and Ni-Ni bond distances after RTA (10 and 60 sec) are close to the measured atomic distances in amorphous film. With increase of dwell time to 180 sec, they increased to the atomic distances of the CTA fully crystallized film (benchmark). The RTA (180 sec) and CTA (1 hr) films possessed the longest range order. Therefore, the RTA (480°C / 180 sec) heat treatment is proposed as an optimal condition to achieve a fully-crystalline sample with a great long-range ordering.
4. The correlation of nanomechanical properties as a function of crystallization holding time in RTA treatment were established for Ti-Ni-Cu thin films. The amorphous thin film showed the lowest elastic modulus of approximately 125 GPa that increased with annealing time to the highest value after RTA for 120 sec. The nanomechanical results along with structural evolution investigations demonstrated the suitability of nanoindentation as a simple and reliable tool to study crystalline domain formation in TiNi-based amorphous thin films.

7.2. Phase Transformation Study of Ti-Ni-Hf Thin Film Library Using Parallel nano-Scanning Calorimetry (PnSC)

Parallel nano-scanning calorimetry (PnSC) was used to study the crystallization and martensitic transformation behavior of a combinatorial library of Ti-Ni-Hf high-temperature shape memory thin films. A systematic study was carried out to compare the PnSC and bulk calorimetry (i.e. traditional DSC) results. The experimental results provide the following revelations:

- 1) The amorphous Ti-Ni-Hf thin films were crystallized by local heating in a process that lasted only tens of milliseconds, resulting in ultra-fine (18 ± 5 nm) grains structure. The glass transition and crystallization behavior of the thin film sample library were explored. The crystallization occurs as a multi-stage process, initiating with surface crystallization followed by volume crystallization of (Ti,Hf)Ni austenite phase. The calorimetric traces of equilibrium precipitates were observed after crystallization. The glass transition temperature (T_g) and crystallization peak temperature (T_c) showed no obvious trend with composition.
- 2) The (Ti,Hf)-rich Ti-Ni-Hf alloy compositions with Ni contents below ~ 49.3 at.% exhibited the martensite-austenite transformation. The transformation temperature increased linearly with increase of Hf content in the range 14-20 at.% at a rate comparable to that observed for bulk materials, but with reduced A_p temperature. The decrease in transformation temperature is caused by the fine nano-scale structure in Ti-Ni-Hf thin samples.

- 3) The martensite–austenite transformation peak in the PnSC is significantly broader than the peak observed in bulk calorimetry. The peak broadening is attributed to the very small grain size and the grain size distribution of the PnSC samples. The large variation in the energy barrier for the martensitic transformation at very small grain size translates into a wide range of transformation temperatures.

7.3. Effect of Thermal Cycling on Transformation Behaviour of Ti-Ni-Hf Thin Films

Parallel nano-scanning calorimetry has been employed to study the effect of high-temperature (850°C) and low-temperature (450°C) thermal cycling on the martensitic transformation behavior as a function of composition. The results of this study lead to the following conclusions:

- 1) Low-temperature cycling ($22^{\circ}\text{C} < T < 450^{\circ}\text{C}$) results in a decrease and stabilization of the transformation temperature. Relaxation of residual stresses by generated dislocations during thermal cycling is suggested as the main mechanism. The PnSC samples demonstrated improved thermal cycling stability (averaging 7.9°C for 100 cycles) compared to Ti-Ni-Hf bulk materials. This was attributed to the nano-scale grain structure in PnSC, which reduces the elastic energy available to nucleate dislocations and creates boundaries to dislocation motion. Alloys with superior thermal cycling stability (approximately 2°C for 100 cycles), $\text{Ti}_{39.6}\text{Ni}_{46.1}\text{Hf}_{14.3}$, $\text{Ti}_{42.3}\text{Ni}_{42.5}\text{Hf}_{15.2}$ and $\text{Ti}_{36.1}\text{Ni}_{49.3}\text{Hf}_{14.6}$ were attained.

-
- 2) The response of the Ti-Ni-Hf thin films to high-temperature cycling ($22^{\circ}\text{C} < T < 850^{\circ}\text{C}$) changes with Ni concentration. For $\text{Ni} \leq 47 \text{ at\%}$, the transformation temperature increases during high-temperature cycling due to precipitation of $(\text{Ti}_{1-x}\text{Hf}_x)_2\text{Ni}$ and the resulting enrichment of Hf in the surrounding matrix. For $\text{Ni} \geq 47.7 \text{ at\%}$, the transformation is gradually suppressed; the transformation temperature decreases and the reverse transformation is suppressed due to insufficient undercooling.
 - 3) The thermal cycling stability is reduced after high-temperature cycling; as high-temperature heat treatments precipitate $(\text{Ti}_{1-x}\text{Hf}_x)_2\text{Ni}$, which increases the internal stresses and enriches the austenite with Hf. The internal stresses and the reduced compatibility between austenite and martensite at greater Hf concentrations both lead to more pronounced thermal fatigue.
 - 4) The ability of PnSC to precisely control the transformation temperature through multiple thermal cycling has been demonstrated. In this manner, the A_P of $\text{Ti}_{38.1}\text{Ni}_{43.3}\text{Hf}_{18.6}$ alloy was controlled precisely between 207 and 260°C through application of appropriate heat treatments protocols.

Chapter 8

Suggestions for Future Work

In this section, some future directions are given based on the findings of this study.

8.1. Investigation of Crystallization Mechanism during RTA Treatment

It is widely known that there is a direct relationship between the martensitic transformation and the microstructures that emerge during crystallization process [18, 19, 73, 187]. Understanding the crystallization mechanism during RTA treatment enables better control of microstructure and consequently optimization of actuation properties.

A combination of high-resolution transmission electron microscopy (HRTEM) and X-ray absorption spectroscopy (XAS) analyses can be employed to explore the crystallization mechanisms. For HRTEM examination, finding an appropriate technique for TEM sample preparation is of paramount importance, since the artifacts will affect the results significantly. This issue is crucial in Ti-Ni-Cu systems, where the martensitic transformation occurs at low temperature ranges ($< 100^{\circ}\text{C}$). For this purpose, ion milling equipped with cold-stage or focused ion beam (FIB) instruments are suggested. Development of a TEM equipped with RTA systems can be also a solution to explore the crystallization mechanism at fast-heating rates.

8.2. Investigation of Shape Memory Effect and Superelasticity in Freestanding SMA Films Crystallized by RTA

As explained in Chapter 4, there are some challenges on characterization of shape memory effect (SME) and superelasticity effect (SE) in Ti-Ni-Cu thin films deposited on a substrate (Section 4-8). One way to overcome these challenges is to synthesize a high-quality freestanding film. For this purpose, a reliable and good sputtering system equipped with at least three DC powers and ultra-high vacuum system (at least 10^{-8} Torr) is required. DC magnetron co-sputtering of pure Ti, Ni and Cu targets is the best way for chemical composition adjustment, where we can easily reproduce a certain composition by optimization of the deposition parameters. The selection of the proper substrate is also an important factor to produce a high quality film. As described in Chapter 3, the Si wafer coated with Si_3N_4 is an appropriate substrate for this purpose, where by deposition of a thick layer of Ti-Ni-X film ($> 3 \mu\text{m}$); the film can be readily removed from the substrate. Finally, by using a micro-tensile machine equipped with cooling system, the functional properties (i.e. SME and SE) can be examined.

8.3. Investigation of the Crystallization Kinetics in SMA Thin Films using PnSC

The crystallization kinetics of the amorphous materials are usually explored using conventional differential scanning calorimetry (DSC), where the material is crystallized at different heating rates (non-isothermal crystallization), and by using the Kissinger's theory [188], the kinetics parameters are derived. There has been extensive research to understand the crystallization mechanisms of TiNi-based thin films by conventional DSC, where the

ramping rates of < 100 °C/min are typically employed [18-20, 26, 73, 106]. As we described in Chapters 3 and 5, the PnSC is able to crystallize thin films at ultra-fast heating rate of approximately 10^4 °C/sec, where the heating rate is modified by adjusting the applied pulse current amplitude [51]. Therefore, the crystallization kinetics at ultra-fast heating rates can be investigated.

8.4. Development of a PnSC to Characterize SMA Thin Films with Low Transformation Temperatures ($< \text{Room Temperature}$)

Currently, parallel nano-scanning calorimeter (PnSC) was used to study the phase transformation characteristics of SMA thin films with transformation temperatures higher than ambient temperature (Chapters 5 and 6). By developing a PnSC operating at lower temperatures ($< \text{RT}$), exploring the SMA materials at nano-scale in a wide range of temperatures is feasible. Developing an adjustable cooling set up at ultra high-vacuum level could be a solution for this purpose.

References

- [1] W.J. Buehler, F.E. Wang, *Ocean Engineering* 1 (1967) 105-120.
- [2] W.L. Benard, H. Kahn, A.H. Heuer, M.A. Huff, *Journal of Microelectromechanical Systems* 7 (1998) 245-251.
- [3] A.D. Johnson, *Journal of Micromechanics and Microengineering* 1 (1991) 34-41.
- [4] M. Kohl, D. Dittmann, E. Quandt, B. Winzek, S. Miyazaki, D.M. Allen, *Materials Science and Engineering A* 273-275 (1999) 784-788.
- [5] P. Krulevitch, A.P. Lee, P.B. Ramsey, J.C. Trevino, J. Hamilton, M.A. Northrup, *Journal of Microelectromechanical Systems* 5 (1996) 270-282.
- [6] E. Makino, T. Mitsuya, T. Shibata, *Sensors and Actuators, A: Physical* 88 (2001) 256-262.
- [7] T. Mineta, N. Kida, S. Nomura, E. Makino, T. Sugawara, S. Toh, T. Shibata, *Sensors and Actuators, A: Physical* 143 (2008) 14-19.
- [8] M. Tomozawa, H.Y. Kim, S. Miyazaki, *Acta Materialia* 57 (2009) 441-452.
- [9] R. Vitushinsky, S. Schmitz, A. Ludwig, *Journal of Microelectromechanical Systems* 18 (2009) 186-194.
- [10] A. Ishida, M. Sato, K. Ogawa, *Materials Science and Engineering A* 481-482 (2008) 91-94.
- [11] A. Ishida, M. Sato, K. Ogawa, K. Yamada, *Materials Science and Engineering A* 438-440 (2006) 683-686.
- [12] S. Miyazaki, T. Hashinaga, A. Ishida, *Thin Solid Films* 281-282 (1996) 364-367.
- [13] M. Cai, Y.Q. Fu, S. Sanjabi, Z.H. Barber, J.T. Dickinson, *Surface and Coatings Technology* 201 (2007) 5843-5849.

References

- [14] Y.Q. Fu, S. Sanjabi, Z.H. Barber, T.W. Clyne, W.M. Huang, M. Cai, J.K. Luo, A.J. Flewitt, W.I. Milne, *Applied Physics Letters* 89 (2006) 171922.
- [15] L. Chang, D.S. Grummon, *Philosophical Magazine A* 76 (1997) 191-219.
- [16] S.H. Chang, S.K. Wu, H. Kimura, *Intermetallics* 15 (2007) 233-240.
- [17] F.F. Gong, H.M. Shen, Y.N. Wang, *Applied Physics Letters* 69 (1996) 2656-2658.
- [18] H.J. Lee, A.G. Ramirez, *Applied Physics Letters* 85 (2004) 1146-1148.
- [19] A.G. Ramirez, H. Ni, H.J. Lee, *Materials Science and Engineering A* 438-440 (2006) 703-709.
- [20] M.J. Vestel, D.S. Grummon, R. Gronsky, A.P. Pisano, *Acta Materialia* 51 (2003) 5309-5318.
- [21] X. Wang, J.J. Vlassak, *Scripta Materialia* 54 (2006) 925-930.
- [22] Q. Xie, W. Huang, M. Hong, W. Song, T.C. Chong, Excimer Laser Annealing of NiTi Shape Memory Alloy Thin Film, in: I. Miyamoto, K.F. Kobayashi, K. Sugioka, R. Poprawe, H. Helvajian (Eds.), *Third International Symposium on Laser Precision Microfabrication*, vol 4830, *Proceedings of SPIE*, Osaka, Japan, 2002, pp. 403-407.
- [23] X. Wang, Y. Bellouard, Z. Xue, J.J. Vlassak, *Applied Physics A: Materials Science and Processing* 90 (2008) 689-694.
- [24] X. Wang, Y. Bellouard, J.J. Vlassak, *Acta Materialia* 53 (2005) 4955-4961.
- [25] Q. He, M.H. Hong, W.M. Huang, T.C. Chong, Y.Q. Fu, H.J. Du, *Journal of Micromechanics and Microengineering* 14 (2004) 950-956.
- [26] Y. Tong, Y. Liu, *Journal of Alloys and Compounds* 449 (2008) 152-155.
- [27] Y. Tong, Y. Liu, Z. Xie, *Journal of Alloys and Compounds* 456 (2008) 170-177.
- [28] Y.Q. Fu, H.J. Du, W.M. Huang, S. Zhang, M. Hu, *Sensors and Actuators, A: Physical* 112 (2004) 395-408.

References

- [29] S. Sanjabi, Y.Z. Cao, S.K. Sadrnezhad, Z.H. Barber, *Journal of Vacuum Science and Technology A: Vacuum, Surfaces and Films* 23 (2005) 1425-1429.
- [30] X.L. Meng, W. Cai, F. Chen, L.C. Zhao, *Scripta Materialia* 54 (2006) 1599-1604.
- [31] D.S. Grummon, *JOM* 55 (2003) 24-32.
- [32] D.N. Abujudom, P.E. Thoma, M. Kao, D.R. Angst, *High Transformation Shape Memory Alloy*, U.S. Patent # 5114504, Johnson Service Company, United States, 1992.
- [33] Y. Tong, Y. Liu, J. Miao, *Thin Solid Films* 516 (2008) 5393-5396.
- [34] S. Sanjabi, Y.Z. Cao, Z.H. Barber, *Sensors and Actuators, A: Physical* 121 (2005) 543-548.
- [35] H.D. Gu, L. You, K.M. Leung, C.Y. Chung, K.S. Chan, J.K.L. Lai, *Applied Surface Science* 127-129 (1998) 579-583.
- [36] D. König, R. Zarnetta, A. Savan, H. Brunken, A. Ludwig, *Acta Materialia* 59 (2011) 3267-3275.
- [37] J.C. Zhao, *Progress in Materials Science* 51 (2006) 557-631.
- [38] X.D. Xiang, *Annual Review of Materials Science* 29 (1999) 149-171.
- [39] I. Takeuchi, O.O. Famodu, J.C. Read, M.A. Aronova, K.S. Chang, C. Craciunescu, S.E. Lofland, M. Wuttig, F.C. Wellstood, L. Knauss, A. Orozco, *Nature Materials* 2 (2003) 180-184.
- [40] K. Rajan, *Annual Review of Materials Research* 38 (2008) 299-322.
- [41] B.J. de Gans, S. Wijnans, D. Woutes, U.S. Schubert, *Journal of Combinatorial Chemistry* 7 (2005) 952-957.
- [42] J. Sakurai, S. Hata, R. Yamauchi, A. Shimokohbe, *Applied Surface Science* 254 (2007) 720-724.
- [43] B.J. Chisholm, M. Berry, J. Bahr, J. He, J. Li, S. Balbyshev, G.P. Bierwagen, *Journal of Coatings Technology Research* 7 (2010) 23-37.

References

- [44] R. Zarnetta, D. König, C. Zamponi, A. Aghajani, J. Frenzel, G. Eggeler, A. Ludwig, *Acta Materialia* 57 (2009) 4169-4177.
- [45] J. Cui, Y.S. Chu, O.O. Famodu, Y. Furuya, J. Hattrick-Simpers, R.D. James, A. Ludwig, S. Thienhaus, M. Wuttig, Z. Zhang, I. Takeuchi, *Nature Materials* 5 (2006) 286-290.
- [46] C. Borgia, S. Olliges, M. Dietiker, G. Pigozzi, R. Spolenak, *Thin Solid Films* 518 (2010) 1897-1913.
- [47] R. Zarnetta, A. Savan, S. Thienhaus, A. Ludwig, *Applied Surface Science* 254 (2007) 743-748.
- [48] O.O. Famodu, J. Hattrick-Simpers, M. Aronova, K.S. Chang, M. Murakami, M. Wuttig, T. Okazaki, Y. Furuya, L.A. Knauss, L.A. Bendersky, F.S. Biancaniello, I. Takeuchi, *Materials Transactions* 45 (2004) 173-177.
- [49] A. Dwivedi, T.J. Wyrobek, O.L. Warren, J. Hattrick-Simpers, O.O. Famodu, I. Takeuchi, *Journal of Applied Physics* 104 (2008) 073501-073505.
- [50] P.J. McCluskey, J.J. Vlassak, *Scripta Materialia* 64 (2010) 264-267.
- [51] P.J. McCluskey, J.J. Vlassak, *Journal of Materials Research* 25 (2010) 2086-2100.
- [52] P.J. McCluskey, J.J. Vlassak, Parallel Nano-differential Scanning Calorimetry: A New Device for Combinatorial Analysis of Complex Nano-scale Material Systems, in: A. Misra, J.P. Sullivan, H. Huang, K. Lu, S. Asif (Eds.), *Mechanics of Nanoscale Materials and Devices*, vol 924E, MRS, Warrendale, PA, 2006, pp. 133-138.
- [53] M. Zarinejad, Y. Liu, *Advanced Functional Materials* 18 (2008) 2789-2794.
- [54] K. Otsuka, X. Ren, *Progress in Materials Science* 50 (2005) 511-678.
- [55] Y. Motemani, M. Nili-Ahmadabadi, M.J. Tan, M. Bornapour, S. Raygan, *Journal of Alloys and Compounds* 469 (2009) 164-168.

References

- [56] Z.G. Wang, X.T. Zu, Y.Q. Fu, *Materials Science and Engineering A* 390 (2005) 400-403.
- [57] K. Otsuka, C.M. Wayman, *Shape Memory Materials*, Cambridge University Press, Cambridge, 1998.
- [58] Y. Li, L. Cui, Y. Zheng, D. Yang, *Materials Letters* 51 (2001) 73-77.
- [59] A. Dlouhy, J. Khalil-Allafi, G. Eggeler, *Philosophical Magazine* 83 (2003) 339-363.
- [60] J. Beyer, P.A. Besselink, A.J. Aartsen, *Thermochimica Acta* 85 (1985) 187-190.
- [61] G.S. Firstov, J. Van Humbeeck, Y.N. Koval, *Scripta Materialia* 50 (2004) 243-248.
- [62] E.A. Olson, M.Y. Efremov, M. Zhang, Z. Zhang, L.H. Allen, *Journal of Microelectromechanical Systems* 12 (2003) 355-364.
- [63] L.H. Allen, S.L. Lai, *Microscale Thermophysical Engineering* 2 (1998) 11-19.
- [64] P.J. McCluskey, J.J. Vlassak, *Thin Solid Films* 518 (2010) 7093-7106
- [65] T.W. Duerig, K.N. Melton, D. Stokel, C.M. Wayman, *Engineering Aspects of Shape Memory Alloys*, Butterworth-Heinemann, UK, London, 1990.
- [66] M. Zarinejad, *Influence of Alloy Chemistry on The Transformation Temperatures And Local Atomic Structure of Shape Memory Alloys: With A Focus On NiTi-based Intermetallics*, Ph.D. Thesis, Nanyang Technological University Singapore, 2009.
- [67] P.K. Kumar, D.C. Lagoudas, *Introduction to Shape Memory Alloys*, in: D.C. Lagoudas (Ed.) *Shape Memory Alloys*, Springer U.S. , New York, 2008.
- [68] A. Falva, *Thermomechanical Characterization of Nickel-Titanium Shape Memory Alloys*, Ph.D. Thesis, University of Della Calabria, Italy, Cosenza, 2008.
- [69] L.C. Chang, T.A. Read, *Transaction AIME* 189 (1951) 47-52.
- [70] W.J. Buehler, J.V. Gilfrich, R.C. Wiley, *Journal of Applied Physics* 34 (1963) 1475-1477.

References

- [71] V. Sánchez-Alarcos, V. Recarte, J.I. Pérez-Landazábal, C. Gómez-Polo, J.A. Rodríguez-Velamazán, *Acta Materialia* 60 (2012) 459-468.
- [72] W.M. Huang, Z. Ding, C.C. Wang, J. Wei, Y. Zhao, H. Purnawali, *Materials Today* 13 (2010) 54-61.
- [73] X. Wang, *Crystallization and Martensitic Transformation Behavior of Nickel-Titanium Shape Memory Alloy Thin Films*, Ph.D. Thesis, Harvard University, United States, Boston, 2007.
- [74] C. Zhang, *Nickel-Titanium and Nickel-Titanium-Hafnium Shape Memory Thin Films*, Ph.D. Thesis, Auburn University, United States, Alabama, 2000.
- [75] J. Van Humbeeck, *Journal of Engineering Materials and Technology*, Transactions of the ASME 121 (1999) 98-101.
- [76] Y. Tong, *Processing and Characterization of NiTi-based Shape Memory Alloy Thin Films*, Ph.D. Thesis, Nanyang Technological University, Singapore, 2008.
- [77] K. Wada, *An Experimental and Macromechanical Study of Two-way Shape Recovery Characteristics in NiTi Alloy*, Ph.D. Thesis, Nanyang Technological University, Singapore, 2008.
- [78] X. Ren, K. Otsuka, *Materials Science Forum* 327 (2000) 429-432.
- [79] W. Tang, *Metallurgical and Materials Transactions A* 28 (1997) 537-544.
- [80] T. Waitz, T. Antretter, F.D. Fischer, N.K. Simha, H.P. Karnthaler, *Journal of the Mechanics and Physics of Solids* 55 (2007) 419-444.
- [81] E.R. Strutt, E.A. Olevsky, M.A. Meyers, *Journal of Materials Science* 43 (2008) 6513-6526.
- [82] Y. Kudoh, M. Tokonami, S. Miyazaki, K. Otsuka, *Acta Metallurgica* 33 (1985) 2049-2056.

References

- [83] J. Khalil-Allafi, W.W. Schmahl, D.M. Toebbens, *Acta Materialia* 54 (2006) 3171-3175.
- [84] V. Antonucci, G. Faiella, M. Giordano, F. Mennella, L. Nicolais, *Thermochimica Acta* 462 (2007) 64-69.
- [85] J. Khalil Allafi, X. Ren, G. Eggeler, *Acta Materialia* 50 (2002) 793-803.
- [86] J. Khalil-Allafi, G. Eggeler, W.W. Schmahl, D. Sheptyakov, *Materials Science and Engineering: A* 438-440 (2006) 593-596.
- [87] Y. Motemani, *Phase Transformation Control in Ni-Ti Shape Memory Alloys*, M.Sc. Thesis, University of Tehran, Iran, Tehran, 2007.
- [88] D. Stroz, Z. Bojarski, J. Ilczuk, Z. Lekston, H. Morawiec, *Journal of Materials Science* 26 (1991) 1741-1748.
- [89] X. Ren, N. Miura, J. Zhang, K. Otsuka, K. Tanaka, M. Koiwa, T. Suzuki, Y.I. Chumlyakov, M. Asai, *Materials Science and Engineering A* 312 (2001) 196-206.
- [90] Y.Q. Fu, S. Zhang, M.J. Wu, W.M. Huang, H.J. Du, J.K. Luo, A.J. Flewitt, W.I. Milne, *Thin Solid Films* 515 (2006) 80-86.
- [91] A. Ishida, A. Takei, S. Miyazaki, *Thin Solid Films* 228 (1993) 210-214.
- [92] T. Lehnert, S. Crevoiserat, R. Gotthardt, *Journal of Materials Science* 37 (2002) 1523-1533.
- [93] Y. Motemani, M.J. Tan, T.J. White, W.M. Huang, *Materials and Design* 32 (2011) 688-695.
- [94] J.A. Walker, K.J. Gabriel, M. Mehregany, *Sensors and Actuators: A. Physical* 21 (1990) 243-246.
- [95] S. Miyazaki, A. Ishida, *Materials Science and Engineering A* 273-275 (1999) 106-133.

References

- [96] J. Zhang, Processing and Characterization of High-Temperature Nickel-Titanium-Hafnium Shape Memory Thin Films, Ph.D. Thesis, Michigan State University, United States, Michigan, 2002.
- [97] C. Craciunescu, J. Li, M. Wuttig, Scripta Materialia 48 (2003) 65-70.
- [98] X. Huang, Y. Liu, Material Science and Engineering A 352 (2003) 314.
- [99] C.L. Shih, B.K. Lai, H. Kahn, S.M. Phillips, A.H. Heuer, Journal of Microelectromechanical Systems 10 (2001) 69-79.
- [100] A. Ohta, S. Bhansali, I. Kishimoto, A. Umeda, Sensors and Actuators, A: Physical 86 (2000) 165-170.
- [101] F. Gil, J. Manero, J. Planell, Journal of Materials Science 30 (1995) 2526-2530.
- [102] S. Takabayashi, K. Tanino, K. Kitagawa, Materials Science Research International 3 (1997) 220-224.
- [103] H.J. Lee, H. Ni, D.T. Wu, A.G. Ramirez, Applied Physics Letters 87 (2005) 124102-124103.
- [104] W.J. Moberly, J.D. Busch, A.D. Johnson, M.H. Berkson, In-situ HVEM Crystallization of Amorphous TiNi Thin Films, in: M. Chen, M.O. Thompson, R.B. Schwarz, M. Libera (Eds.), Phase Transformation Kinetics in Thin Films Symposium, vol 230, MRS, Anaheim, CA, USA, 1991, pp. 85-90.
- [105] H. Ni, H.J. Lee, A.G. Ramirez, Journal of Materials Research 20 (2005) 1728-1734.
- [106] P. Schlossmacher, N. Boucharat, H. Rosner, G. Wilde, A.V. Shelyakov, Journal De Physique. IV : JP 112 II (2003) 731-734.
- [107] Y. Xu, X. Huang, A.G. Ramirez, Journal of Alloys and Compounds 480 (2009) L13-L16.
- [108] X. Wang, M. Rein, J.J. Vlassak, Journal of Applied Physics 103 (2008) 023501.

References

- [109] L.H. Allen, G. Ramanath, S.L. Lai, Z. Ma, S. Lee, D.D.J. Allman, K.P. Fuchs, *Applied Physics Letters* 64 (1994) 417-419.
- [110] Q. He, W.M. Huang, X.Y. Gao, M.H. Hong, *Smart Materials and Structures* 14 (2005) 1320-1324.
- [111] A. Ishida, A. Takei, M. Sato, S. Miyazaki, Shape Memory Behavior of Ti-Ni Thin Films Annealed at Various Temperatures, in: *Material Research Society Symposium*, vol 360, MRS , Boston, MA, USA, 1995, pp. 381-386.
- [112] T.B. Massalski, H. Okamoto, P.R. Subramanian, L. Kacprzak, *Binary Alloy Phase Diagrams*, ASM International, United States, Materials Park, OH., 1990.
- [113] Y. Nakata, T. Tadaki, H. Sakamoto, A. Tanaka, K. Shimizu, *Journal of de Physique Colloque IV C8* (1995) 671-676.
- [114] S. Kajiwara, K. Ogawa, T. Kikuchi, T. Matsunaga, S. Miyazaki, *Philosophical Magazine Letters* 74 (1996) 395-404.
- [115] T. Kikuchi, K. Ogawa, S. Kajiwara, T. Matsunaga, S. Miyazaki, Y. Tomota, *Philosophical Magazine A* 78 (1998) 467-489.
- [116] T. Saburi, T. Komatsu, S. Nenno, Y. Watanabe, *Journal of The Less-Common Metals* 118 (1986) 217-226.
- [117] A.D. Johnson, V.V. Martynov, E.J. Shahoian, High-transition Temperature Shape Memory Alloy Film, in: A. Peter Jardine (Ed.) *Smart Structures and Materials 1995: Smart Materials*, vol 2441, *Proceedings of SPIE*, San Diego, CA, USA, 1995, pp. 165-170.
- [118] S. Besseghini, E. Villa, A. Tuissi, *Materials Science and Engineering A* 273-275 (1999) 390-394.
- [119] Y.Q. Fu, W.M. Huang, H.J. Du, X. Huang, J. Tan, X. Gao, *Surface and Coatings Technology* 145 (2001) 107-112.

References

- [120] Y.Q. Fu, J.K. Luo, A.J. Flewitt, W.M. Huang, S. Zhang, H.J. Du, W.I. Milne, *International Journal of Computational Materials Science and Surface Engineering* 2 (2009) 208-226.
- [121] J.J. Gill, D.T. Chang, L.A. Momoda, G.P. Carman, *Sensors and Actuators, A: Physical* 93 (2001) 148-156.
- [122] H.G. Machens, P. Mailaender, B. Rieck, A. Berger, *Microsurgery* 15 (1994) 778-786.
- [123] T. Sugawara, K.-i. Hirota, M. Watanabe, T. Mineta, E. Makino, S. Toh, T. Shibata, *Sensors and Actuators A: Physical* 130-131 (2006) 461-467.
- [124] Y. Motemani, M.J. Tan, T.J. White, A. Banas, *Surface and Coatings Technology* 205 (2011) 3147-3157.
- [125] H.O. Moser, B.D.F. Casse, E.P. Chew, M. Cholewa, C.Z. Diao, S.X.D. Ding, J.R. Kong, Z.W. Li, M. Hua, M.L. Ng, B.T. Saw, S. Bin Mahmood, S.V. Vidyaraj, O. Wilhelmi, J. Wong, P. Yang, X.J. Yu, X.Y. Gao, A.T.S. Wee, W.S. Sim, D. Lu, R.B. Faltermeier, *Nuclear Instruments and Methods in Physics Research, Section B: Beam Interactions with Materials and Atoms* 238 (2005) 83-86.
- [126] T. Ressler, *Journal De Physique. IV : JP 7* (1997) 269-270.
- [127] G.R. Purdy, J.G. Parr, *Transactions of the Metallurgical Society of Aime* 221 (1961) 636- 639.
- [128] A.L. Ankudinov, B. Ravel, J.J. Rehr, S.D. Conradson, *Physical Review B* 58 (1998) 7565-7576.
- [129] W.C. Oliver, G.M. Pharr, *Journal of Materials Research* 7 (1992) 1564-1580.
- [130] W.C. Oliver, G.M. Pharr, *Journal of Materials Research* 19 (2004) 3-20.
- [131] M. Zhao, X. Chen, Y. Xiang, J.J. Vlassak, D. Lee, N. Ogasawara, N. Chiba, Y.X. Gan, *Acta Materialia* 55 (2007) 6260-6274.

References

- [132] A.F. Lopeandía, E. Leon-Gutierrez, G. Garcia, F. Pi, A. Bernardi, A.R. Goñi, M.I. Alonso, J. Rodríguez-Viejo, *Materials Science in Semiconductor Processing* 9 (2006) 806-811.
- [133] S.L. Lai, J.R.A. Carlsson, L.H. Allen, *Applied Physics Letters* 72 (1998) 1098-1100.
- [134] M.Y. Efremov, E.A. Olson, M. Zhang, F. Schiettekatte, Z. Zhang, L.H. Allen, *Review of Scientific Instruments* 75 (2004) 179-191.
- [135] S.L. Lai, G. Ramanath, L.H. Allen, P. Infante, Z. Ma, *Applied Physics Letters* 67 (1995) 1229-1231.
- [136] S.L. Lai, J.Y. Guo, V. Petrova, G. Ramanath, L.H. Allen, *Physical Review Letters* 77 (1996) 99-102.
- [137] M.Y. Efremov, E.A. Olson, M. Zhang, Z. Zhang, L.H. Allen, *Macromolecules* 37 (2004) 4607-4616.
- [138] M.Y. Efremov, E.A. Olson, M. Zhang, Z. Zhang, L.H. Allen, *Physical Review Letters* 91 (2003) 085703.
- [139] R.K. Kummamuru, L. De La Rama, L. Hu, M.D. Vaudin, M.Y. Efremov, M.L. Green, D.A. Lavan, L.H. Allen, *Applied Physics Letters* 95 (2009) 181911-181913.
- [140] M.Y. Efremov, F. Schiettekatte, M. Zhang, E.A. Olson, A.T. Kwan, R.S. Berry, L.H. Allen, *Physical Review Letters* 85 (2000) 3560-3563.
- [141] E.A. Olson, M.Y. Efremov, M. Zhang, Z. Zhang, L.H. Allen, *Journal of Applied Physics* 97 (2005) 034304.
- [142] M. Zhang, M.Y. Efremov, E.A. Olson, Z.S. Zhang, L.H. Allen, *Applied Physics Letters* 81 (2002) 3801-3803.
- [143] R. Singh, M. Fakhrudin, K.F. Poole, *Applied Surface Science* 168 (2000) 198-203.
- [144] R. Singh, S. Sinha, R.P.S. Thakur, P. Chou, *Applied physics Letter* 58 (1991) 1217-1219.

References

- [145] R. Singh, Journal of Applied Physics 63 (1988) R56-R114.
- [146] Y.Q. Fu, H.J. Du, S. Zhang, W.M. Huang, Materials Science and Engineering A 403 (2005) 25-31.
- [147] X. Huang, Y. Liu, Surface and Coatings Technology 190 (2005) 400-405.
- [148] J. F. Moulder, W.F. Stickle, P.E. Sobol, K.D. Bomben, Handbook of X-ray Photoelectron Spectroscopy: A Reference Book of Standard Spectra for Identification and Interpretation of XPS Data, Physical Electronics, 1995.
- [149] L. Tan, W.C. Crone, Acta Materialia 50 (2002) 4449-4460.
- [150] P.A. Lee, P.H. Citrin, P. Eisenberger, B.M. Kincaid, Reviews of Modern Physics 53 (1981) 769 -806.
- [151] S.H. Lim, N. Phonthammachai, T. Liu, T.J. White, Journal of Applied Crystallography 41 (2008) 1009-1018.
- [152] W. Ni, Y.T. Cheng, D.S. Grummon, Applied Physics Letters 82 (2003) 2811-2813.
- [153] X.G. Ma, K. Komvopoulos, Applied Physics Letters 83 (2003) 3773-3775.
- [154] K. Komvopoulos, X.G. Ma, Applied Physics Letters 87 (2005) 1-3.
- [155] X.G. Ma, K. Komvopoulos, Applied Physics Letters 84 (2004) 4274-4276.
- [156] M.F. Doerner, W.D. Nix, Journal of Material Research 1 (1986) 601-609.
- [157] A. Kumar, D. Singh, D. Kaur, Surface and Coatings Technology 203 (2009) 1596-1603.
- [158] R. Zarnetta, S. Kneip, C. Somsen, A. Ludwig, Materials Science and Engineering A 528 (2011) 6552-6557.
- [159] J. Amorsolo Alberto Villar, TiSi₂ Formation by Rapid Thermal Processing: Effects of Processing on Material Properties, Ph.D. Thesis, University of Rochester, United States, New York, 1996.

References

- [160] C.A. Schuh, C.E. Packard, A.C. Lund, *Journal of Materials Research* 21 (2006) 725-736.
- [161] C.A. Schuh, J.K. Mason, A.C. Lund, *Nature Materials* 4 (2005) 617-621.
- [162] R. Löbel, S. Thienhaus, A. Savan, A. Ludwig, *Materials Science and Engineering: A* 481-482 (2008) 151-155.
- [163] Y.Q. Fu, H.J. Du, *Materials Science and Engineering A* 339 (2003) 10-16.
- [164] A. Ludwig, J. Cao, J. Brugger, I. Takeuchi, *Measurement Science and Technology* 16 (2005) 111-118.
- [165] R. Zarnetta, R. Takahashi, M.L. Young, A. Savan, Y. Furuya, S. Thienhaus, B. Maaß, M. Rahim, J. Frenzel, H. Brunken, Y.S. Chu, V. Srivastava, R.D. James, I. Takeuchi, G. Eggeler, A. Ludwig, *Advanced Functional Materials* 20 (2010) 1917-1923.
- [166] Y. Motemani, P.J. McCluskey, C. Zhao, M.J. Tan, J.J. Vlassak, *Acta Materialia* 59 (2011) 7602-7614.
- [167] ASTM E 1356, *Standard Test Method for Assignment of the Glass Transition Temperatures by Differential Scanning Calorimetry*, ASTM International, 2008.
- [168] W.H. Jiang, F.X. Liu, Y.D. Wang, H.F. Zhang, H. Choo, P.K. Liaw, *Materials Science and Engineering: A* 430 (2006) 350-354.
- [169] M. Peterlechner, J. Bokeloh, G. Wilde, T. Waitz, *Acta Materialia* 58 (2010) 6637-6648.
- [170] A. Slipenyuk, J. Eckert, *Scripta Materialia* 50 (2004) 39-44.
- [171] G.A. Yurko, J.W. Barton, J.G. Parr, *Acta Crystallographica* 12 (1959) 909-911.
- [172] M. Zarinejad, Y. Liu, T.J. White, *Intermetallics* 16 (2008) 876-883.
- [173] A. Gyobu, Y. Kawamura, H. Horikawa, T. Saburi, *Materials Transactions, JIM* 37 (1996) 697-702.

References

- [174] X.L. Meng, W. Cai, Y.F. Zheng, Y.B. Rao, L.C. Zhao, *Materials Letters* 57 (2003) 4206-4211.
- [175] T. Waitz, V. Kazykhanov, H.P. Karnthaler, *Acta Materialia* 52 (2004) 137-147.
- [176] A. Gyobu, Y. Kawamura, T. Saburi, H. Horikawa, *Nippon Kinzoku Gakkaishi/Journal of the Japan Institute of Metals* 63 (1999) 201-207.
- [177] S. Miyazaki, Y. Igo, K. Otsuka, *Acta Metallurgica* 34 (1986) 2045-2051.
- [178] N.G. Jones, S.L. Raghunathan, D. Dye, *Metallurgical and Materials Transactions A: Physical Metallurgy and Materials Science* 41 (2010) 912-921.
- [179] S.H. Kang, H.J. Im, H.W. Lee, T.H. Nam, *Metals and Materials International* 7 (2001) 201-205.
- [180] G. Eggeler, E. Hornbogen, A. Yawny, A. Heckmann, M. Wagner, *Materials Science and Engineering A* 378 (2004) 24-33.
- [181] P.J. McCluskey, C. Zhao, O. Kfir, J.J. Vlassak, *Acta Materialia* 59 (2011) 5116-5124.
- [182] M.F.X. Wagner, S.R. Dey, H. Gugel, J. Frenzel, C. Somsen, G. Eggeler, *Intermetallics* 18 (2010) 1172-1179.
- [183] X.L. Meng, Y.X. Tong, K.T. Lau, W. Cai, L.M. Zhou, L.C. Zhao, *Materials Letters* 57 (2002) 452-456.
- [184] R.D. James, Z. Zhang, A Way to Search for Multiferroic Materials with “Unlikely” Combinations of Physical Properties, in: A. Planes, L. Mañosa, A. Saxena (Eds.), *Magnetism and Structure in Functional Materials*, vol 79, Springer Berlin Heidelberg, 2005.
- [185] K. Gall, H.J. Maier, *Acta Materialia* 50 (2002) 4643-4657.
- [186] B. Kockar, I. Karaman, J.I. Kim, Y. Chumlyakov, *Scripta Materialia* 54 (2006) 2203-2208.
- [187] H.Y. Kim, M. Mizutani, S. Miyazaki, *Acta Materialia* 57 (2009) 1920-1930.
- [188] H.E. Kissinger, *Analytical Chemistry* 29 (1957) 1702-1706.

References