Processing and characterization of NiTi-based shape memory alloy thin films

Tong, Yunxiang

2008

Tong, Y. X. (2008). Processing and characterization of NiTi-based shape memory alloy thin films. Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/13440>

<https://doi.org/10.32657/10356/13440>

Processing and Characterization of NiTi-based Shape Memory Alloy Thin Films

Tong Yunxiang

School of Mechanical and Aerospace Engineering

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

2008

Acknowledgements

The author would like to express his gratitude towards many individuals who help to complete this thesis.

First of all, I would like to thank my supervisors, associate professors Liu Yong and Miao Jianmin, for the opportunity to develop, learn, and interact with many people in the scientific community. I have learned and acquired many personal and professional skills from them. They have been great advisors, mentors. I am grateful and honored to have the opportunity to learn and work with them. Thanks for their encouragement, guidance, patience and support throughout the course of this work.

I would like to thank assistant professor Xie Zeliang for help in texture analysis and fruitful discussion.

I would like to thank all my group members, Dr. Li Guang, Dr. Huang Xu, Mr. Xiong Feng, Mr. Wada Kiyohide and Mr. Mehrdad Zarinejad. Without the help and inspiration we provided each other, I probably would have gone insane. Special thanks also go to Mr. Mehrdad Zarinejad for help in Rietveld refinement and fruitful discussion.

I would like to thank Mr. Leong Kwok Phui, Mr. Koh Soon Hong, Mr. Sa'don Ahmad, Mr. Lew Sui Leung, Mr. Chang Set Chiang, Mrs. Yee-Yong Mei Yoke, Mrs. Chow Shiau Kee, Mrs. Yeong Peng Neo, Sandy, the technicians in Materials Laboratory, for their various assistances in doing the project. I would also like to thank Mr. Hong Sin Poh, Mr. Pek Soo Siong, the technicians in MicroMachine Center, for help in sputtering deposition.

I wish thank my friends and those who have helped me during the period of my study, Mrs. Cheng Guiping, Mr. Li Yibin, Mr. Wang Yongsheng, Mr. Wang Huili, Dr. Su Jincai, Mrs. Wang Chunmei, Mrs. Wang Zhiying, for being great labmates and encouragement and support.

Finally, my most sincere thanks go to my parents, who raised and supported me in all aspects before and during this endeavor, and my wife for her consistent love, caring, patience and her being who she is. Without them, this thesis would never have been possible.

List of Publications

1. **Tong Y. X.**, Y. Liu, J. M. Miao, L. C. Zhao. Characterization of a nanocrystalline NiTiHf high temperature shape memory alloy thin film. *Scripta Materialia* 52 (10) 2005, 983-987.
2. Liu Y., Z. L. Xie, **Y. X. Tong**, C. W. Lim. Properties of rapidly annealed Ti₅₀Ni₂₅Cu₂₅ melt-spun ribbon. *Journal of Alloys and Compounds* 416(1-2) 2006, 188-193.
3. **Tong Y.X.**, Y. Liu. Properties of Ti₅₀Ni₂₅Cu₂₅ melt-spun ribbon. *Proceedings of the 47th AIAA/ASME/ASCE/AHS/ASC Structures, Structural Dynamics, and Materials Conference, 1 - 4 May 2006, Newport, Rhode Island, USA*, MS AIAA-2006-1769 (2006) pp. 1-6.
4. **Tong Y.X.**, Y. Liu. Crystallization behavior of a Ti₅₀Ni₂₅Cu₂₅ melt-spun ribbon. *Journal of Alloys and Compounds* 449 (2008) 152-155.
5. **Tong Y. X.**, Y. Liu, Z. L. Xie. Characterization of a rapidly annealed Ti₅₀Ni₂₅Cu₂₅ melt-spun ribbon. *Journal of Alloys and Compounds* 456 (2008) 170-177.
6. **Tong Y.X.**, Y. Liu, Z. L. Xie, M. Zarinejad. Effect of precipitation on the shape memory effect of Ti₅₀Ni₂₅Cu₂₅ melt-spun ribbon. *Acta Materialia* 56 (2008) 1721-1732.
7. **Tong Y. X.**, Y. Liu, J. M. Miao. Phase transformation in NiTiHf shape memory alloy thin films. *Thin Solid Films* 2008 (in press).

Abstract

In the present work, the properties of two NiTi-based shape memory alloy thin films, namely $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon and Ni-Ti-Hf thin films, and the influencing factors have been extensively studied. Major attention has been paid to rapid thermal annealing of the initially amorphous materials and their resulted properties, including crystallization behavior, microstructure evolution, transformation characteristics and constraint shape memory effect. As a result, the processing-microstructure-property relationship has been established, which provides guidelines on optimization of the properties.

The crystallization behavior of NiTi-based thin films is characterized by a single-stage transformation. The addition of Cu reduces the crystallization temperature and activation energy of the initially amorphous alloy; whereas, the addition of Hf has a contrary effect. With the help of rapid thermal annealing, the initially amorphous $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon can be fully crystallized by annealing at 400 °C for 30 s, which is significantly lower than the crystallization temperature under conventional thermal annealing. This is attributed to the assistance of the extra energy available from the higher internal stress field associated with free volume in amorphous state.

In addition to B11 TiCu, a new precipitate, $\text{Ti}_2(\text{Ni,Cu})$ phase is present. B11 TiCu is metastable and converts to $\text{Ti}_2(\text{Ni,Cu})$ at higher temperatures or longer holding duration. With increasing annealing temperature or time, the room temperature microstructure changes in the sequence of $\text{B19} \rightarrow \text{B19} + \text{B11 TiCu} \rightarrow \text{B19} + \text{B11 TiCu} + \text{Ti}_2(\text{Ni,Cu}) \rightarrow \text{B19} + \text{Ti}_2(\text{Ni,Cu})$. The results further show that the annealing

temperature at which B11 TiCu or $\text{Ti}_2(\text{Ni,Cu})$ forms is lower than that under conventional thermal annealing.

The relation between precipitation (volume fraction, morphology and type) and shape recovery properties of the $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon was investigated. The shape memory effect is found to depend on both the volume fraction and distribution of the precipitates. The former affects the shape recovery strain through a reduction of the transformation volume participating in the shape recovery; the latter affects the shape recovery strain through strengthening the matrix thus reducing the martensite strain especially at low constraint stress. Precipitation strengthening, on the other hand, reduces the tendency of dislocation generation/movement, thus reducing the irreversible strain and improving the shape recovery strain. An optimized shape recovery strain of 2.91% can be obtained through annealing at 500 °C for 300 s that produces fine dispersed precipitates to strengthen the matrix and yet to have low volume fraction. This understanding provides guidelines on optimization of the shape memory properties via post-processing annealing.

Table of Contents

Acknowledgements	I
List of Publications.....	III
Abstract	IV
Table of Contents	VI
List of Figures	X
List of Tables.....	XX
List of Abbreviations and Symbols.....	XXI
Chapter 1 Introduction	1
1.1 Background	1
1.2 Objective and Scope.....	3
1.3 Organization	5
Chapter 2 Literature Review	7
2.1 Shape Memory Alloys and Related Phenomena	7
2.1.1 Martensitic Transformation.....	7
2.1.2 Shape Memory Effect.....	9
2.1.3 Superelasticity	11
2.1.4 Two-way Memory Effect	12
2.2 Crystallographic Theory of Martensitic Transformation	13
2.2.1 Crystal Structure of NiTi-based Shape Memory Alloys	13
2.2.2 Phenomenological Theory	15
2.3 Thermodynamic Aspects of Martensitic Transformation	16

2.4 NiTi-based Shape Memory Alloy Thin Films.....	20
2.4.1 Fabrication Methods.....	20
2.4.2 Crystallization Behavior of NiTi-based Thin Films.....	24
2.4.3 Microstructure	28
2.4.4 Martensitic Transformation Behavior	32
2.4.5 Shape Memory Properties	39
2.4.6 Mechanical Properties of NiTi-based Thin Films	43
2.4.7 Development of Ti-Ni-Cu Melt-spun Ribbon.....	45
2.4.8 Development of Ni-Ti-Hf Thin Films.....	50
2.5 Applications of NiTi-based Thin Films	51
2.5.1 Ni-Ti Thin Film Micropump	52
2.5.2 Ni-Ti Thin Film Microwrapper	53
Chapter 3 Experimental Procedures.....	55
3.1 Fabrication Methods.....	55
3.1.1 Fabrication of NiTi-based Thin Films.....	55
3.1.2 Post-processing Heat Treatment.....	56
3.2 Characterization Methods	58
3.2.1 Chemical Composition.....	58
3.2.2 Phase Transformation.....	58
3.2.3 Crystal Structure.....	59
3.2.4 Quantitative Analysis	60
3.2.5 Texture Measurement.....	61
3.2.6 Microstructure	62

3.2.7 Thermomechanical Property	62
Chapter 4 Crystallization Behavior of NiTi-based Thin Films	66
4.1 Crystallization Behavior of $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ Ribbon	66
4.1.1 Structure of As-spun Ribbon.....	66
4.1.2 Crystallization Behavior under Conventional Annealing	69
4.1.3 Effect of Heating Rate on Martensitic Transformation.....	71
4.1.4 Low Temperature Crystallization by Rapid Thermal Annealing	76
4.1.5 Discussion on Low Temperature Crystallization	82
4.1.6 Effect of Annealing Time on Martensitic Transformation.....	86
4.2 Crystallization Behavior of Ni-Ti-Hf Thin Films	88
4.2.1 Effect of Applied Power on Composition	88
4.2.2 Crystallization Behavior under Conventional Annealing	90
4.3 Effect of Alloying Element on Crystallization Behavior	93
4.4 Summary	96
Chapter 5 Phase Transformation Characteristics and Microstructure.....	98
5.1 Microstructure of $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ Ribbon.....	99
5.1.1 Martensite Structure of $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon	99
5.1.2 Precipitation of Rapidly Annealed $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ Ribbon	101
5.1.3 Discussion on the Precipitation Behavior	109
5.2 Texture of $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ Ribbon	110
5.3 Martensitic Transformation of $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ Ribbon	113
5.3.1 Effect of Annealing Temperature.....	113
5.3.2 Effect of Thermal Cycling.....	116

5.4 Microstructure of Ni-Ti-Hf Thin Films.....	118
5.5 Martensitic Transformation of Ni-Ti-Hf Thin Films	125
5.5.1 Effect of Composition	125
5.5.2 Effect of Annealing Temperature.....	126
5.5.3 Effect of Thermal Cycling.....	129
5.6 Summary	132
Chapter 6 Thermomechanical Properties	134
6.1 Thermomechanical Properties of $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ Ribbon	135
6.1.1 Deformation of B19 Martensite	135
6.1.2 Two-way Memory Effect Developed by Martensite Deformation	140
6.1.3 Martensite Stabilization	143
6.1.4 Constraint Shape Recovery Property	145
6.1.5 Explanation on the Structure-Property Relation	154
6.2 Shape Recovery of Ni-Ti-Hf Thin Films	163
6.3 Summary	164
Chapter 7 Conclusions and Recommendations.....	166
7.1 Conclusions	166
7.2 Recommendations	168
References	171

List of Figures

- Figure 2-1. Stress-strain-temperature curves showing the deformation behavior of a Ni-Ti alloy deformed below M_f (a), above A_f (b) and above M_d (c). The curves are associated with shape memory effect, superelasticity and ordinary plastic deformation, respectively [24]. 9
- Figure 2-2. Mechanism of shape memory effect: (a) original parent single crystal, (b) self-accommodated martensite, (c-d) deformation of martensite proceeds by the growth of one variant at the expense of the other, (e) upon heating to a temperature above A_f , each variant reverts to the parent phase in the original orientation by the reverse transformation [25]. 10
- Figure 2-3. Schematic diagram showing the region of shape memory effect and superelasticity in temperature-stress coordinates [26]. 12
- Figure 2-4. Schematic illustration of Gibbs free energy for both parent and martensite phases, and their relation to M_s and A_s temperatures. ΔT is the supercooling required for the transformation. 17
- Figure 2-5. Schematic illustration of the melt-spinning process. 20
- Figure 2-6. Phase diagram of a Ni-Ti alloy [106]. 28
- Figure 2-7. Pseudo-phase diagram of Ti-Ni and Ti-Cu alloy [108]. 29
- Figure 2-8. Various microstructure of Ti-rich Ni-Ti thin films heat treated at different temperature for 1 h [15]: Solid squares (■) are Ti_2Ni particles with random orientation (a); open squares (□) are Ti_2Ni precipitates with the same orientation as that of the matrix (b); open triangles(Δ) are plate

precipitates and oriented Ti_2Ni precipitates (c); solid circles (●) are plate precipitates (high-temperature form)(d) and plate precipitates (low temperature form)(e); open circles (○) indicate no precipitates; solid triangles (▲) indicate amorphous films. All graphs are on the same scale as shown in (e).....	31
Figure 2-9. Effect of Ni content on M_s temperature for binary Ni-Ti alloys. Different data symbols represent data from different authors. The solid line is given by thermodynamic calculations [113].	33
Figure 2-10. Effect of alloying elements on martensitic transformation temperature for Ni-Ti alloys: (a) wide alloying range (b) narrow alloying range [117].	35
Figure 2-11. Effect of Cu-content on transformation temperatures in $\text{Ti}_{50}\text{Ni}_{50-x}\text{Cu}_x$ alloys [17].....	37
Figure 2-12. Effect of composition and heat treatment temperature on martensitic transformation behavior in Ni-rich Ni-Ti thin films. The thin films were heat-treated at several temperatures below 580 °C for 1 h [130].	39
Figure 2-13. Change in curvature of $\text{Ni}_{51.3}\text{Ti}_{48.7}$ thin film aged at 300 °C (a), 350 °C (b), 400 °C (c), 450 °C (d) and 500 °C (e) for 1, 10 and 100 h. ●, in iced water, ○ in boiling water [135].	43
Figure 2-14. Stress-strain curves of $\text{Ni}_{48.3}\text{Ti}_{51.7}$, $\text{Ni}_{50}\text{Ti}_{50}$ and $\text{Ni}_{51.5}\text{Ti}_{48.5}$ thin films tested at 42 °C. The $\text{Ni}_{48.3}\text{Ti}_{51.7}$ and $\text{Ni}_{50}\text{Ti}_{50}$ thin films were annealed at 500 °C for 5 min and 1 h, respectively. The $\text{Ti}_{48.5}\text{Ni}_{51.5}$ thin film was aged at 400 °C for 1 h after solution treatment at 700 °C for 1 h [139].	44

Figure 2-15. TEM bright field (a) and two dark field images (b, c) of the same area of a melt-spun $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon annealed at 410 °C for 48 h. The precipitation takes place within the grains. Beam direction is parallel to [100] direction of the parent B2-phase for all three images. Note that only the variant of platelets perpendicular to the encircled streak which marks the corresponding g-vector is visible in (b) and (c), respectively [145].	46
Figure 2-16. Work output per volume versus cycling frequency for various microactuators [162].	52
Figure 2-17. Micropump structure with SMA thin film actuator: (a) pressurization type; (b) evacuation type [163].	53
Figure 2-18. Illustration of microwrapper: (a) plan view of microwrappers; (b) schematic diagram of actuation [164].	54
Figure 3-1. A typical temperature profile for an RTA treatment showing the setting temperature and the sample temperature.	57
Figure 3-2. A typical DSC curve showing the determining method of martensitic transformation temperatures.	59
Figure 3-3. Definition of the rotation angle β and tilt angle α in a pole figure.	61
Figure 3-4. Schematic strain-temperature curve representing shape memory behavior under constraint. The transformation temperatures are determined by tangent intercept method.	64
Figure 3-5. Schematic illustration of the strain-temperature behavior of the deformed sample under zero load. The reverse transformation temperatures are also indicated.	65

Figure 4-1. XRD patterns of free side and wheel side of the as-spun $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon at room temperature.	67
Figure 4-2. TEM bright field image of the as-spun $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon. The corresponding SAED pattern is inserted.	68
Figure 4-3. DSC curves of the as-spun $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon.	69
Figure 4-4. DSC curves with different heating rates from 350 °C to 550 °C for the as-spun $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon under 1 °C /min, 5 °C /min, 10 °C /min, 15 °C /min, 20 °C/min and 40 °C /min, respectively.	70
Figure 4-5. Kissinger's plot for the DSC data of Figure 4-4.	71
Figure 4-6. DSC cooling (a) and heating (b) curves for the $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbons annealed at different heating rates, 1 °C/min, 5 °C/min, 10 °C/min, 15 °C/min, 20 °C/min and 40 °C/min, respectively.	72
Figure 4-7. Transformation temperatures and ΔT as a function of the heating rate for the crystallized $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon.	73
Figure 4-8. TEM bright image of the $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ sample annealed at 15 °C /min.	74
Figure 4-9. XRD patterns of the $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon annealed at different heating rates, 1 °C/min, 5 °C/min, 10 °C/min, and 40 °C/min, respectively.	76
Figure 4-10. XRD patterns of the $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon annealed under RTA at 400 °C for 5 s, 10 s, 20 s, 30 s, 60 s and 300 s, respectively.	77
Figure 4-11. TEM bright field images and the corresponding SAED patterns of the $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon annealed under RTA at 400 °C for 10 s (a), 20 s (b) (c), 30 s (d) and 60 s (e), respectively.	79

Figure 4-12. TEM bright field image (a) and the corresponding SAED pattern (b) of the $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon annealed under RTA at 400 °C for 300 s. The incident electron beam is parallel to the $[100]_{\text{B19}}$	80
Figure 4-13. TEM bright field image showing the typical locations where EDX analysis was performed. The sample was annealed at 400 °C for 20 s.	81
Figure 4-14. DSC curve of the as-spun $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon under 10 °C/min from 40 °C to 550 °C. The inset is the enlargement of the region around the arrow.....	83
Figure 4-15. DSC curve (10 °C/min) of the as-spun $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon pre-annealed under CTA at 400 °C for 15 min. The inset is the enlargement of the curve.	84
Figure 4-16. Comparison of the XRD pattern of $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ samples. (a) The as-spun ribbon was annealed under CTA at 400 °C for 15 min followed by annealed under RTA at 400 °C for 30 s. (b) The as-spun ribbon was directly annealed under RTA at 400 °C for 30 s.	85
Figure 4-17. DSC cooling (a), (c) and heating (b), (d) curves for the $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbons annealed under RTA at 400 °C for 5 s, 10 s, 20 s, 30 s, 60 s and 300 s, respectively.....	87
Figure 4-18. Transformation temperatures as a function of annealing time for the $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon annealed under RTA at 400 °C	88
Figure 4-19. Chemical composition of as-deposited Ni-Ti-Hf thin films as a function of the power applied on Hf target. The power of the $\text{Ni}_{50}\text{Ti}_{50}$ target was fixed at 200 W.....	89

Figure 4-20. XRD patterns of the as-deposited $\text{Ni}_{48}\text{Ti}_{37.7}\text{Hf}_{14.3}$ (a), $\text{Ni}_{47.9}\text{Ti}_{35.7}\text{Hf}_{16.4}$ (b) and $\text{Ni}_{45}\text{Ti}_{32}\text{Hf}_{23}$ (c) thin films at room temperature....	90
Figure 4-21. DSC curves with different heating rates from 673K to 873K for the as-deposited $\text{Ni}_{48}\text{Ti}_{37.7}\text{Hf}_{14.3}$ (a) and $\text{Ni}_{45}\text{Ti}_{32}\text{Hf}_{23}$ (b) thin films.	92
Figure 4-22. Kissinger's plots for the DSC data of the as-deposited $\text{Ni}_{48}\text{Ti}_{37.7}\text{Hf}_{14.3}$, $\text{Ni}_{47.9}\text{Ti}_{35.7}\text{Hf}_{16.4}$ and $\text{Ni}_{45}\text{Ti}_{32}\text{Hf}_{23}$ thin films.	93
Figure 4-23. Comparison of the activation energy of Ni-Ti-Hf thin films and $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon with those of other NiTi-based ribbon and thin films.	94
Figure 5-1. TEM bright field image (a) and the SAED patterns (b), (c) of martensite in the ribbon annealed at 500 °C for 300 s under RTA. The SAED patterns (b), (c) correspond to the areas B, C in (a), respectively. The beam directions are parallel to the $[100]_{\text{M,T}}$ (b) and $[\bar{1}2\bar{1}]_{\text{M,T}}$ (c).	99
Figure 5-2. TEM bright field image (a) of martensite in the ribbon annealed at 700 °C for 300 s under RTA. The SAED pattern (b) shows the (011) compound twin. The incident beam direction is parallel to the $[100]_{\text{M,T}}$ . .	101
Figure 5-3. XRD patterns of the ribbons annealed at different conditions under RTA showing the formation of precipitates due to annealing.	102
Figure 5-4. TEM bright field images of the ribbon annealed at 800 °C for 300 s under RTA showing the morphology and distribution of precipitates.	103
Figure 5-5. SAED patterns from $\text{Ti}_2(\text{Ni}, \text{Cu})$ precipitates. The incident beam directions are parallel to $[100]_{\text{Ti}_2(\text{Ni,Cu})}$ (a), $[011]_{\text{Ti}_2(\text{Ni,Cu})}$ (b) and $[\bar{1}2\bar{3}]_{\text{Ti}_2(\text{Ni,Cu})}$ (c), respectively.	104

Figure 5-6. XRD patterns of the ribbons rapidly annealed at 700 °C for 1200 s (a) and conventionally annealed at 700 °C and 800 °C for 1200 s (b), respectively.....	105
Figure 5-7. Microstructure of the ribbon as a function of annealing temperature and time under RTA.	106
Figure 5-8. TEM bright field images of the ribbons annealed at 500 °C (a), 600 °C (b), and 700 °C (c) for 300 s, respectively. The SAED pattern in (d) was taken from (b). The incident beam is parallel to $[101]_{B19}/[221]_{B11}$	108
Figure 5-9. Volume fractions of B11 TiCu and $Ti_2(Ni,Cu)$ precipitates in the ribbons annealed for 300 s at different temperatures shown.....	109
Figure 5-10. $\{111\}$ pole figures of the ribbons annealed for 300 s at 400 °C (a), 500 °C (b), 600 °C (c), 700 °C (d) and 800 °C (e) under RTA showing no significant texture.....	112
Figure 5-11. DSC curves upon cooling (a) and heating (b) of the $Ti_{50}Ni_{25}Cu_{25}$ ribbons annealed at 500 °C, 600 °C, 700 °C and 800 °C for 300 s, respectively.....	114
Figure 5-12. Effect of annealing temperature on the transformation temperatures (a) and ΔT (b) of the ribbons annealed for 300 s.	115
Figure 5-13. Transformation peak temperatures of the ribbon annealed at 800 °C for 300 s as a function of the number of thermal cycling.	118
Figure 5-14. XRD pattern of $Ni_{47.9}Ti_{35.7}Hf_{16.4}$ thin film annealed at 600 °C for 25 s under RTA.	119

Figure 5-15. TEM bright field images and the corresponding SAED patterns of $\text{Ni}_{47.9}\text{Ti}_{35.7}\text{Hf}_{16.4}$ thin films annealed at 550 °C (a), 600 °C (b), 650 °C (c) 700 °C (d) and 750 °C (e) for 25 s, respectively.....	121
Figure 5-16. Histograms of the grain size distributions of $\text{Ni}_{47.9}\text{Ti}_{35.7}\text{Hf}_{16.4}$ thin film annealed at 600 °C (a), 650 °C (b), 700 °C (c), and 750 °C (d) for 25 s, respectively. The dash lines present the corresponding Gauss fitting curves.	122
Figure 5-17. TEM bright field image (a) of $\text{Ni}_{47.9}\text{Ti}_{35.7}\text{Hf}_{16.4}$ thin film annealed at 700 °C for 25 s under RTA. The SAED pattern (b) corresponds to the region A in (a). The incident electron beam in (b) is parallel to $[100]_{\text{M}}$	123
Figure 5-18. DSC curves of the $\text{Ni}_{48}\text{Ti}_{37.7}\text{Hf}_{14.3}$, $\text{Ni}_{47.9}\text{Ti}_{35.7}\text{Hf}_{16.4}$ and $\text{Ni}_{45}\text{Ti}_{32}\text{Hf}_{23}$ thin films annealed at 600 °C for 25 s.	126
Figure 5-19. M_s and A_s temperatures of the $\text{Ni}_{47.9}\text{Ti}_{35.7}\text{Hf}_{16.4}$ thin film as a function of annealing temperature.....	127
Figure 5-20. Effect of thermal cycling on the transformation peak temperatures of Ni-Ti-Hf thin films annealed at 650 °C for 25 s under RTA.....	131
Figure 5-21. The difference of the transformation peak temperatures between the 1 st and the N th cycles (ΔT_H) of Ni-Ti-Hf thin films annealed at 650 °C for 25 s under RTA.....	132
Figure 6-1. Stress-strain curves of the ribbons annealed at 400 °C (a), 500 °C (b), 600 °C (d), 700 °C (d) and 800 °C (e) for 300 s under RTA, respectively (tests performed at room temperature).....	136

Figure 6-2. Strain-temperature curve of the ribbon annealed at 400 °C for 300 s after 5.5% deformation at room temperature.	137
Figure 6-3. Effect of tensile strain on ε_{EL} , ε_{RE} , ε_{IR} , ε_A and η . The sample was annealed under RTA at 400 °C for 300 s.	138
Figure 6-4. Effect of annealing temperature on ε_{EL} , ε_{RE} , ε_A (a), ε_{IR} and η (b). The deformation strain is 4.5%.	139
Figure 6-5. Effect of tensile strain on ε_{TW} of the ribbons annealed for 300 s at different temperatures.	141
Figure 6-6. Effect of annealing temperature on ε_{TW} . The ribbons were deformed to 4% and 4.5%, respectively.	141
Figure 6-7. Strain-temperature curves of the ribbon annealed at 800 °C for 300 s after 4.5% deformation under thermal cycling (a) and ε_{TW} as a function of number of thermal cycling (b).	142
Figure 6-8. DSC curves of the deformed ribbons annealed at 400 °C (a), 500 °C (b), 600 °C (c), 700 °C (d) and 800 °C (e) for 300 s, respectively. The tensile strain is 4.5%.	144
Figure 6-9. Effect of tensile strain on the reverse transformation temperature (A_s) upon first heating. The ribbon annealed at different temperatures for 300 s under RTA.	145
Figure 6-10. Strain-temperature curves of the samples annealed for 300 s at 400 °C (a), 500 °C (b), 600 °C (c), 700 °C (d) and 800 °C (e), respectively. The constraint stress is 30 MPa.	146
Figure 6-11. Effect of annealing temperature and constraint stress on ε_M	147

Figure 6-12. Strain-temperature curves of the samples annealed for 300 s at 400 °C (a), 500 °C (b), 600 °C (c), 700 °C (d) and 800 °C (e) for 300 s, respectively. The constraint stress is 300 MPa.	149
Figure 6-13. Effect of stress on M_s temperature (a) and ΔT (b) for the samples annealed at different temperatures. The slope of the stress- M_s temperature as a function of annealing temperature is plotted in the insert of (a).	150
Figure 6-14. Effect of constraint stress on ε_P in the samples annealed at different temperatures for 300 s.	151
Figure 6-15. Critical stress (σ_s) for plastic deformation of 0.1% strain for the samples annealed for 300s at various temperatures shown.	152
Figure 6-16. Effect of constraint stress on ε_R of the ribbons annealed for 300 s at different temperatures.	153
Figure 6-17. Effect of annealing temperature on $\varepsilon_R^{\max}$ of the ribbons annealed for 300 s at different temperatures. The corresponding constraint stresses are also shown.	153
Figure 6-18. Comparison of the experimentally determined values of shape recovery strains and estimated values based on the volume fraction of precipitate. The samples were annealed for 300 s at different temperatures shown. The constraint stresses are 30 MPa (a), 50 MPa (b) and 150 MPa (c), respectively. The maximum recovery strain is shown in (d).	158
Figure 6-19. Photographs showing SME in the $\text{Ni}_{47.9}\text{Ti}_{35.7}\text{Hf}_{16.4}$ thin film annealed at 600 °C for 25s, (a) original shape (b) deformed shape (c)-(f) shape recovery upon heating.	164

List of Tables

Table 2-1. Comparison of crystallographic data for Ni-Ti martensite [36].	14
Table 2-2. Twinning models in NiTi-based SMAs	16
Table 2-3. Relationship between microstructure and related properties of Ni-Ti thin films by thermal cycling tests under an applied stress of 400 MPa [15].	40
Table 4-1. Average chemical compositions from the EDX measurements on different regions in the $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon annealed at 400 °C for 20 s. ...	81
Table 4-2. The onset of crystallization (T_x) and the crystallization temperatures (T_p) of the as-deposited $\text{Ni}_{47.9}\text{Ti}_{35.7}\text{Hf}_{16.4}$ thin film under different heating rates.	92
Table 4-3. Atomic radius mismatch and binary mixing enthalpy of Ti, Ni, Cu and Hf.	96
Table 5-1. Transformation temperatures and transformation enthalpy for $\text{Ni}_{47.9}\text{Ti}_{35.7}\text{Hf}_{16.3}$ thin film annealed at different temperatures for 25s.	127
Table 6-1. Summary of the present observations and major results reported in the literature.	155
Table 6-2. Lattice parameters of B19 martensite of the $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbons annealed for 300 s at different temperatures.	156

List of Abbreviations and Symbols

Abbreviations

ALCHEMI	Atom location by channeling enhanced microanalysis
BCC	Body centered cubic
BM	Bowles-Mackenzie
CSRO	Chemical short range order
CTA	Conventional thermal annealing
DSC	Differential scanning calorimetry
EDX	Energy dispersive X-ray spectrometry
e.m.	Electromagnetic
e.s.	Electrostatic
GP	Guinier-Preston
JCPDS	Joint committee for powder diffraction standards
MEMS	Microelectromechanical system
ND	Normal direction
PIPS	Precision ion polishing system
PZT	Piezoelectric
RD	Rolling direction
RTA	Rapid thermal annealing
RTP	Rapid thermal processor
SAED	Selected area electron diffraction
SEM	Scanning electron microscopy

SMA	Shape memory alloy
SME	Shape memory effect
TEM	Transmission electron microscopy
TD	Transverse direction
TSRO	Topological short range order
TTT	Transformation-temperature-time
TWME	Two-way memory effect
WLR	Wechsler-Lieberman-Read
XRD	X-ray diffraction

Symbols

A_f	Reverse transformation finish temperature upon heating
A_p	Reverse transformation peak temperature upon heating
A_s	Reverse transformation start temperature upon heating
a	Lattice parameter: unit cell x-axial length
B	Lattice deformation matrix
b	Lattice parameter: unit cell y-axial length
c	Lattice parameter: unit cell z-axial length
d	Interplanar distance
d_l	Unit column vector in the direction of the shape strain
E	Crystallization activation energy
$E_{fr}^{p \rightarrow m}$	Frictional energy
F	Force generated by microactuator

G^m	Gibbs free energy of the martensite
G^p	Gibbs free energy of the parent phase
I	Identity matrix
K_1	Twinning plane
K_2	Undistorted plane
M_d	Temperature at which martensite is no longer stress-induced
M_f	Martensitic transformation finish temperature upon cooling
M_p	Martensitic transformation peak temperature upon cooling
M_s	Martensitic transformation start temperature upon cooling
m_1	Magnitude of the shape strain
P_1	Shape strain matrix
P_2	Lattice invariant shear matrix
p_1'	Unit row vector in the direction normal to the invariant plane
Q_p	wavenumber
R	Gas constant, $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$
R_b	Bragg reliability factor
R_t	Lattice rotation matrix
S	Twinning shear
T_a	Annealing temperature
T_c	Crystallization temperature
T_g	Glass transition temperature
T_m	Melting temperature
T_p	Crystallization peak temperature

T_x	Onset of crystallization
T_0	Equilibrium temperature between parent phase and martensite
u	Displacement produced by microactuator
v	Volume produced by microactuator
V_P	Volume fraction of the precipitate
W	Work output per unit volume
$\Delta G^{p \rightarrow m}$	Change of the total free energy in martensitic transformation
$\Delta G_{ch}^{p \rightarrow m}$	Chemical free energy change
$\Delta G_{el}^{p \rightarrow m}$	Elastic strain energy
$\Delta G_{non-ch}^{p \rightarrow m}$	Non-chemical free energy change
ΔH^*	Enthalpy of the transformation per unit volume
ΔS	Entropy of the transformation per unit volume
ΔT	Transformation hysteresis
ΔT_H	Difference of the transformation peak temperatures between the 1 st and the N th cycle
α	Heating rate
β	Lattice parameter: unit cell y-z interaxial angle
ε	Tensile strain
ε_A	Recovery strain
ε_{EL}	Spring-back strain after unloading to zero stress
ε_{IR}	Irreversible strain after heating
ε_M	Martensite strain under constraint stress

ε_P	Irreversible strain produced during the thermal cycling
ε_R	Recovery strain under constraint stress
ε_R'	Estimated recovery strain
$\varepsilon_R^{\text{exp}}$	Experimental recovery strain of the precipitate-free sample
$\varepsilon_R^{\text{max}}$	Maximum recovery strain under constraint stress
ε_{RE}	One-way memory strain after heating to parent phase
ε_t	Transformation strain
ε_{TW}	Two-way memory strain after cooling to martensite
η	Strain recovery ratio
η_1	Twinning shear direction
η_2	The intersection of the plane of shear and the K_2 plane
θ	Diffraction angle
λ	Wavelength of X-ray
σ	Uniaxial stress
σ_s	Critical stress for slip

Chapter 1 Introduction

1.1 Background

In the past decades, shape memory alloys (SMAs) have attracted much attention due to their combined functions of sensing and actuating associated with shape memory effect (SME) or superelasticity. The unique SME and superelasticity realized in SMAs are the results of a thermoelastic martensitic transformation and its reverse transformation. SME is a particular phenomenon in which a specimen is deformed in the lower temperature phase (martensite) and subsequently recovers to the original shape upon heating to above a certain temperature by reverse martensitic transformation [1-3]. Superelasticity, another important property of SMAs, occurs at a higher temperature range (in parent phase). After the specimen undergoes a nonlinear deformation, it can completely recover upon unloading at a constant temperature due to the reverse stress-induced martensitic transformation [4].

So far, many alloy systems have been found to be SMAs, such as Ni-Ti [5], Cu-Al-Ni [6], Cu-Zn-Al [7], Fe-Mn-Si [8], Ni-Al [9, 10], etc. As compared to other SMAs, near-equiatomic Ni-Ti alloys are the most commercially successful SMAs due to their large recovery strain and stress, excellent corrosion resistance and good fatigue resistance as well as biocompatibility with human body. As a result, various applications of Ni-Ti alloys utilizing SME and superelasticity have been achieved in the areas of industry, aerospace and biomedicine, such as couplings [11], actuators [11], orthodontic arches, stents and bendable surgical tools [3, 12].

Recently with the development of microelectromechanical system (MEMS), the requirement for microactuators has resulted in the development of Ni-Ti alloys from bulk material to thin films [13-15]. In fact, Ni-Ti thin films are also the only SMA thin films that are successfully used to drive some MEMS components because of their large work output force per unit volume, large displacement and compatibility with silicon wafer. The shape memory properties of Ni-Ti thin films are comparable to those of bulk materials. However, the applications of Ni-Ti thin films are limited by the intrinsic drawbacks, i.e. the slow response speed and the lower transformation temperature. It is generally accepted that the properties of Ni-Ti alloys can be readily changed by the addition of an alloying element. The first drawback can be significantly improved by the addition of Cu which greatly reduces the transformation hysteresis, thus increases the response speed [16]. For instance, the transformation hysteresis of $\text{Ti}_{50}\text{Ni}_{30}\text{Cu}_{20}$ bulk material is about 4 °C [17], which is much smaller than the typical value (about 40 °C) of Ni-Ti binary alloys. In order to increase the transformation temperatures of NiTi-based alloys, the substitution of Hf, Zr for Ti or Pt, Pd, Au for Ni has been proved to be an effective way [18].

Sputtering deposition is the most common method to prepare NiTi-based SMA thin films, including Ni-Ti-Hf and Ti-Ni-Pd [19, 20]. Among them, Ni-Ti-Hf thin films have demonstrated higher transformation temperatures. Melt-spinning technique is an alternative way to prepare almost ready-to-use ribbon with a thickness of about 30 μm . This technique has an advantage of fabricating NiTi-based alloys with specific compositions which are difficult to deform by rolling or drawing, for example, Ti-Ni-Cu alloys with Cu content higher than 12 at.% [17, 21]. Compared to the sputtering

deposited thin films, the composition of the melt-spun ribbons is more uniform. This is of crucial importance for the practical applications since the properties of NiTi-based SMAs are strongly dependent on the composition. From the viewpoint of applications in MEMS, it seems that the sputtering deposition is more suitable because the thin films can be directly deposited on silicon and easily applicable to the silicon batch process. The integration of melt-spun ribbons may be improved to some extent by a hybrid integration process [22, 23].

In the present study, both the sputtering deposition and melt-spinning techniques have been employed to produce Ni-Ti-Hf thin films and $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon, respectively. The as-spun ribbon and the as-deposited thin films are likely amorphous, and they require post-annealing to achieve the desired shape memory properties. Thus, it is of primary importance to understand how the annealing condition affects the properties of NiTi-based thin films.

1.2 Objective and Scope

The purpose of this research is to investigate the processing-microstructure-property relationship of NiTi-based thin films, including $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ melt-spun ribbon and Ni-Ti-Hf thin films. Based on the results, the mechanism behind the property is established from a microstructure point of view. In view of applications, such understanding provides a guidance to optimize the shape memory properties. The scope of the present study is listed in detail in the following:

(1) Crystallization Behavior

The as-spun ribbon or the thin films are fully or partially amorphous depending on the processing parameters, and they require post annealing to obtain SME. It is

important to completely understand the crystallization behavior for controlling the microstructure and, consequently, transformation behavior and shape memory properties.

In the present study, effect of rapid thermal annealing (RTA) on the crystallization behavior of $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon is investigated. A plausible crystallization mechanism is proposed. The effect of different alloying elements, Hf and Cu, on crystallization temperature and activation energy of NiTi-based alloys is investigated and compared.

(2) Microstructure and Martensitic Transformation

Microstructure is generally governed by crystallization mechanism and heat-treatment. In the present study, the effect of rapid annealing on microstructure evolution of NiTi-based thin films is investigated. The precipitation behavior of $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon under RTA is systematically revealed. The annealing dependence of grain size in Ni-Ti-Hf thin films is studied. The effects of composition, annealing and thermal cycling on martensitic transformation of NiTi-based thin films are also studied and discussed.

(3) Thermomechanical Properties

Thermomechanical properties are very important issues for the design of MEMS devices and applications of NiTi-based thin films. However, the effect of annealing on shape memory behavior of $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon has not been completely established to date. In the present study, the thermomechanical properties of $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon are systematically investigated as a function of annealing condition by tensile tests and thermal cycling tests under constraint stress. The thermomechanical properties mainly include recovery strain, critical stress for slip and two-way memory strain. Based on

the resulted microstructure, the thermomechanical behavior is explained in detail and the relationship of processing-microstructure-property is established.

1.3 Organization

The main body of the present thesis begins with a literature review on NiTi-based SMA films, and then the detailed experimental procedures and methods followed by the experimental results and discussion. The detailed organization is as follows:

- (1) Chapter 2 gives a literature review on SMAs, especially fundamental aspects of SMAs and NiTi-based alloys thin films.
- (2) Chapter 3 presents a detailed description of the experimental techniques and procedures employed, including annealing treatments, microstructure characterization and transformation behavior measurement as well as thermomechanical property measurement.
- (3) In Chapter 4, crystallization behavior of $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon and Ni-Ti-Hf thin films under different conditions are studied and the crystallization mechanism is suggested.
- (4) In Chapter 5, phase transformation characteristics and microstructure evolution are presented with a focus on the precipitation behavior of $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon under RTA.
- (5) In Chapter 6, the thermomechanical properties of $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon are presented. The relationship of processing-structure-property is established and explained on the basis of the microstructure evolution.

- (6) Chapter 7 presents conclusions and recommendations.

Chapter 2 Literature Review

In this chapter, a literature survey on SME and NiTi-based SMAs thin films is presented. Fundamental notions are explained, such as martensitic transformation, the mechanism of SME and superelasticity, two-way memory effect. Furthermore, the crystallographic phenomenological theory and thermodynamics aspects of martensitic transformation are briefly reviewed. Following the brief introduction to SMAs and related phenomena, particular attention is paid to the recent progress in NiTi-based SMA thin films. The applications of NiTi-based SMA thin films are also introduced at the end.

2.1 Shape Memory Alloys and Related Phenomena

2.1.1 Martensitic Transformation

Solid-state phase transformation can be divided into two types: diffusional and displacive. Martensitic transformation belongs to the latter, which is a first-order transformation and does not require long range movement of atoms. The atoms move in a cooperative manner during transformation. So it is also called diffusionless transformation. Although the definition of martensite has been controversial for many years, some important features are widely accepted. The volume fraction of martensite is usually dependent on temperature, but not time. There is a hysteresis related with the transformation. During martensitic transformation, the martensite remains the same composition and atomic order as the parent phase.

The martensitic transformation is often described by a shear mechanism. In order to accommodate a volume change or a shape change produced by the martensitic transformation, slip or twinning mechanisms are required. Slip is a permanent process and unable to realize reversible shape change due to dislocation introduced during deformation. Twinning cannot accommodate volume change, however, can accommodate shape change in a reversible way.

Generally, martensitic transformation is divided into two categories: thermoelastic transformation and non-thermoelastic transformation. The former is characterized by a small driving force and a small transformation hysteresis (a few to several tens of degrees) as well as crystallography reversibility, while the latter is just in the opposite side [1]. Both SME and superelasticity are based on the thermoelastic martensitic transformation.

Since the structures of martensite and parent phase are quite different, many physical properties change with temperature during transformation, which can be used to determine the characteristic temperatures, such as, electrical resistivity, enthalpy and magnetic susceptibility. The characteristic transformation temperatures are defined as follows:

M_s : martensitic transformation start temperature upon cooling;

M_f : martensitic transformation finish temperature upon cooling;

M_p : martensitic transformation peak temperature upon cooling;

A_s : reverse transformation start temperature upon heating;

A_f : reverse transformation finish temperature upon heating;

A_p : reverse transformation peak temperature upon heating.

2.1.2 Shape Memory Effect

Shape memory effect (SME) is such a phenomena that a sample is deformed in low temperature phase (martensite), it recovers its original shape upon heating to above certain temperature through the reverse transformation. A typical stress-strain curve of a Ni-Ti alloy demonstrating the SME is shown in Figure 2-1 (a) [24].

Figure 2-1. Stress-strain-temperature curves showing the deformation behavior of a Ni-Ti alloy deformed below M_f (a), above A_f (b) and above M_d (c). The curves are associated with shape memory effect, superelasticity and ordinary plastic deformation, respectively [24].

A simplified model proposed by Otsuka is used to explain the mechanism of SME, as shown in Figure 2-2 [25]. When the sample is cooled from parent phase to a temperature below M_f , martensites are formed in a self-accommodation fashion. During this process, the shape of the sample does not change. The correspondence variants are twin-related and quite mobile. If an external stress is applied, the twin

boundaries move in order to accommodate the strain. If the external stress is enough high, a single variant of martensite will form. If heated to above A_f , the reverse transformation occurs, the original shape is regained if the transformation is thermoelastic. During reverse transformation, although the movement of each atom is small (less than one inter-atomic distance), the macroscopic shape change appears since all the atoms move in the same direction in a variant. Depending on the deformation temperature regions, the mechanism of SME is slightly different, but naturally the same as above.

Figure 2-2. Mechanism of shape memory effect: (a) original parent single crystal, (b) self-accommodated martensite, (c-d) deformation of martensite proceeds by the growth of one variant at the expense of the other, (e) upon heating to a temperature above A_f , each variant reverts to the parent phase in the original orientation by the reverse transformation [25].

2.1.3 Superelasticity

Another important property of most SMAs is superelasticity. The stress-strain curve in Figure 2-1 (b) clearly shows the unique deformation behavior. When the sample is deformed at above A_f , the strain can be recovered after unloading the applied stress. In this case, a strain far exceeding the elastic limit can be fully or partially recovered. So the particular stress-strain behavior is called superelasticity. This is due to stress-induced martensitic transformation and its reverse transformation. Since martensitic transformation occurs by a shear-like mechanism, it is possible that it occurs even above M_s if an external stress is applied. It is also possible to induce martensitic transformation even above A_f if the applied stress is not enough to induce slip deformation. Since the stress-induced martensite is unstable, if the stress is absent at above A_f , the reverse transformation occurs. Thus the strain recovers due to the nature of thermoelastic martensitic transformation.

According to the above explanation, we can find the critical stress for slip is vitally important to realize large recoverable strain. This is because slip is an irreversible process. If the applied stress is over the critical stress for slip, slip occurs instead of stress-induced transformation, which seriously deteriorates superelasticity of SMAs. A schematic illustration of relationship between superelasticity and critical stress for slip is presented in Figure 2-3 [26]. In this figure, the relationship between SME and superelasticity is also shown. In principle, both SME and superelasticity can be observed in the same sample depending on the test temperature if the critical stress for slip is high enough. Comparison of the figures in Figure 2-1 shows that the deformation behavior of NiTi-based SMAs is strongly influenced by deformation

temperature. When the deformation temperature is above M_d , at which the critical stress for slip is equal to the critical stress to induce martensitic transformation, the parent phase shows the ordinary plastic deformation. Several methods are known to increase the critical stress for slip in order to obtain good SME and superelasticity, including work-hardening, aging-hardening, and solution hardening [27] as well as grain refinement.

Figure 2-3. Schematic diagram showing the region of shape memory effect and superelasticity in temperature-stress coordinates [26].

2.1.4 Two-way Memory Effect

The SME stated in section 2.1.2 is often called one-way SME because only the shape of parent phase is remembered. However, it is possible to partially remember the shape of martensite besides that of the parent phase under certain conditions. In contrast to the one-way SME, this is called two-way memory effect (TWME). The

origin of TWME results from the feature of martensitic transformation in nature that martensite nucleation is very sensitive to stress field [25]. Therefore, some specifically thermomechanical treatments are usually necessary in order to create the specific stress field then to realize the TWME, which is unlike the one-way SME. The specific processes include the following methods: introduction of severe deformation [28], constraining in the martensitic state followed by heating above A_f in the constrained state [29], thermal cycling [30] and precipitation [31].

2.2 Crystallographic Theory of Martensitic Transformation

2.2.1 Crystal Structure of NiTi-based Shape Memory Alloys

The crystal structure of parent phase in NiTi-based shape memory alloys is BCC (body-centered cubic) B2 structure. The lattice parameters of the B2 parent phase is about 0.301-0.305 nm. The crystal structure of martensite in Ni-Ti alloy is more complex. The first report in 1961 by Purdy and Parr [32] claimed that the martensite has a hexagonal structure. In 1965, Dautovich et al [33] reported that it is triclinic by using electron diffraction and X-ray powder diffraction. Since then, several crystal structures were proposed to be that of martensite. In 1971, Otsuka et al. [34] and Hehemann and Sandrock [35] determined that the crystal structure is monoclinic. More recently, Kudoh et al. [36] carried out a complete analysis on a $\text{Ni}_{49.2}\text{Ti}_{50.8}$ martensite single crystal by using X-ray 4-circle diffractometer and precession camera. Their results clearly showed that the crystal structure of martensite is monoclinic with a space group of $P2_1/m$. Table 2-1 summarizes the crystal structure proposed by different researchers.

Table 2-1. Comparison of crystallographic data for Ni-Ti martensite [36].

	Otsuka et al.[34]	Hehemann et al.[35]	Kudoh et al.[36]	Michel et al.[37]
a (nm)	0.2889	0.2883	0.2898(1)	0.2885(4)
b (nm)	0.4120	0.4117	0.4108(2)	0.4120(5)
c (nm)	0.4622	0.4623	0.4646(3)	0.4622(5)
β (°)	96.8	96.8	97.78(4)	96.8(1.0)
V (nm ³)	0.05463	0.05449	0.05479(4)	0.05455
Atoms per unit cell	4	4	4	4
Space group	$P2_1/c$	$P2_1/m$	$P2_1/m$	$P2_1/m$

The addition of alloying elements may influence the structure of NiTi-based alloys. The addition of Hf or Zr increases the lattice parameters of the martensite and the parent phase, does not change the crystal structure [38-40]. Potapov et al. [40] reported that the lattice parameters of a , c and β increases with increasing Hf content in $\text{Ni}_{49.8}\text{Ti}_{50.2-x}\text{Hf}_x$ martensite, but b keeps constant. The addition of Cu or Pd changes not only the lattice parameters, but also the crystal structure of martensite from B19' to B19 [41-44]. The martensite in $\text{Ti}_{50}\text{Ni}_{50-x}\text{Cu}_x$ ($x=10-30$ at.%) is determined to be orthorhombic (B19). The space group is found to be $Pmmb$ in $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon [43]. The lattice parameters of the parent phase and the martensite in $\text{Ti}_{49.5}\text{Ni}_{40.5}\text{Cu}_{10}$ alloy reported by Saburi et al. [42] are :

Parent phase: $a = 0.3030$ nm

Martensite: $a = 0.2881$ nm

$b = 0.4279$ nm

$c = 0.4514$ nm

2.2.2 Phenomenological Theory

Crystallographic characteristics of martensitic transformations are now well understood by phenomenological theory which is developed by Wechsler-Lieberman-Read (WLR) [45, 46] and Bowles-Mackenzie (BM) [47], independently. The theory describes martensitic transformation by the following three processes: (1) a lattice deformation B creating the martensite structure from the parent phase, (2) a lattice invariant shear P_2 and (3) a lattice rotation R_t . Thus the total shape strain P_1 can be expressed by the following matrix form:

$$P_1 = R_t P_2 B \quad (2.1)$$

The theory requires that the shape strain is described by an invariant plane strain, i.e. a plane of no distortion and no rotation, which is macroscopically homogeneous and consists of a shear strain parallel to the habit plane and a volume change. Therefore, the shape strain can be expressed by the following equation:

$$P_1 = I + m_1 d_1 p_1' \quad (2.2)$$

where, d_1 is a unit column vector in the direction of the shape strain, I is the (3×3) identity matrix, m_1 is the magnitude of the shape strain and p_1' is a unit row vector in the direction normal to the invariant plane.

According to this theory, only the following three parameters are required to calculate the crystallographic parameters and determine orientation relationship: (1) lattice parameters of the parent and martensite phases, (2) a lattice correspondence and (3) a lattice invariant shear. In Ni-Ti alloys, this theory has been applied to quantitatively predict the transformation strain, to explain the self-accommodation phenomenon and set up models for polycrystalline alloys.

The lattice invariant shear can be introduced by twinning, slip, or faulting, but in most cases, only twinning is desired since it does not introduce irreversible deformation. When a crystal is composed of parts that are oriented with respect to one another according to some symmetry rule, the crystal is said to be twinned. The twinning process is in general described by five twinning elements, K_1 represents the shearing plane, K_2 is the second undistorted plane, η_1 represents the shearing plane and η_2 is the intersection of K_2 and the plane of shear. According to the symmetry rule, the twinning is divided into three kinds, type I, type II and compound twinning. There are many twinning models reported in NiTi-based alloys. Table 2-2 summaries several main twinning modes reported in NiTi-based B19' and Ti-Ni-Cu B19 martensite.

Table 2-2. Twinning models in NiTi-based SMAs

Twinning mode	K_1	η_1	K_2	η_2	S	Ref.
{111} type I (Ni-Ti)	(111) ($\bar{1}\bar{1}\bar{1}$)	$[\bar{1}.5\bar{1}0.511]$ $[\bar{1}.5\bar{1}0.511]$	$(\bar{0}.670.331)$ $(\bar{0}.670.331)$	$[211]$ $[2\bar{1}\bar{1}]$	0.14	[48]
$\langle 011 \rangle$ type II (Ni-Ti)	$(\bar{0}.72\bar{1}\bar{1})$ $(\bar{0}.7211)$	$[011]$ $[01\bar{1}]$	(011) $(01\bar{1})$	$[\bar{1}.57\bar{1}\bar{1}]$ $[\bar{1}.5711]$	0.28	[49]
Compound (Ni-Ti)	(001) (100)	$[100]$ $[001]$	(100) (001)	$[001]$ $[100]$	0.24	[49]
Compound (Ni-Ti-Hf)	(001)	$[100]$	(100)	$[001]$		[39]
{111} type I (Ti-Ni-Cu)	(111)	$[\bar{1}.140.141]$	$(\bar{0}.540.081)$	$[211]$	0.16	[50]
Compound (Ti-Ni-Cu)	(011)	$[01\bar{1}]$	$(01\bar{1})$	$[011]$	0.11	[50]

2.3 Thermodynamic Aspects of Martensitic Transformation

Martensitic transformation does not involve the compositional change, so the driving force for the transformation results from the Gibbs free energy difference between

parent phase and martensite. Figure 2-4 schematically shows the dependence of Gibbs free energy of parent phase and martensite on the temperature, where T_0 represents the equilibrium temperature between parent phase and martensite, usually taken as $1/2(M_s + A_s)$ [51], $\Delta G^{p \rightarrow m} |_{M_s} = G^m - G^p$ is the driving force for martensite nucleation, G^m and G^p are the Gibbs free energy of martensite and parent phase, respectively. Hornbogen [52] proposed that T_0 depends on chemical composition, degree of order and hydrostatic stress.

Figure 2-4. Schematic illustration of Gibbs free energy for both parent and martensite phases, and their relation to M_s and A_s temperatures. ΔT is the supercooling required for the transformation.

For a thermoelastic martensitic transformation, a local equilibrium between the chemical and non-chemical contributions is reached for all of the transformation interfaces at each temperature. The non-chemical term includes the elastic strain

energy and the friction energy. Martensitic transformation is associated with shape and volume changes, which is elastically self-accommodated in the system. The elastic strain energy results from two contributions: the interfacial energy associated with the existence of a single or multiple interfaces, and the elastic strain energy due to elastic strains [53, 54]. The elastic energy is responsible for the transformation intervals since it resists the growth of the martensite unless a further driving force is given. The frictional term originates from three contributions: friction stresses required to move the interfaces between parent phase and martensite, free energy changes associated with defects induced by the transformation and partial plastic accommodation of the transformation shape and volume changes [53, 54]. The frictional energy is responsible for the transformation hysteresis. For NiTi-based alloys, the transformation temperature hysteresis is usually several to several tens degrees.

During the forward martensitic transformation, the driving force is balanced by the increase in elastic strain energy and interfacial energy, and by resistive forces against interfacial movement. Half of the chemical free energy change is stored as the elastic energy [55]. During the reverse transformation, the elastic energy previously stored promotes the reverse transformation together with the driving force. Thus, the change of the total free energy in the transformation can be express as [53, 56]

$$\Delta G^{p \rightarrow m} = -\Delta G_{ch}^{p \rightarrow m} + \Delta G_{non-ch}^{p \rightarrow m} = -\Delta G_{ch}^{p \rightarrow m} + \Delta G_{el}^{p \rightarrow m} + E_{fr}^{p \rightarrow m} \quad (2.3)$$

where $\Delta G_{ch}^{p \rightarrow m}$ represents the chemical free energy change, $\Delta G_{non-ch}^{p \rightarrow m}$ represents the non-chemical free energy change, $\Delta G_{el}^{p \rightarrow m}$ is the elastic strain energy and $E_{fr}^{p \rightarrow m}$ is the frictional energy. The superscript $p \rightarrow m$ denotes the forward transformation from

parent phase to martensite. The quantities are taken in absolute value, and if they are negative, it is indicated by a minus sign.

Since martensitic transformation can be described by a shear mechanism, the stress always influences martensitic transformation. Following Patel and Cohen [57], martensitic transformation interacts with an external applied stress, and whether the stress assist or oppose the transformation is easily determined by calculating the work done on the system by the external stress. Obviously, if the work is positive, the stress assists the transformation, and vice versa. After discussion on the mechanical work, it was concluded that a shear stress always assists the transformation, but a normal stress may assist or resist it, depending on the sign of the stress and the volume change associated with the transformation.

The effect of stress on martensitic transformation usually is analyzed by using the following Clausis-Clapeyron equation:

$$\frac{d\sigma}{dT} = -\frac{\Delta S}{\varepsilon_t} = -\frac{\Delta H^*}{\varepsilon T_0} \quad (2.4)$$

where σ is a uniaxial stress, ε_t the transformation strain, ΔS the entropy of transformation per unit volume, and ΔH^* the enthalpy of the transformation per unit volume, T_0 is the equilibrium temperature between parent phase and martensite. However, M_s is often used if the driving force is independent of temperature and stress. The critical stress to induce martensitic transformation follows the Clausis-Clapeyron equation, as shown in Figure 2-3. It is reported that the slope of the critical stress-temperature line, $d\sigma/dT$ for NiTi-based SMAs is between 4 and 20 MPa/°C [58].

2.4 NiTi-based Shape Memory Alloy Thin Films

2.4.1 Fabrication Methods

2.4.1.1 Melt-spinning

It is known that the properties of Ni-Ti binary SMAs can be changed by the alloying of the third elements, including Hf, Zr, Cu et al. However, most of the ternary alloys are too brittle to be deformed plastically. The melt-spinning technology is introduced to skip the thermomechanical shaping procedure and to achieve the fine grain after the conventional casting since 1990's [59]. Figure 2-5 schematically shows the melt-spinning process. During the process, the mother alloy is induction melted in a quartz crucible and then ejected with a pressurized argon gas out of a nozzle onto a high speed rotating copper roller quenched by water.

Figure 2-5. Schematic illustration of the melt-spinning process.

Since the melt-spinning is a non-equilibrium technique, the structure of the as-spun ribbon sensitively depends on the cooling rate controlled by the processing parameters such as the wheel speed, gas pressure, melting temperature and nozzle-wheel gap etc. The melting temperature is the most effective processing parameter to control the cooling rate. Recently, Nam et al. [60, 61] investigated the melting temperature dependence of the structure and properties of Ti-Ni-Cu ribbon. By increasing the melting temperature, the initial structure of the as-spun $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon changes from partially to fully amorphous. The transformation temperatures of the as-spun $\text{Ti}_{50}\text{Ni}_{35}\text{Cu}_{15}$ ribbon decrease with increasing the melting temperature due to the grain size effect and the internal strain.

The as-spun Ni-Ti ribbons are fully crystalline, while, the structure of the as-spun Ti-Ni-Cu ribbons is related to Cu content under similar melt-spinning conditions [62]. The ribbons with high content of Cu are partially or fully amorphous. This is because that increase in alloying elements favors formation of amorphous state according to the empirical rule proposed by Inoue [63]. It is easy to control the microstructure through post-annealing of the amorphous materials. This is also one of the probable reasons to select ternary alloy to do the melt-spinning.

Most of the investigations on the melt-spun SMAs ribbon focus on Ti-Ni-Cu ribbon, which is probably due to the reduced transformation hysteresis, good thermal stability et al. The melt-spinning technique is also used to investigate the Ni-Ti alloys [62], Ni-Ti-Hf high temperature SMAs [64, 65], Ni-Ti-Hf-Re [66, 67] and Ti-Ni-Cu-Zr [68] alloys.

Generally, there are several advantages of the melt-spinning over the conventional casting techniques. These include the ability to form metastable phases, increasing the solubility above the equilibrium solubility, decreasing the segregation of additions, and refining the microstructure. In view of the applications, the best advantage is probably that almost-ready-to use ribbons are directly produced, avoiding the typical rolling or drawing procedure after the conventional casting. However, the melt-spun ribbons are not easily incorporated in the MEMS devices. It is expected that this disadvantage may be overcome by a hybrid integration process [69] .

2.4.1.2 Sputtering Deposition

NiTi-based SMA thin films have been successfully fabricated by different ways, including sputter deposition [70], vacuum vapor deposition [71], laser ablation [72]. Recently plasma ion plating was also employed to fabricate SMA thin films [73]. Among them, sputtering deposition is the major technology obtaining perfect SMA thin films because of good reproducibility.

Sputtering deposition is the process that the particles are firstly ejected from the solid surface of target by the momentum transferring from other particles which are usually gaseous ions and then condense onto various substrates [74]. In the present study, the Ar ion was used to sputter Ti, Ni and Hf atoms from NiTi and Hf targets.

Although sputtering deposition has been used to make thin film for many years, it is difficult to find a theory which enable one to predict the results yet. This is because many parameters are involved during sputter deposition, such as applied power, Ar gas pressure, substrate-target distance, substrate and its temperature, and the target used.

This complexity causes many troublesome problems for sputtering deposition of SMA thin films, including structure and composition deviation.

The structure of SMA thin films is significantly affected by the sputtering conditions. For instance, if the substrate is not heated, the as-deposited thin film is in amorphous state. But if the substrate is heated to around 200 °C or higher, the crystallized thin film will be produced. By increasing the substrate temperature, the crystallized thin films demonstrate different microstructures [75]. In addition, the thin films prepared at low pressure exhibit a flat and featureless structure, while high sputtering pressure produces a well-defined clustered columnar structure [70].

Compared with the composition of target, a lack of Ti formed by sputtering deposition usually occurs because Ti is very active resulting in oxide formation and the sputtering yield of Ni is higher than Ti. As well known, the composition strongly affects the transformation temperature of SMAs. For binary Ni-Ti bulk material, in general, the transformation temperature will drop around 100 °C if Ti decreases by 1 at.% [76]. So how to achieve an optimized composition that is equivalent to the bulk target is always concern of researchers. Various attempts have been performed on this aspect. The earliest and usual method is to put some Ti chips on the top of target or utilize the Ti-rich target [77]. But the former method requires many parameters, including number, geometry, size and position of plates. It is too difficult to precisely adjust the composition of SMA thin films. Using a separate Ti target as the compensator is another possibility. Instead of compensating for Ti loss by modifying the target, several unique methods are also developed to achieve the optimum composition, such as using the heated targets instead of the common ones [78, 79],

sputter deposited Ti/Ni multilayer and subsequent heat treatment [80] and adjusting the power applied to each target [81].

2.4.2 Crystallization Behavior of NiTi-based Thin Films

The as-spun ribbon and the as-deposited thin films are partially or fully amorphous depending on the processing parameters. Such amorphous thin films cannot be directly employed as micro-actuator materials. Thus, proper post-annealing to crystallize the amorphous materials is essential to obtain SME. Crystallization is such a transformation during which an amorphous phase crystallizes into one or more metastable or stable polycrystalline phases. The driving force for crystallization is the Gibbs free energy difference between the amorphous and the crystalline states. Based on the transformation mechanism, the crystallization behavior is divided into three kinds: polymorphous, eutectic and primary crystallization. Most of the crystallization in amorphous NiTi-based SMAs is polymorphous transformation [82-85], i.e. an amorphous phase crystallizes into a single crystalline phase with same chemical composition. In this mechanism, the grains grow rapidly and isotropically and the growth rate is linear with time, since long distance diffusion is not required.

2.4.2.1 Influencing Factors

The crystallization behavior of NiTi-based alloys is significantly influenced by composition. The crystallization temperature and activation energy first increase and then decrease with increasing Ni content from 24 to 64 at.% in amorphous Ni-Ti ribbons [86]. Once the composition is off that of intermetallic compound (Ti_2Ni , TiNi), the growth kinetics of amorphous ribbon cannot be described by the polymorphous

mechanism [87]. This is consistent with the results found in Ni-Ti thin films [83]. The addition of Cu in near-equiatomic alloy does not change the transformation path, but reduces the crystallization temperature and activation energy which are two important indicators of the thermal stability of amorphous materials [88, 89]. Therefore, this indicates that the addition of Cu reduces the thermal stability of Ni-Ti-Cu amorphous alloy. This is different from the role of Si in the crystallization behavior of Ni-Ti-Si alloys. The Ti_2Ni alloy with small amount of Si (less than 4 at.%) still crystallizes in a single step. However, with increasing Si content, the transformation changes to a two-step one, primary crystallization followed by a eutectic reaction [87].

The crystallization behavior is also affected by annealing condition. With increasing annealing temperature, nucleation mode changes from continuous to site-saturation one, as reflected by Avrami exponents [90]. The grain size shows little dependence on the annealing temperature under low temperature crystallization. The microstructure of the crystallized NiTi-based alloys is also sensitive to annealing temperature [15, 91, 92]. For Ti-rich NiTi-based thin films, annealing at a low temperature, typically 50 °C below the crystallization temperature, produces fine Guinier-Preston (GP) zone precipitates first which are effective in increasing the critical stress for slip. With increasing annealing temperature, GP zone precipitates disappear and small spherical Ti_2Ni precipitates form.

2.4.2.2 Structural Relaxation

The atomic structure of an amorphous alloy changes towards states of lower energy and higher density during annealing since it is metastable. This behavior is known as structural relaxation [93]. No crystallization is involved in this process. The structural

relaxation involves the atomic cooperative rearrangement, and then leads to change in free volume or configuration entropy [94]. Several physical properties may be substantially changed due to structural relaxation, with typical increases of up to 5-7% in Young's modulus, 2-3% in electrical resistivity, 20-30 °C in Curie temperature of $\text{Fe}_{27}\text{Ni}_{53}\text{P}_{14}\text{B}_6$ amorphous alloy [95] and two orders of magnitude in viscosity as well as length and density changes [96]. All above phenomena may be used to characterize structural relaxation.

The structural relaxation is usually observed as an irreversible process, but sometimes a reversible process occurs [97]. The irreversible process occurs at a temperature around T_g (Glass transition temperature). This process involves a reduction and a redistribution of free volume, which is associated with the changes in topological short range order (TSRO) and an increase in chemical short range order (CSRO). After such a process, the state of the amorphous alloy cannot be retrieved unless the fabrication is repeated. The TSRO change refers to changes in atom packing independent of chemical bonding. The CSRO means the chemical distribution of atomic near neighbors. The reversible structural relaxation usually takes place at a temperature below T_g and is caused by the changes in CSRO [93]. It is such a process that during annealing below T_g , the atomic distribution is adjusted and more atoms are repopulated to a lower energy level; upon reheating, the atoms at low energy level acquire thermal energy and are re-excited to resume original configuration.

Since it occurs prior to crystallization, structural relaxation may influence the crystallization behavior. Terunuma et al. [98, 99] reported the structural relaxation in amorphous $\text{Ni}_{50}\text{Ti}_{50}$ alloy prepared by ball milling. With the increasing ball milling

time, NiTi_2 and Ni_3Ti phases appear as the crystallization products besides NiTi phase. This is attributed to the fact that the structural relaxation occurred during prolonged milling time causes local phase separation or compositional fluctuation. The structural relaxation is also observed in amorphous near-equiatomic Ni-Ti thin films fabricated by sputtering deposition [100].

2.4.2.3 Rapid thermal Annealing

The crystallization of amorphous thin films by annealing can be greatly aided by rapidly bringing the films up to the annealing temperature, so called rapid thermal annealing (RTA). The conventional furnace annealing typically involves heating rates of order 1-10 °C/s and annealing times of the order of 1 h. However, the heating rates realized by RTA can reach up to 100 °C/s or higher. The high heating rates have been proved to affect the mechanism and kinetics of phase transformation and the formation of modified microstructure in comparison of conventional heat treatments, for instance grain refinement [101]. Successful use of RTA has been reported to heat-treat a wide variety of materials, such as amorphous silicon [102], ZnO thin films [103], InGaAs/GaAs quantum wells [104] and the sol-gel indium tin oxide thin films [105]. However, up to date, the applications of RTA in SMA ribbon or thin films have not been reported. In the present study, RTA was employed to heat-treat $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon and Ni-Ti-Hf thin films, respectively.

2.4.3 Microstructure

2.4.3.1 Phase Diagrams

Since all heat-treatment for improving the shape memory properties is based on phase diagram, Ni-Ti binary phase diagram is first reviewed, as shown in Figure 2-6 [106]. In most cases, Ni-Ti alloys can exhibit the SME when Ni and Ti have nearly equivalent content, scattering in the central region. On the Ti-rich side, Ti_2Ni phase is the only product during annealing since the phase boundary is almost vertical and the solubility shows little dependence on annealing temperature. However, on the Ni-rich side, there are several annealing products depending on the annealing conditions. According to the transformation-temperature-time (TTT) diagram in Ni-rich $\text{Ni}_{52}\text{Ti}_{48}$ alloy [107], the precipitation occurs in the following sequence with increasing aging temperature and time:

Figure 2-6. Phase diagram of a Ni-Ti alloy [106].

TiNi₃ precipitate is an equilibrium phase, both Ti₃Ni₄ and Ti₂Ni₃ phases are intermediate ones. Ti₃Ni₄ phase is the most important one since it can be used to strengthen parent phase and improve the shape memory properties due to its thin plates and densely dispersed distribution in matrix. The precipitation strengthening by Ti₂Ni is impossible in bulk material. However, in sputtering deposition thin films or other amorphous alloys, precipitation strengthening by Ti₂Ni is also available since the precipitation can be well controlled by adjusting annealing from initially amorphous state.

Ti-Cu alloy has a phase diagram very similar to that of Ni-Ti alloy. A pseudo-phase diagram for Ti-Ni and Ti-Cu alloys is shown in Figure 2-7 [108]. Different from B2 TiNi phase at high temperature, TiCu phase has a tetragonal structure. This indicates that up to about 30% Cu is soluble in the cubic B2 phase at high temperature. The solubility of Cu in Ni-Ti, much larger than other elements in Ni-Ti alloys, means that the shape memory properties will be retained for higher alloying content of Cu than for other ternary additions. This diagram also indicates that the precipitation of TiCu phase occurs when Ti-Ni-Cu alloy with high concentration of Cu is annealed.

Figure 2-7. Pseudo-phase diagram of Ti-Ni and Ti-Cu alloy [108].

2.4.3.2 Effect of Annealing on Microstructure of NiTi-based Thin Films

Ni-rich Ni-Ti SMA thin films demonstrate the same microstructure evolution as the bulk materials after solution-treatment followed by aging treatment. The Ti_3Ni_4 precipitates are produced during aging at intermediate temperature. The size and density of the precipitates depend on aging temperature and time.

As for Ti-rich Ni-Ti SMA thin films, while, peculiar microstructure evolution never reported in the bulk materials has been revealed. The microstructure of Ti-rich Ni-Ti thin films is strongly related to the composition and annealing temperature. Figure 2-8 summaries various microstructure of Ti-rich Ni-Ti SMA thin films heat treated at different temperatures [15]. If the heat treatment temperature of the amorphous specimen is lower than T_c (crystallization temperature), typically $T_c-50^\circ\text{C}$, large number of thin plate precipitates along (100) planes constitute the boundaries of nanocrystals, as shown in Figure 2-8 (a). For the heat treatment temperature at around T_c , thin coherent plate precipitates are produced in parent phase, as shown in Figure 2-8 (b). The thin precipitates are uniformly distributed and are regarded as a Ti-rich GP zone. After annealing at higher temperature, the microstructure is characterized by the mixture of plate precipitates and spherical Ti_2Ni phase shown in Figure 2-8 (c) and oriented spherical Ti_2Ni phase displayed in Figure 2-8 (d).

In the case of heat treatment blow T_c [91], the parent phase with exact equiatomic composition is formed and crystallized. Consequently, the excess Ti atoms are ejected and accumulate in the amorphous region facing the interface between crystal and amorphous. To relieve the excess Ti atoms, Ti-rich coherent plate precipitates are formed and a new parent phase grain is nucleated adjacent to the precipitates. If heat

treatment temperature is at T_c [92], rapid growth of the interface between crystals and amorphous should be responsible for the formation of thin plate precipitates. The excess Ti atoms will cluster because the matrix tends to form the exact equiatomic Ni-Ti composition and the temperature is not high enough to allow long-range diffusion for formation of Ti_2Ni phase. Therefore, the precipitates are produced as GP zone. The unique microstructure has also been observed in a Ti-rich $Ti_{50.8}Ni_{43}Cu_{6.2}$ thin film besides the Ti-rich Ni-Ti thin film [109].

Figure 2-8. Various microstructure of Ti-rich Ni-Ti thin films heat treated at different temperature for 1 h [15]: Solid squares (■) are Ti_2Ni particles with random orientation (a); open squares (□) are Ti_2Ni precipitates with the same orientation as that of the matrix (b); open triangles (Δ) are plate precipitates and oriented Ti_2Ni precipitates (c); solid circles (●) are plate precipitates (high-temperature form) (d) and plate precipitates (low temperature form) (e); open circles (○) indicate no precipitates; solid triangles (▲) indicate amorphous films. All graphs are on the same scale as shown in (e).

Melt-spun ribbons of NiTi-based ribbons show some interesting behavior due to the non-equilibrium feature under rapid solidification processes. The coherent Ti_2Ni precipitates are observed to densely distribute in the grain interior of Ti-rich Ni-Ti ribbon [110, 111], even in $\text{Ti}_{50}\text{Ni}_{45}\text{Cu}_5$ and Ni-rich $\text{Ti}_{49}\text{Ni}_{46}\text{Cu}_5$ ribbons [111]. This is attributed to different dependences of undercooling on composition. All ribbons are fully crystallized in as-spun condition. With increasing annealing temperature, the coherency strain around Ti_2Ni precipitates disappears because of the growth of precipitates. Khantachawana et al. [112] reported that Ti_2Ni precipitates are observed at grain boundaries in $\text{Ti}_{49}\text{Ni}_{51}$ ribbon. But the mechanism of the unusual precipitation is not established to date. In addition to Ti_2Ni precipitates, disc precipitates on $\{100\}\text{B}_2$ plane of the matrix are also observed in $\text{Ni}_{49}\text{Ti}_{51}$, $\text{Ni}_{50}\text{Ti}_{50}$ and $\text{Ni}_{51}\text{Ti}_{49}$ ribbons and result in good shape memory properties. The disc precipitates are not identified and the precipitation mechanism is also understood as yet. All specific microstructure observed in the ribbons are believed to affect the transformation behavior and shape memory properties.

2.4.4 Martensitic Transformation Behavior

The transformation temperature is of importance for the practical application because the transformation is related to almost all the shape memory properties. The most effective way of controlling the transformation temperature is to change the composition, i.e. Ni content or the addition of alloying elements. Another way is to control the microstructure by annealing, such as precipitation, grain size. The effect of precipitation on transformation temperature results from two mechanisms: one is the

decomposition due to the precipitation, the other one is related to the stress field around the precipitates.

2.4.4.1 Effect of Composition on Martensitic Transformation

Figure 2-9. Effect of Ni content on M_s temperature for binary Ni-Ti alloys. Different data symbols represent data from different authors. The solid line is given by thermodynamic calculations [113].

It is known that 1 at.% change in composition may change the transformation temperatures by more than 100 °C for the solution-treated Ni-rich Ni-Ti alloys. The solution-treated Ni-Ti alloys show one-stage transformation from B2 parent phase to B19' martensite. Figure 2-9 shows the dependence of transformation temperature on the Ni-content for binary Ni-Ti alloys [113]. For the Ti-rich alloys, the transformation temperature is not sensitive to the composition. This is because of the solubility limit

of NiTi phase on Ti-rich side. For the Ni-rich alloys, the transformation temperature drastically decreases with increasing Ni content. The compositional dependence of martensitic transformation temperature has been understood by considering the elastic constant change during transformation [114].

The transformation behavior strongly depends on the addition of the alloying elements. According to their effect on transformation temperature, the alloying elements can be divided into two groups, one is to lower the transformation temperature, and the other one is to raise the transformation temperature. The former includes the substitution of Al for Ti [115] and the substitution of Cr, Fe, Mn, V and Co for Ni [116]. The latter mainly includes the substitution of Au, Pt, Pd for Ni and the substitution of Zr and Hf for Ti [18]. The substitution of Zr and Hf for Ti seems to be more practical because of the low cost. Otsuka et al. [117] summarized the effect of most of the alloying elements on transformation temperature, as shown in Figure 2-10. The addition of the alloying elements not only changes the transformation temperature, but also possibly affects the transformation path. A typical example is the addition of Fe in Ni-Ti alloys [118-120]. The addition of 3 at.% Fe reduces M_s temperature to about -196 °C, furthermore, separates the R-phase transformation and B19' martensitic transformation.

Figure 2-10. Effect of alloying elements on martensitic transformation temperature for Ni-Ti alloys: (a) wide alloying range (b) narrow alloying range [117].

The intrinsic mechanism of the effect of alloying elements on martensitic transformation has not been well understood to date. Several important factors are considered to be related to this mechanism, such as electron configuration, chemical affinity and atomic size effect. The experiment of atom location by channeling enhanced microanalysis (ALCHEMI) by Nakata et al. [121] reveals that electron configuration cannot simply correlate with this mechanism. Thus, the above influencing factors should be considered together when dealing with the effect of alloying elements. This needs further investigations to understand these influencing factors.

Among the alloying elements, the effect of Cu is unique. The addition of Cu substitutes Ni in Ni-Ti alloys if adding Cu with formula $\text{Ti}_{50}\text{Ni}_{50-x}\text{Cu}_x$ [117]. The addition of Cu does slightly change the transformation temperature, but changes the transformation path and drastically reduces the transformation hysteresis. Nam et al. [17, 21] studied the Cu-content dependence of martensitic transformation temperature in Ti-Ni-Cu alloys. Addition of 7.5 at.% Cu can change the transformation path into B2-B19-B19', as shown in Figure 2-11. With increasing Cu content, the transformation temperature from B19-B19' decreases. Recently, it is found that the B19-B19' transformation occurs at about -81 °C in $\text{Ti}_{50}\text{Ni}_{30}\text{Cu}_{20}$ alloy by synchrotron radiation [122]. The increase in the Cu content results in the reduction of the transformation hysteresis. The smallest transformation hysteresis is about 4 °C for $\text{Ti}_{50}\text{Ni}_{30}\text{Cu}_{20}$ alloy [17]. A small transformation hysteresis means fast response frequency, which is desirable by the actuator applications. This small value is comparable to that of R-phase transformation, but B2-B19 transformation shows much

larger transformation strain than that of R-phase transformation. The small transformation temperature hysteresis is due to the strengthening of parent phase by increasing Cu content, because the frictional stress for twin boundary movement decreases if the dislocation movement is suppressed by increasing Cu content [21]. The addition of Cu also reduces the compositional sensitivity of martensitic transformation [123] and increases the thermal cycling stability [124].

Figure 2-11. Effect of Cu-content on transformation temperatures in $\text{Ti}_{50}\text{Ni}_{50-x}\text{Cu}_x$ alloys [17].

2.4.4.2 Martensitic Transformation in NiTi-based Thin Films

Martensitic transformation of NiTi-based thin films strongly depends on the sputtering conditions [125-127] and metallurgical conditions [128, 129]. For example, the transformation temperature of Ni-Ti thin films deposited on Si substrate is slightly

higher than that of the thin films deposited on SiO₂ buffer layer [125]. The transformation behavior are also influenced by deposition temperature [127], thickness of the thin films [126]. It is found by Surbled et al. [128] that the transformation temperatures are below room temperature and show little dependence on the annealing temperature for solution-treated Ni-rich thin films. However, unlike Ni-rich thin films, the transformation temperatures of the Ti-rich thin films are very sensitive to the composition and heat treatment and above room temperature. This is correlated to the unique precipitation process during the heat treatment.

The transformation behavior of Ni-rich Ni-Ti thin films is strongly influenced by aging because of the precipitation of Ti₃Ni₄ phase, which is quite similar to the bulk Ni-rich Ni-Ti alloys. Figure 2-12 summarizes the martensitic transformation behavior of Ni-rich Ni-Ti thin films [130]. The as-deposited thin films were crystallized and concurrently aged at several temperatures below 580 °C for 1 h. The transformation behavior can be divided into the following three types depending on the Ni-content and heat-treatment temperature. (1) Two-steps transformation occurs upon both cooling and heating: B2-R-B19'. (2) The transformation occurs in two steps as B2-R-B19' during cooling, single step as B19'-B2 upon heating. (3) Single step transformation as B2-B19' occurs upon both cooling and heating. Miyazaki et al. [131] studied the effect of aging time on the transformation temperatures of Ni_{51.9}Ti_{48.1} thin film. The film was first annealed at 700 °C for 1 h and then aged at 500 °C for various time. The as-annealed thin film does not show the R phase transformation. However, with increasing aging time, M_s and A_s both increase and R phase transformation appears. Furthermore, when the aging time is increased to 100 h, M_s and A_s raise by

about 100 °C. This indicates that the aging is an effective method to increase the transformation temperature of Ni-rich Ni-Ti thin films.

Figure 2-12. Effect of composition and heat treatment temperature on martensitic transformation behavior in Ni-rich Ni-Ti thin films. The thin films were heat-treated at several temperatures below 580 °C for 1 h [130].

2.4.5 Shape Memory Properties

Ni-Ti SMAs thin films have been proved to show desirable shape memory characteristics, including SME and superelasticity, which are comparable to those of bulk materials. After annealed at 500 °C for 1 h, $\text{Ni}_{48}\text{Ti}_{52}$ thin film shows perfect SME, but superelasticity is not good, $\text{Ni}_{50}\text{Ti}_{50}$ thin film does not show perfect SME and superelasticity and $\text{Ni}_{51}\text{Ti}_{49}$ thin film shows both perfect SME and superelasticity [132].

Shape memory properties are closely related to microstructure of SMAs. Table 2-3 summaries a group of data on relationship between microstructure and related properties of thin films with different heat treatments and compositions [15, 92]. This

table shows that $\text{Ni}_{47.9}\text{Ti}_{52.1}$ thin film annealed at 450 °C for 1 h containing GP zones possesses the same transformation strain as $\text{Ni}_{50}\text{Ti}_{50}$ thin film, but no permanent strain is detected. In contrast, the thin film annealed at 550 °C for 1 h containing Ti_2Ni precipitates shows smaller transformation strain and permanent strain. In the case of heat treatment at a temperature below or near T_c , the thin plate precipitates impede the movement of the slip dislocations, but cannot resist the martensite growth. In the case of heat treatment above T_c , Ti_2Ni precipitates suppress the martensite growth and dislocation motion [92]. With increasing Ti content, the transformation strain decreases. The Ti-rich Ni-Ti SMAs thin films annealed at T_c-50 °C show better shape memory properties than those annealed at around T_c [109, 133].

Table 2-3. Relationship between microstructure and related properties of Ni-Ti thin films by thermal cycling tests under an applied stress of 400 MPa [15].

Composition (at.%)	Heat treatment (°C) 1 h	Precipitates	Available transformation strain (%)	Permanent strain (%)
$\text{Ni}_{50}\text{Ti}_{50}$	500	None	5.5	1.1
$\text{Ni}_{47.9}\text{Ti}_{52.1}$	450	GP zones	5.5	0.0
$\text{Ni}_{47.9}\text{Ti}_{52.1}$	500	GP zones + Ti_2Ni	5.1	0.1
$\text{Ni}_{47.9}\text{Ti}_{52.1}$	550	Ti_2Ni	3.9	0.4

Ishida et al. [134] reported that the thickness effect of $\text{Ni}_{50}\text{Ti}_{50}$ thin films on the deformation behavior. Both transformation and plastic strains increase gradually with decreasing film thickness from 5 μm to around 2 μm and then drop dramatically after reaching a maximum value. Furthermore, with the increasing applied stress, the

maximum value shifts to a lower one. The constraints from neighboring grains and surface oxide layers formed during heat treatment may be responsible for this.

It is generally accepted that near-equiatomic and Ni-rich Ni-Ti bulk alloys are expected to show TWME after training process. The special heat treatments are also found to be suitable for Ni-rich Ni-Ti thin films [130, 135]. Furthermore, in recent, the TWME is documented in Ti-rich Ni-Ti SMAs thin films fabricated by sputter deposited Ni/Ti multilayers [80, 136] and conventional sputtering deposition [137]. Since they are able to recover the original shape of not only parent phase but also the martensite upon cooling or heating without any bias force, the thin films with TWME could be used to simplify and miniaturize the micromachines.

The TWME in the Ni/Ti multilayer is related to the residual intrinsic stress and can be obtained without any special treatments except annealing at the lower temperature for crystallization. Lehnert et al. [136] found that $\text{Ni}_{46}\text{Ti}_{54}$ thin films fabricated with multiplayer method show the TWME after annealed at 400 °C for 30 min. Such annealing process is not enough to homogenize completely the composition and release the stress. The stress generated during deposition may act as driving force of reverse transformation upon cooling. After annealed at relatively high temperature, such as 600 °C for 30 min, the thin films do show a one-way SME because the residual stresses have released. Even that, the TWME still favors reducing the fabrication procedure of microactuators. More recently, the intrinsic TWME is also demonstrated in Ti-Ni-Pt and Ti-Ni-Pd thin films [138].

Plate-shape precipitates form on the $\{100\}$ planes of B2 parent phase in as-deposited Ti-rich Ni-Ti thin films after heat-treatment at around or below T_c . The

TWME of Ti-rich Ni-Ti thin films just originates from the stress fields produced by the plate-shape precipitates [137]. The spontaneous shape memory change associated with B2-R transformation and B2-R-B19' is about 0.08% and 0.34%, respectively.

The TWME of Ni-rich Ni-Ti thin films is strongly affected by heat-treatment because it is related to the precipitation process of Ti_3Ni_4 . Figure 2-13 shows the shape change for $\text{Ni}_{51.3}\text{Ti}_{48.7}$ thin films which are put in boiling water and in ice water, the films have been aged at various temperatures for various times [135]. The shape change is described by a parameter r_i/r_t ; r_i represents the curvature radius of a film under constraint, while r_t curvature radius of the film at a given temperature. The corresponding strain at the inner surface can be calculated by the equation, $\varepsilon = -t/2r$ (ε : strain at the inner surface, t : film thickness, r : curvature radius of a film), and is also shown on the right-hand scale. In these figures the open circles represent the film shape in boiling water, where the film is in the parent phase. The closed circles represent the film shape in ice water, where the film is in the R-phase. When a film is aged at 300 °C for 1 h, the film bends in the constrained direction upon cooling. However, as aging time increases, the bending direction changes and the film aged for 100 h bends backward upon cooling and shows all-round shape memory effect. This effect becomes stronger by increasing aging temperature and time. However, at highest aging temperatures of 450 °C and 500 °C, the effect gradually decreases with increasing aging time. A good TWME is obtained above room temperature when $\text{Ni}_{51.3}\text{Ti}_{48.7}$ thin film is aged at 400 °C for 100 h.

Figure 2-13. Change in curvature of $\text{Ni}_{51.3}\text{Ti}_{48.7}$ thin film aged at 300 °C (a), 350 °C (b), 400 °C (c), 450 °C (d) and 500 °C (e) for 1, 10 and 100 h. ●, in iced water, ○ in boiling water [135].

2.4.6 Mechanical Properties of NiTi-based Thin Films

In order to understand the mechanical properties of NiTi-based SMA thin films, another important problem for practical applications, the strength and elongation of three types of Ni-Ti thin films were measured from the stress-strain curves [132, 139, 140]. For $\text{Ni}_{50}\text{Ti}_{50}$ thin film, after annealing at 500 °C for 1 h, the thin films exhibit a high yield stress and a small elongation as compared to bulk $\text{Ni}_{50}\text{Ti}_{50}$ alloy. The yield stress can reach up to 650 MPa and elongation 40%, the former is higher than bulk samples which results from fine grain of thin films and the latter is smaller than bulk samples which is possibly due to the higher defect density caused by sputtering process. For Ni-rich $\text{Ni}_{51.5}\text{Ti}_{48.5}$ thin film, after solution treatment at 700 °C for 1 h

followed by age treatment at 400 °C for 1 h, a yield stress of 1.4 GPa can be obtained. This is associated with the presence of the coherent Ti_3Ni_4 and the fine grain size. For Ti-rich $\text{Ni}_{48.3}\text{Ti}_{51.7}$ thin film annealed at 500 °C for 5 min, its stress-strain curve shows a similar behavior with $\text{Ni}_{50}\text{Ti}_{50}$ thin film. But the yield stress is much higher than the latter, which is attributed to the distribution of the fine coherent GP zones. The elongation of $\text{Ni}_{48.3}\text{Ti}_{51.7}$ thin film is about 20% at around M_s temperature, which is not observed in the bulk Ti-rich Ni-Ti alloys. Their stress-strain curves are shown in Figure 2-14. It is obvious that Ni-Ti thin films possess enough mechanical properties for practical applications. It seems that $\text{Ni}_{48.3}\text{Ti}_{51.7}$ thin film has a balance between the ductility and strength. For this thin film, the ductility is sensitive to the heat treatment [139]. Annealing at 600 °C for 1 h produces Ti_2Ni precipitates, resulting in decrease in ductility.

Figure 2-14. Stress-strain curves of $\text{Ni}_{48.3}\text{Ti}_{51.7}$, $\text{Ni}_{50}\text{Ti}_{50}$ and $\text{Ni}_{51.5}\text{Ti}_{48.5}$ thin films tested at 42 °C. The $\text{Ni}_{48.3}\text{Ti}_{51.7}$ and $\text{Ni}_{50}\text{Ti}_{50}$ thin films were annealed at 500 °C for 5 min and 1 h, respectively. The $\text{Ti}_{48.5}\text{Ni}_{51.5}$ thin film was aged at 400 °C for 1 h after solution treatment at 700 °C for 1 h [139].

2.4.7 Development of Ti-Ni-Cu Melt-spun Ribbon

2.4.7.1 Microstructure of Ti-Ni-Cu Melt-spun Ribbon

Microstructure of $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon was first studied by Xie et al. [141]. The microstructure of the as-spun ribbon consists of mainly amorphous and a small amount of crystalline particles embedded in amorphous matrix. After annealing at different temperatures, B19 martensite variants are self-accommodated with (011) and (111) twins. The structure of the B19 martensite in $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon was further studied by XRD [43]. The results reveal that the structure is different from the standard B19 type since atoms shift from the centro-symmetric positions in the $(010)_{\text{ORT}}$ layers of the orthorhombic martensite. After partial crystallization at 420 °C, the microstructure of $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon is characterized by some curious structure and morphology [142-144]. In addition to the perfect spherical single grains, multi-grain BCC particles showing twinning relations between their grains are observed by TEM. Each grain of the multi-grain particles grows radically to the same distance from the center of the particles, resulting in isotropic growth. These results are helpful for understanding of the nucleation and growth mechanism of $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ alloy.

Rösner et al. [145] studied the microstructure of $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon annealed at 410 °C for 22-48 h and found that a high density of thin plate-like precipitates is formed homogeneously within the grains, as shown in Figure 2-15. The density of the precipitates increases with increasing annealing time [145, 146]. The thin-plate precipitates are determined to be a tetragonal B11 TiCu phase with a slight solution of Ni into Cu lattice sites. The habit planes of the precipitates are found to be $\{100\}_{\text{B2}}$ or $\{011\}_{\text{B19}}$ when the matrix is martensite. When the ribbon is annealed at a temperature

near or below the crystallization temperature for a long time, the precipitates are coherent with the matrix and form a cell structure [147, 148]. However, when the ribbon is annealed at 600 °C for 48 h, the relationship between the precipitates and the matrix becomes semi-coherent [148]. The densely B11 TiCu precipitates are possibly related to the high density defects produced during rapid cooling in the ribbon.

Figure 2-15. TEM bright field (a) and two dark field images (b, c) of the same area of a melt-spun $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon annealed at 410 °C for 48 h. The precipitation takes place within the grains. Beam direction is parallel to [100] direction of the parent B2-phase for all three images. Note that only the variant of platelets perpendicular to the encircled streak which marks the corresponding g-vector is visible in (b) and (c), respectively [145].

2.4.7.2 Martensitic Transformation of Ti-Ni-Cu Melt-spun Ribbon

Since melt-spinning is a non-equilibrium process, the melt-spun ribbons show some specific microstructure which influences the martensitic transformation behavior. Rösner et al. [149] reported a two-stage B2-B19+B2-B19' transformation in $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon annealed at 410 °C. The two-stage transformation is first ascribed to the high density of TiCu precipitates. After two years, the same authors [150] further studied martensitic transformation in $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon and corrected their understanding on the two-stage transformation. The mechanism is then attributed to the influence of the initial crystalline particles with larger grain size in the “free surface”. The same mechanism is also applicable to the results found in $\text{Ti}_{50}\text{Ni}_{35}\text{Cu}_{15}$ ribbon [61]. Morgiel et al. [151] investigated the martensitic transformation by *in situ* TEM observations and concluded that the B2-B19 transformation occurs in the following order: large grains, newly formed small grains and heavily dislocated strip grown at the surface of primary large grains upon cooling. Their results are consistent with the mechanism proposed by Rösner et al. [150] and exclude the B19-B19' transformation [141]. The amorphous ribbon also provides an opportunity to study martensitic transformation in partially crystallized sample. The amorphous-crystalline interface has the same effect as the smaller grain size, i.e. lower the transformation temperature by increasing the non-chemical energy [152].

It seems that $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon is likely appropriate candidate to separately study the effect of internal stress on martensitic transformation since the addition of Cu reduces the compositional sensitivity [124]. Based on this consideration, Rösner et al. [147] studied the effect of coherent thin plate B11 TiCu precipitates on martensitic

transformation. The coherent B11 TiCu precipitates were produced by annealing at the temperature close to the crystallization temperature (455 °C). The densely distributed B11 TiCu precipitates broaden the transformation peak and lower the transformation temperature due to the internal stresses. However, the dependence of semi-coherent TiCu precipitates produced by annealing at 600 °C on transformation temperature shows an opposite effect as compared to that of coherent ones [148]. The semi-coherent B11 TiCu precipitates raise the transformation temperature because the dislocations around the interface between the precipitates and the matrix can act as the nucleation sites.

The annealing dependence of martensitic transformation was also investigated [146, 153, 154]. Cheng et al. [146, 153] annealed the initially amorphous $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon at different temperatures for 15 min. The transformation temperature increases when the ribbon is annealed below 500 °C and then decreases by annealing at higher temperatures, which is ascribed to the combined effect arising from the B11 TiCu precipitates and grain size. Chang et al. [154] reported that increase of the annealing time elevates the transformation temperature when annealing at 500 °C. But the transformation temperature is quite lower than the values reported by other researchers. It is surprising that annealing at 500 °C for 3 h cannot fully crystallize $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon, although the crystallization temperature of 467 °C under a heating rate of 10 °C/min is very close to other results [141, 149]. Since it is not fully crystallized, the ribbon does not show any precipitates. According to the above results, one can see that martensitic transformation behavior of $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon still remains controversial and is not reproducible.

2.4.7.3 Deformation Behavior of Ti-Ni-Cu Melt-spun Ribbon

As compared to the bulk material produced by conventional casting method, Ti-Ni-Cu ribbons show better shape recovery properties, including larger transformation strain and higher critical stress for slip. Furuya et al. [59, 155] studied the Cu-content dependence of deformation behavior of the ribbons with different Cu-content from 0-20 at.%. The Ti-Ni-Cu ribbons shows larger transformation strain when less than 10 at.% Cu is added. However, the transformation strain decreases with increasing Cu-content when more than 10 at.% Cu is added [62, 155]. Furthermore, the recent results in $\text{Ti}_{50}\text{Ni}_{30}\text{Cu}_{20}$ ribbon demonstrates better shape recovery properties than the counterpart bulk material [156]. The improved properties are ascribed to the refined grain size, the large density of defects and the texture. The effect of annealing on shape recovery properties of $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon was studied by Cheng et al. [153, 157] and Chang et al. [154]. The transformation strain decreases by increasing annealing temperature from 450 °C to 700 °C, or by increasing the annealing time when annealing at 500 °C. The transformation under constraint stress also shows good thermal cycling stability [153]. Santamarta et al. [62] reported that TWME can be induced in as-spun $\text{Ti}_{50}\text{Ni}_{45}\text{Cu}_5$ ribbon by thermomechanical cycling training. However, the TWME in the $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon annealed at about 600 °C for 3.5 min is inhibited because of the precipitation of B11 TiCu.

Superelasticity of Ti-Ni-Cu ribbons is better than that of the bulk material as the critical stress for slip is effectively increased resulting from the refined grain size and high density of defects [158]. Santamarta et al. [62] and Liu [159] observed superelasticity in $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon. With the increasing cycling number, the critical

stress to induce martensite and the recovery strain decrease in the first 10 cycles [159]. The addition of Cu also reduces the stress hysteresis [158]. The stress hysteresis decreased with increasing the number of cycling [159]. In $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon, the smallest stress hysteresis is about 30 MPa after annealing at 465 °C for 1 h [60]. The deformation behavior of Ti-Ni-Cu ribbon has been investigated by some researchers, however, several problems remains unclear. Further understanding of the relationship between the stress hysteresis and the single-pair variant is needed. How the single-pair martensite variant forms and how it affects the stress-hysteresis are unknown. Another problem is related to the effect of thin plate B11 TiCu precipitates on the thermomechanical properties. Our knowledge on how the type, volume fraction and distribution of the precipitates vary with the annealing temperature or duration, and how they affect the subsequent shape memory properties, is missing.

2.4.8 Development of Ni-Ti-Hf Thin Films

Ni-Ti-Hf bulk materials have been considered as the promising candidates for high temperature applications due to their considerable shape memory properties and lower cost compared with Ti-Ni-Pd and Ti-Ni-Pt alloys. So Ni-Ti-Hf thin films maybe one of the potential materials for high temperature conditions.

Ni-Ti-Hf thin films have been fabricated using sputtering deposition [160] or laser ablation of composite targets [19, 161]. Depending on Hf content, the transformation peak temperatures of Ni-Ti-Hf thin films can reach up to 175 °C, 228 °C upon cooling and heating, respectively. R-phase transformation that is never observed in Ni-Ti-Hf bulk materials occurs in a $\text{Ti}_{36.63}\text{Ni}_{50.04}\text{Hf}_{13.33}$ thin film [19]. It is suggested that this

presence of R-phase transformation is related to the refined grain size of thin films resulting from the dimensional constraints during the crystallization process

Zhang et al. [160] investigated the transformation peak temperatures (M_p and A_p) as functions of deposition temperature and heat treatment temperature. M_p and A_p increases by increasing the deposition temperature and heat treatment temperature. When the deposition temperature is low, the heat treatment has significant effect on the transformation temperature. With increasing deposition temperature, the transformation temperatures become less sensitive to the annealing temperature. But their results do not show R-phase transformation, different from the results obtained by Gu et al. [19].

2.5 Applications of NiTi-based Thin Films

With the progress in MEMS technique, several mechanisms have been proposed as the microactuators, such as electrostatic, magnetic, thermal bimorph, piezoelectric and thermopneumatic as well as SMAs. In general, four critical parameters are often used to evaluate the characteristics of microactuators, including force, displacement, and volume as well as response frequency. Work output per unit volume is related to those parameters except for the response frequency and often used to compare the properties of different microactuators, defined in the following equation:

$$W = \frac{F \cdot u}{v} \quad [162] \quad (2.5)$$

where F stands for the generated force, u is displacement and v volume.

Figure 2-16 shows the relationship between the work output per unit volume and the cycling frequency for several microactuators [162], in which SMA refers to Ni-Ti

SMA thin film, e.m. electromagnetic, e.s. electrostatic, PZT piezoelectric. From this figure, one can see that SMA thin film microactuators can generate the largest work output per volume at reasonably fast cycling frequencies. Therefore, many efforts have been made to develop the applications of SMA thin films in MEMS field. In the following, several microdevices based on SMA thin films are to be reviewed.

Figure 2-16. Work output per volume versus cycling frequency for various microactuators [162].

2.5.1 Ni-Ti Thin Film Micropump

As the basic components for micro fluidic handling devices in micro chemical analysis and micro dosage systems, micropump based on Ni-Ti SMA thin films has been realized. Figure 2-17 shows two kinds of diaphragm type micropump structures based on SMA thin films, (a) pressurization and (b) evacuation [163]. The micropump consists of two main components: an SMA thin film microactuator and a check valve

structure. The SMA actuator is built up with a Ni-Ti thin film diaphragm with a memorized flat shape and a glass cap, which forms a chamber between them. When an external force is applied to the chamber, the diaphragm deforms. Then, when the diaphragm is heated by current heating or other methods, it recovers the original shape. Thus liquid can be pushed out or sunk in depending on the movement of the SMA thin film diaphragm which controls the inlet and outlet ports in the valve.

Figure 2-17. Micropump structure with SMA thin film actuator: (a) pressurization type; (b) evacuation type [163].

2.5.2 Ni-Ti Thin Film Microwrapper

It is well known that Ni-Ti alloys exhibit not only superior shape memory characteristics but also excellent biocompatibility. Therefore, Ni-Ti thin films are also considered as the potential candidates in biomedical field. Micrograbbing devices are one of those applications. The micrograbbing devices (i.e. microwrapper) are designed to grab the microsize objects in a living organism or pieces of cancerous tumor for

removal from the body [164]. Figure 2-18 illustrates the actuation scheme of the proposed SMA thin film microwrapper. Figure 2-18 (a) represents a plan-view of the microwrapper, in which the gray outline is the Ni-Ti thin film area. The bonding pad, current path and central parts of arms are attached to the substrate, other parts are unattached. The unattached arms have two stable states: (1) curled-up shape, (2) flat shape (Figure 2-18 (b)). When released from substrate, the arms curl up to form a cage-like structure. After heated, the arms become flat due to SME. Joule heat passing the current path is used to actuate microwrapper.

Figure 2-18. Illustration of microwrapper: (a) plan view of microwrappers; (b) schematic diagram of actuation [164].

Chapter 3 Experimental Procedures

In this chapter, the experimental methods and procedures used in the present study are described in detail. Melt-spinning and sputtering deposition have been used to prepare Ti-Ni-Cu ribbon and Ni-Ti-Hf thin films, respectively. Annealing at different conditions by rapid thermal processor was carried out to crystallize the amorphous sample. Thermal analysis was performed to investigate the crystallization behavior and martensitic transformation. The structural analysis, including crystal structure and microstructure, was conducted by X-ray diffraction technique, electron diffraction and transmission electron microscopy. The thermomechanical properties of the sample were studied by tensile test and thermal cycling test under constraint stress.

3.1 Fabrication Methods

3.1.1 Fabrication of NiTi-based Thin Films

Two NiTi-based thin films were investigated. One is $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ melt-spun ribbon, which is about 0.03 mm thick and 23 mm wide. The other one is Ni-Ti-Hf thin film fabricated by using planar D.C. magnetron sputtering method in micro machine laboratory. The sputtering system (Coaxial MSS3A/LL) is composed of vacuum chamber, four 3-inch planar high performance water-cooled magnetrons, a rotatable 10-inch substrate holder designed to accommodate 4×4 -inch wafers, and D.C power supply connected to target and substrate. The vacuum chamber, evacuated by an Edwards A6117DC36A mechanical pump and an Ultek-12 cryo-pump, could be pumped to 10^{-7} Torr.

Ni-Ti-Hf thin films were co-sputtering deposited at ambient temperature by a Ni₅₀Ti₅₀ target and an Hf target with a purity of 99.99%. Thin films were deposited after about 10⁻⁷ Torr base vacuum was achieved, 99.999%-purity Ar gas was introduced during sputtering as working gas. The pressure of the working gas was controlled by an MKS1259B mass flow controller and measured by an MKS 127 Barometer. During deposition, the flow rate and the working gas pressure was kept at 40 mls/min and 2.3 mTorr, respectively. The sputter power was defined as the produce of the voltage between target surface and substrate and the current. The D.C. power of Ni₅₀Ti₅₀ target was fixed at 200 W, the D.C. power of Hf target was adjusted from 40 W to 80 W to obtain different compositions. The working distance, the distance from target to substrate, was fixed at 25 mm. The substrates were 4-inch diameter (100) single-crystal silicon wafer. During deposition, the substrate was kept rotating with a speed of 30 rpm to minimize the compositional inhomogeneity. The deposition duration was 3 h. With these conditions, the thickness of the as-deposited thin films is about 3 μm measured by a Dektak³ST surface profiler (Veeco Instruments).

3.1.2 Post-processing Heat Treatment

Crystallization annealing is necessary for those amorphous SMAs thin films in order to render them with SME. In the present study, rapid thermal annealing (RTA) was used to heat-treat Ti₅₀Ni₂₅Cu₂₅ ribbon and Ni-Ti-Hf thin films by a Jipelec Jetfirst 100 rapid thermal processor (RTP). The apparatus equips with 12 infrared lamps corresponding to a maximum power of 30 kW. The temperature measurement and control system can provide accurate and repeatable thermal control across the temperature range. The following steps were involved in the procedure:

- 1). Program the temperature profile for the annealing treatment;
- 2). Load the sample into the system;
- 3). Evacuate the chamber to 10^{-2} Torr and then purge the system using 99.99% Ar gas at a flow of about 2000 sccm for about 90 s;
- 4). Repeat the step 3 for more than ten times to minimize the remnant oxygen;
- 5). Apply power and heat the sample according to the program;
- 6). Remove the sample from the chamber after the temperature is below 100 °C.

The samples were initially heated up to 200 °C in 10 s, isothermally held for 20 s followed by heating to different temperatures at a rate of 50 °C/s and maintaining for different durations. Figure 3-1 shows a typical temperature profile for an RTA treatment.

Figure 3-1. A typical temperature profile for an RTA treatment showing the setting temperature and the sample temperature.

3.2 Characterization Methods

3.2.1 Chemical Composition

The composition of the thin films was analyzed by energy dispersive X-ray spectrometry (EDX) mounted on a Leica S360 scanning electron microscopy (SEM). The operating voltage is 20 kV. Before measurement, the EDX system was carefully calibrated. A $100\times$ magnification was chosen in order to get average compositional data over a relatively large area. For each sample, the measurement of chemical composition was performed for seven times in different regions. The mean value was taken as the composition.

3.2.2 Phase Transformation

Both crystallization of amorphous materials and martensitic transformation of SMAs are first-order phase transformations accompanying by change of enthalpy. Accordingly differential scanning calorimetry (DSC), one of most commonly used methods, can be used to determine the transformation temperatures and other thermodynamic parameters. In this study, a TA instrument DSC 2920 was employed to determine the crystallization temperature of Ni-Ti-Hf thin films and $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon. The Ni-Ti-Hf samples were first peeled from the substrate and then sealed in an aluminum pan. To ensure good resolution, the weight of the samples was at least 5-7 mg. The temperature ranges were from 350 °C to 600 °C. The different heating rates from 1 °C/min to 40 °C/min were used to evaluate the crystallization behavior.

Other DSC experiments were also carried out using the same DSC instrument to characterize martensitic transformation behavior of as-annealed Ni-Ti-Hf thin film and

Ti₅₀Ni₂₅Cu₂₅ ribbon. The weight of the sample was at least 5 mg. The sample sealed in aluminum pan was first heated up to 300 °C for Ni-Ti-Hf thin film or 100 °C for Ti₅₀Ni₂₅Cu₂₅ ribbon and isothermally held for 5 min under helium atmosphere to obtain thermal equilibrium. Then the sample was cooled down to 50 °C for Ni-Ti-Hf thin film or 0 °C for Ti₅₀Ni₂₅Cu₂₅ ribbon at a constant rate of 5 °C /min. After isothermal holding for 5 min, the sample was heated up to 300 °C or 100 °C at the same rate again, respectively.

Figure 3-2 shows a typical DSC curve of martensitic transformation, and the transformation temperatures can be determined using a slope line extension method.

Figure 3-2. A typical DSC curve showing the determining method of martensitic transformation temperatures.

3.2.3 Crystal Structure

The crystal structure of NiTi-based thin films was analyzed by X-ray diffraction (XRD) using a Philips PW3179 diffractometer with accelerating voltage of 40 kV, tube current of 30 mA, Cu-K α radiation and normal $\theta/2\theta$ scanning mode. The time per step

is 1 s, the scan rate was 0.02°/s and the scan range was from 10° to 90°. All experiments were performed at room temperature.

The interplanar distance corresponding to every peak was calculated by the Bragg equation:

$$2d \sin \theta = \lambda \quad (3.1)$$

in which d is the interplanar distance, θ the diffraction angle and λ the wavelength of Cu-K α radiation. Then the measured d values were compared with those of possible phases with known structures obtained from Joint Committee for Powder Diffraction Standards (JCPDS) database to find the best match. The next indexing step is to determine the unknown structure. The existence of cubic phases was first determined according to the ratio of $\sin^2\theta$ since cubic lattice is characterized by an integral sequence of that ratio. In case that more complicated phase existed, the d values were compared to those of known structure obtained from literature. Then the plane indices corresponding to every peak were assumed. Based on this assumption, the d values were calculated and compared to the measured values. This procedure was repeated until a reasonable match between calculated values and measured ones was achieved.

3.2.4 Quantitative Analysis

The quantitative phase analysis was conducted using the fundamental parameter Rietveld procedure as implemented in TOPAS [165]. The crystallographic models of orthorhombic B19 martensite ($Pmmb$) [43], tetragonal B11 TiCu ($P4/nmm$) [166] and cubic Ti₂(Ni,Cu) ($Fd\bar{3}m$) [167] were used. For each refinement, the background parameter, scale factor, cell parameters, zero point correction, Lorentzian crystal size, and isotropic thermal parameters were refined, while the strain factors and preferred

orientation parameters were not considered. The refinements yielded good fits to the experimental data and Bragg Reliability factor (R_b) between 2% to 5%.

3.2.5 Texture Measurement

Texture measurements were carried out using a texture goniometer in a Rigaku DMAX 2200 diffractometer. Sample size was $20 \times 18 \text{ mm}^2$. Prior to the texture measurement, the Bragg diffraction angles, 2θ , of each pole were determined by θ - 2θ scan. Schultz method was used to measure pole figure within the range of rotation angle (β) from 0 to 360° and that of the tilt angle (α) from 0 to 70° . The definitions of rotation angle β and tilt angle α in pole figure are shown in Figure 3-3, in which RD is the melt-spinning direction and TD is perpendicular to the spinning direction. Schulz formula was applied for correction of the pole figure intensity. Correction for background intensity was performed separately for each sample by off-Bragg angle measurements.

Figure 3-3. Definition of the rotation angle β and tilt angle α in a pole figure.

3.2.6 Microstructure

The plan-view microstructure of Ni-Ti-Hf thin films and $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon annealed at different temperatures was observed by a JEOL 2010 transmission electron microscopy (TEM) operated at 200 kV. The possible oxide layer on the Ni-Ti-Hf thin film surface was carefully eliminated using a 0.5 μm diamond lapping film. The sample was mechanically polished to about 50 μm thick from substrate side. The polished sample was glued on 3mm diameter copper grid. The sample was thinned by a Gatan Model 691 precision ion polishing system (PIPS) using a 4 kV Ar-ion beam at an incidence angle of 4° to an electrontransparent thickness. Then, the sample was mounted on a side-entry type double tilt specimen stage for TEM observation.

For $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon, some thin foils were prepared by a conventional twin-jet polishing technique using an electrolyte consisting of 66% methanol and 34% nitric acid in volume at -30°C .

3.2.7 Thermomechanical Property

Thermomechanical properties of $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon were investigated by tensile tests on an Instron 8800 micro-force system. The samples were cut from the ribbon along the spinning direction by using a low speed diamond cutter. In order to cut the samples, the ribbon was tightly clamped between two aluminum plates. Then the samples were cut together with the aluminum plates. The sample edges were smoothed by mechanical grinding. The tensile machine is equipped with a thermal chamber in which the testing temperature can be controlled between -75 and 250°C . The gauge length was fixed at 18 mm between the clamps. The load cell has a maximum load

capacity of 50 N with an accuracy of 0.025 N. Pull rods made of quartz bars were used to minimize thermal expansion.

The thermal cycling tests under various constraint stresses were carried out to evaluate the shape memory property of the annealed ribbon. Figure 3-4 shows a typical strain-temperature curve under a constant load. The sample was first heated to a temperature higher than A_f temperature under zero load. A constraint stress was then applied and the sample was cooled to below M_f temperature. Then the sample was heated up to above A_f temperature again under constraint. The cooling and heating rate was fixed at 2 °C/min. In Figure 3-4, ε_M represents the martensite strain induced by martensitic transformation from parent phase to martensite upon cooling. ε_R is the recovery strain due to the reverse martensitic transformation from martensite to parent phase upon heating. ε_p is the irreversible strain produced during the thermal cycling. The constraint stress was subsequently increased to 30, 50, 100, 150, 200, 250 and 300 MPa, respectively, on the same sample. The transformation temperatures under applied stress were also determined by tangent intercept method, as indicated by the blank arrows in Figure 3-4.

Figure 3-4. Schematic strain-temperature curve representing shape memory behavior under constraint. The transformation temperatures are determined by tangent intercept method.

The deformation behavior of B19 martensite was also evaluated by tensile tests. During testing, the tensile strain was increased subsequently from 1% to 5.5% with an interval of 0.5%. All the tensile experiments were carried out at room temperature. Following each unloading process, the sample was heated to recover the deformation and then cooled to room temperature. A same sample was used throughout the test. A thermal couple softly attached on the sample was used to record the temperature. The strain rate was fixed at $2 \times 10^{-5} \text{s}^{-1}$. Figure 3-5 schematically shows the strain-temperature curve of the sample, in which several characteristic parameters could also be defined as follows:

$\mathcal{E}$: tensile strain,

ε_{EL} : spring-back strain after unloading to zero stress,

ε_{RE} : one-way memory strain after heating to parent phase,

ε_A : recovery strain, $\varepsilon_A = \varepsilon_{EL} + \varepsilon_{RE}$,

ε_{IR} : irreversible strain after heating,

ε_{TW} : two-way memory strain after cooling to martensite,

η : recovery ratio, $\eta = \frac{\varepsilon_A}{\varepsilon} \times 100\%$

The reverse transformation temperatures upon first heating were determined from the heating curve under zero load, as indicated by the blank arrows.

Figure 3-5. Schematic illustration of the strain-temperature behavior of the deformed sample under zero load. The reverse transformation temperatures are also indicated.

Chapter 4 Crystallization Behavior of NiTi-based Thin Films

The as-spun ribbon or as-deposited NiTi-based thin films are likely amorphous depending on the processing parameters and do not show any shape recovery since SME is related to the crystallographic reversibility. It is known that the martensitic transformation and SME are strongly dependent on the microstructure controlled by crystallization process. Thus, it is of primary importance to fully understand the crystallization behavior in order to obtain desired properties.

In this chapter, the crystallization behavior of $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon was first studied. The structure of as-spun ribbon, crystallization temperature and activation energy are determined. A low temperature crystallization of the ribbon was achieved by RTA and the crystallization mechanism was discussed. In the second part, the crystallization behavior of Ni-Ti-Hf thin films was investigated. The roles of the third alloying elements, Cu and Hf, were compared and discussed in the last section.

4.1 Crystallization Behavior of $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ Ribbon

4.1.1 Structure of As-spun Ribbon

It is generally accepted that the as-spun ribbon has two different surfaces, one is wheel side which contacts with the Cu wheel, the other one is the opposite side and called free side. The two sides of the ribbon may have different structures. Figure 4-1 shows the XRD patterns from free side and wheel side of the as-spun $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon at room temperature. The broad and low intensity peak appearing at 2θ value of about 41° indicates that the as-spun $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon was mainly amorphous. XRD peaks

indicated by arrows imply some crystalline particles may exist in the free surface of the sample, which is consistent with the previous reports [150]. These peaks can be indexed as B19 martensite with a space group of $Pmmb$ using the following lattice parameters: $a = 0.2918 \text{ nm}$, $b = 0.429 \text{ nm}$, $c = 0.4504 \text{ nm}$ [43]. The existence of some crystalline particles was also confirmed by TEM observation, as shown in Figure 4-2. The corresponding selected area electron diffraction (SAED) pattern shows a diffuse ring and some diffraction spots, indicating that the co-existence of crystalline particle and amorphous matrix. Some crystalline particles embed in the amorphous matrix. The boundary between matrix and crystalline phase is smooth and well delineated. This may imply that the crystalline particles formed before rapid solidification.

Figure 4-1. XRD patterns of free side and wheel side of the as-spun $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon at room temperature.

Figure 4-2. TEM bright field image of the as-spun Ti₅₀Ni₂₅Cu₂₅ ribbon. The corresponding SAED pattern is inserted.

The presence of crystalline martensite particles in the as-spun ribbon can also be revealed by DSC results, as shown in Figure 4-3. One can see that weak peaks corresponding to the martensitic transformation and its reverse transformation appear at above room temperature during cooling and heating. The existence of some crystalline particles in the as-spun ribbon is possibly related to the inhomogeneous solidification process. A lower cooling rate occurred in the free side because the heat transfer was less effective than that of the wheel side during rapid solidification, thus leading to some crystalline particles on the free side and fully amorphous on the wheel side, as evidenced by XRD results.

Figure 4-3. DSC curves of the as-spun $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon.

4.1.2 Crystallization Behavior under Conventional Annealing

DSC curves of the as-spun $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon at different heating rates are plotted in Figure 4-4. It is seen that the as-spun $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon crystallized through a single-step exothermic transformation and the peak temperature of $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon is associated with the heating rate in such continuous heating experiments. With increasing the heating rate from 1 °C/min to 40 °C/min, the peak temperature increased from 434 °C to 473 °C, close to the results reported [82, 141].

Figure 4-4. DSC curves with different heating rates from 350 °C to 550 °C for the as-spun $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon under 1 °C /min, 5 °C /min, 10 °C /min, 15 °C /min, 20 °C/min and 40 °C /min, respectively.

The peak shift and the effective activation energy can be correlated to each other by means of Kissinger's equation [168]:

$$\frac{d(\ln(\alpha / T_p^2))}{d(1/T_p)} = -\frac{E}{R} \quad (4.1)$$

where R is the gas constant ($R = 8.314 \text{ Jmol}^{-1}\text{K}^{-1}$) and E is the crystallization activation energy, α is the heating rate, Kmin^{-1} . T_p is the sample temperature at which the maximum deflection in the DSC curve is recorded. It seems reasonable that the peak temperature of DSC curve in this reaction is defined as T_p temperature. According to the data of Figure 4-4, $\ln(\alpha / T_p^2)$ is plotted as a function of $1/T_p$ in Figure 4-5. The crystallization activation energy estimated from the slope of the fitted linear regression line is 406 kJ/mol, which is close to the value reported by other researchers [82] and

lower than that of the Ni-Ti binary alloys [89] and Ti-Ni-Cu-Zr alloys [68]. This indicates that the present $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon is less thermal stable than Ni-Ti binary alloys and Ti-Ni-Cu-Zr alloys.

Figure 4-5. Kissinger's plot for the DSC data of Figure 4-4.

4.1.3 Effect of Heating Rate on Martensitic Transformation

In order to characterize the effect of crystallization process on martensitic transformation, the transformation behavior of the $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon was studied as a function of heating rate during crystallization. The samples used were those crystallized under different heating rates (Section 4.1.2). The DSC curves in Figure 4-6 show the transformation characteristics of these samples. These curves have been normalized with respect to the mass of the samples. During these DSC tests, the heating/cooling rate was 5 °C/min. Both forward and reverse transformation curves of all samples clearly show two-stage transformation. As the heating rate was decreased from 40 °C /min to 1 °C /min, the transformation peaks became broad. For the peaks at

higher temperature side, no obvious effect of heating rate is observed. However, for the peaks at lower temperature side, the transformation temperatures are strongly dependent on the heating rates.

Figure 4-6. DSC cooling (a) and heating (b) curves for the $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbons annealed at different heating rates, 1 °C/min, 5 °C/min, 10 °C/min, 15 °C/min, 20 °C/min and 40 °C/min, respectively.

The peak transformation temperatures and the transformation hysteresis (ΔT), defined as the difference between the peak temperatures upon cooling and heating, as a function of the heating rate are plotted in Figure 4-7. It is seen that when the heating rate was lower than 10 °C/min, both M_p and A_p increased quickly and the transformation hysteresis decreased as the heating rate was increased. When the heating rate was higher than 10 °C/min, both M_p and A_p as well as the ΔT keep constant.

Figure 4-7. Transformation temperatures and ΔT as a function of the heating rate for the crystallized $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon.

The substitution of Ni by about 7.5 at.% Cu leads to the two-stage transformation from $\text{B2} \rightarrow \text{B19} \rightarrow \text{B19}'$, and when the content of Cu exceeds about 15 at.%, a one stage transformation from $\text{B2} \rightarrow \text{B19}$ occurs in bulk material at room temperature [17]. Accordingly, it is suggested that the two-stage martensitic transformation observed in the present case is due to the inhomogeneous microstructure resulting from the melt-

spinning process and the subsequent heat-treatment, not due to the transformation to two different martensitic structures (B19 and B19'). This agrees well with other reports [61, 150]. Some crystalline particles have formed in the free surface of the $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon, as demonstrated by XRD pattern (Figure 4-1). The coarse particles have a large grain size up to 22 μm and formed before the fast solidification [141]. On the other hand, in the case of the present study, besides the large particles, much smaller grains have formed after heating the sample to 550 $^{\circ}\text{C}$ at different rates, as typically shown in Figure 4-8. Smaller grain size usually results in a decrease of transformation temperature by increasing the nucleation barrier. Similar effect of grain size on the transformation temperature has been reported for several NiTi-based alloys [169].

Figure 4-8. TEM bright image of the $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ sample annealed at 15 $^{\circ}\text{C}/\text{min}$.

The formation of thin coherent plate-like precipitates of the B11 TiCu phase is expected to occur when annealing $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon at the temperature below 800 $^{\circ}\text{C}$

based on the pseudo-binary TiCu-TiNi phase diagram [16]. Figure 4-9 shows the microstructure evolution with the heating rates studied by XRD tests. All of the XRD patterns can be indexed as B19 martensite or a mixture of B19 martensite and B11 TiCu precipitate using the following lattice parameters: B19, $a = 0.2918$ nm, $b = 0.429$ nm, $c = 0.4504$ nm [42] and B11, $a = b = 0.3108$ nm, $c = 0.5887$ nm [166], respectively. The diffraction peak of (020)-B19 martensite overlaps with that of (102)-B11 TiCu precipitates according to their lattice parameters. No other obvious diffraction peaks from B11 TiCu precipitates can be found except for the sample heated at 1 °C/min where a diffraction peak from (110)-B11 precipitates is visible. This implies that lower heating rate results in the higher volume density of B11 TiCu precipitates. The B11 TiCu precipitates hindered martensitic transformation and caused the transformation peak broaden. The change in Ni content in the matrix due to B11 TiCu precipitation may also contribute to the change of the transformation temperature. Therefore, in the present case, the effect of the crystallization heating rate on the martensitic transformation behavior is attributed to a combined effect arising from the microstructure inhomogeneity and the precipitation.

Figure 4-9. XRD patterns of the $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon annealed at different heating rates, 1 °C/min, 5 °C/min, 10 °C/min, and 40 °C/min, respectively.

4.1.4 Low Temperature Crystallization by Rapid Thermal Annealing

Figure 4-10 shows the XRD patterns of the wheel side of the ribbon as a function of the annealing time at 400 °C under RTA. The crystallization process can be clearly observed from these XRD patterns. With the increasing annealing time, the wide and diffuse peak representing the amorphous phase fades away and the sharp peaks representing the crystalline phase become distinct. After annealed for 30 s, the ribbon was fully crystallized. All the XRD patterns can only be indexed as martensite with B19 structure. No diffraction peaks from precipitates are visible. These diffraction

patterns show that the ribbon directly transformed from amorphous phase into crystalline phase without passing through intermediate phase.

Figure 4-10. XRD patterns of the $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon annealed under RTA at 400 °C for 5 s, 10 s, 20 s, 30 s, 60 s and 300 s, respectively.

In order to further understand the unique crystallization behavior of the $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon under RTA, microstructure observation was carried out. Figure 4-11 shows the typical features of the microstructure of the ribbon annealed at 400 °C for 10 s, 20 s, 30 s and 60 s, respectively. The corresponding SAED patterns were also inserted in the TEM images. The TEM image of the sample annealed at 400 °C for 5 s was ignored because the microstructure did not show any obvious difference from that of the as-spun ribbon. After annealed for 10 s, the microstructure of the partially crystallized sample is characterized by a few crystalline particles embedded in amorphous matrix. Some multi-grain particles have been observed, as shown in Figure

4-11(a). The multi-grain particles show nearly spherical shape and the interface between the adjacent grains is not straight. Similar multi-grain particles have been reported by Santamarta et al. [144] in the $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon annealed under conventional thermal annealing (CTA) at 420 °C for 10 min. In their case, each grain in the multi-grain particle grows radially from the center of the particle. However, in the present case, such features are not observed and the grains seem randomly impinge each other.

After annealed for 20 s, the sample was partially crystallized, which agrees well with the XRD results shown in Figure 4-10. Two kinds of distinct morphologies were found in the partially crystallized sample, as shown in Figure 4-11 (b) and (c). In Figure 4-11 (b), the crystalline phase shows perfectly spherical feature, suggesting that the growth is isotropic and interface-controlled. This is consistent with the characteristic of the polymorphic mechanism. Some grains are also observed to nucleate at the interface between the amorphous matrix and crystalline phase since such interface with higher energy can preferentially act as the nucleation site during crystallization. Figure 4-11(c) shows another morphology observed in the same sample annealed for 20 s. It is clear that the crystallization has completed in this area. The corresponding SAED pattern also shows the polycrystalline feature. These different morphologies suggest that the crystallization process is heterogeneous. The growth rate is estimated to be 0.037 $\mu\text{m/s}$ without taking into account the incubation time, apparently higher than that of the Ni-Ti thin film annealed under CTA (0.015 $\mu\text{m/s}$) [84]. After annealed for 30 s, the grain growth has consumed the entire amorphous matrix and the grains impinged each other. Figure 4-11(d) and (e) are the

microstructures of the ribbons annealed for 30 s and 60 s, respectively. Single-pair martensite variants have formed in most of the grains, similar to the $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon fully crystallized under CTA [141, 146]. The grain size increases with increasing annealing time.

Figure 4-11. TEM bright field images and the corresponding SAED patterns of the $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon annealed under RTA at 400 °C for 10 s (a), 20 s (b) (c), 30 s (d) and 60 s (e), respectively

For the $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon, the B11 TiCu precipitates have formed when annealed at 410 °C for a long duration under CTA [149]. In the present case, however, after annealed at 400 °C for 300 s, no B11 TiCu precipitates can be detected, as shown in Figure 4-12.

Figure 4-12. TEM bright field image (a) and the corresponding SAED pattern (b) of the $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon annealed under RTA at 400 °C for 300 s. The incident electron beam is parallel to the $[100]_{\text{B19}}$

EDX measurements were performed on different regions of the partially crystallized $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon. Figure 4-13 shows typical locations where the EDX measurements were analyzed: amorphous matrix far from crystalline particle (points 1 and 7), amorphous regions close to the interface with the crystalline particle (points 2 and 6) and crystalline regions close to the interface with amorphous matrix (points 3 and 5) as well as interior of the crystalline particle (point 4). The sample was annealed at 400 °C for 20 s under RTA. The chemical composition has been worked out for a large number of regions and subsequently averaged for each region. The results are summarized in Table 4-1. A small amount of silicon was also detected, which possibly

dissolved from the quartz crucible during the melt-spinning process. The results are far from the nominal composition since the EDX attached on transmission electron microscopy can only qualitatively measure the composition. However, the EDX results still clearly reveal that the composition does not change during crystallization. This implies that the crystallization of the $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon is governed by polymorphous mechanism.

Figure 4-13. TEM bright field image showing the typical locations where EDX analysis was performed. The sample was annealed at 400 °C for 20 s.

Table 4-1. Average chemical compositions from the EDX measurements on different regions in the $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon annealed at 400 °C for 20 s.

	1	2	3	4	5	6	7
Ti (at.%)	38.9	38.8	38.5	38.4	38.7	39.1	39.4
Ni (at.%)	30.7	30.2	30.9	30.7	30.7	29.8	29.8
Cu (at.%)	30.1	30.5	30.1	30.5	30.2	30.7	30.3
Si (at.%)	0.3	0.5	0.5	0.4	0.4	0.4	0.5

4.1.5 Discussion on Low Temperature Crystallization

The full crystallization of the $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon was normally achieved by CTA at a temperature higher than 450 °C [141, 149]. In the present study, RTA was employed to heat-treat $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon which has not been used before on SMAs. The initially amorphous ribbon was fully crystallized by RTA at 400 °C for 30 s, as evidenced by XRD and TEM observations. Although Rösner et al. [149] once reported that annealing at 410 °C under CTA can fully crystallize the ribbon, it has to take at least 24 h. The precipitation of coarse and dense B11 TiCu phase unavoidably occurs during such a long annealing time, which deteriorates the mechanical properties of the $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon [145]. It must be emphasized that no precipitates were found in the present low temperature crystallized sample. This can be attributed to the combination of lower annealing temperature and short annealing duration that allows avoiding the formation of the B11 TiCu phase.

It is important to understand the crystallization path that begins with amorphous phase and ends with B2 parent phase. As shown in Figure 4-10, no intermediate-phase formed during crystallization. In the as-spun ribbon, the atoms are randomly arranged with excess energy stored in the metastable structure. Structural relaxation usually occurs during annealing, which changes the metastable state to the state with lower energy [93]. Figure 4-14 plots again the DSC curve of the as-spun ribbon under 10 °C/min from 40 °C to 550 °C. A weak and diffuse exothermic peak indicated by arrow was observed before the sharp crystallization peak, as shown in the inset of Figure 4-14. The origin of this peak is due to the structural relaxation of amorphous ribbon prior to crystallization. Similar feature was also observed in sputter-deposited Ni-Ti thin films

[100]. In the present case, the transformation path is likely to be the amorphous-structural relaxation-crystalline phase.

Figure 4-14. DSC curve of the as-spun $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon under 10 °C/min from 40 °C to 550 °C. The inset is the enlargement of the region around the arrow.

The as-spun amorphous ribbon contains a large number of defects that are mainly free volume [170] and short-range-ordered clusters. Structural relaxation is usually associated with the annihilation of the free volume characterized by the wide and diffuse exothermal peak in DSC curve of Figure 4-14. After crystallization, the free volume can be totally annealed out. In order to investigate the role of the annihilation of the free-volume on crystallization, a sample was heated up to 400 °C with a heating rate of 10 °C/min and then kept isothermally for 15 min. XRD results show that the sample was still mainly amorphous, same as the as-spun ribbon. This pre-annealed sample was then tested in DSC, and the results are shown in Figure 4-15. As compared

with Figure 4-14, no weak and diffuse peak was observed prior to crystallization, indicating no obvious structure relaxation in the second heating. This pre-annealed sample shows identical crystallization temperature with the as-spun ribbon. This further suggests that the structural relaxation does not have obvious effect on the crystallization under CTA. The above pre-annealed sample was also heated up under RTA from room temperature to 400 °C and remained for 30 s. The XRD results shown in Figure 4-16 (a) reveal that the sample was partially crystallized, different from the results of the as-spun ribbon directly annealed under RTA shown in Figure 4-16 (b). This suggests that the crystallization of the ribbon became more difficult after structure relaxation. During RTA, the structural relaxation was shifted to higher temperature because of the rapid heating. The excess energy due to a higher internal stress field associated with the free-volume can provide an additional driving force for crystallization.

Figure 4-15. DSC curve (10 °C/min) of the as-spun $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon pre-annealed under CTA at 400 °C for 15 min. The inset is the enlargement of the curve.

Figure 4-16. Comparison of the XRD pattern of $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ samples. (a) The as-spun ribbon was annealed under CTA at 400 °C for 15 min followed by annealed under RTA at 400 °C for 30 s. (b) The as-spun ribbon was directly annealed under RTA at 400 °C for 30 s.

It has been found that some short-range-ordered clusters exist in the same as-spun $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon [146]. This may result from the fact that Ti-Ni pair has a much larger mixing enthalpy than Ti-Cu and Ni-Cu pairs in the present alloy (Ti-Ni: -35 kJ/mol, Ti-Cu: -9 kJ/mol, and Ni-Cu: +4 kJ/mol) [171]. Thus Ti should have strong interaction with Ni, which possibly leads to the formation of short-range-ordered clusters of Ti-Ni pair in the liquid state. During melt-spinning, the metastable atomic configuration is frozen in the amorphous matrix. During RTA, the short-range-ordered clusters can act as the nucleation sites.

In summary, the low temperature crystallization under RTA is naturally related to the effect of the heating rate, as compared to the crystallization under CTA. The structural relaxation may assist the crystallization by providing an extra energy. The

low temperature crystallization under RTA may reduce the processing cost as compared to the crystallization under CTA. Such processing is also beneficial to obtain the desired microstructure, such as grain size and size of the precipitates, thus control the properties.

4.1.6 Effect of Annealing Time on Martensitic Transformation

The transformation behavior of the $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon was subsequently studied as a function of annealing time. Figure 4-17 shows the DSC curves for the samples annealed at 400 °C for different durations. Both forward and reverse transformation curves of all samples show multiple-step transformation except for the sample annealed for 10 s. When the annealing time was less than 30 s, the weak and wide transformation peaks are found in the DSC curves. On the contrary, the sharp and well-defined DSC peaks are visible after annealed at 400 °C for more than 30 s. The peak transformation temperatures of the samples as a function of annealing time are plotted in Figure 4-18. The transformation temperatures of the as-spun ribbon shown in Figure 4-3 are also included in this figure. It is obvious that all the transformation temperatures increase with the increasing annealing time. Several microstructural factors should be considered notably to be responsible for the dependence of martensitic transformation on annealing time, amorphous matrix, grain size and precipitates. The effect of the precipitates can be firstly ruled out since no precipitates were found in the annealed ribbon based on the results of XRD tests and TEM observation. So the others factors might be responsible for this dependence. The effect of amorphous-crystalline interface on the martensitic transformation is the same as that of a smaller grain size [152, 169]. Both hinder the transformation by increasing

the non-chemical energy terms. When annealed for less than 30 s, the samples were only partially crystallized. With increasing annealing time, the volume of amorphous matrix reduced and the grain size increased, causing the increase in the transformation temperature. After annealed for more than 30 s, the samples were fully crystallized. The newly generated grains usually have a smaller size than the pre-existed grains formed during rapid solidification of the as-spun ribbon. With the increasing annealing time, the grain size increases, which causes the transformation shift to higher temperature side.

Figure 4-17. DSC cooling (a), (c) and heating (b), (d) curves for the $Ti_{50}Ni_{25}Cu_{25}$ ribbons annealed under RTA at 400 °C for 5 s, 10 s, 20 s, 30 s, 60 s and 300 s, respectively.

Figure 4-18. Transformation temperatures as a function of annealing time for the $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon annealed under RTA at 400 °C

4.2 Crystallization Behavior of Ni-Ti-Hf Thin Films

4.2.1 Effect of Applied Power on Composition

In this research, the composition control was realized by adjusting the DC power of Hf target under the constant power of $\text{Ni}_{50}\text{Ti}_{50}$ target. The composition of as-deposited NiTiHf thin films was measured by EDX. The results are plotted in Figure 4-19 as a function of the power of Hf target when the power of the $\text{Ni}_{50}\text{Ti}_{50}$ target was fixed at 200 W. It can be seen that with the increasing power of Hf target from 40 W to 80 W, Ni and Ti contents decreased near-linearly from 49.5 to 41.1 at.%, 37.7 to 31.4 at.% respectively, while Hf content increased from 12.8 to 27.6 at.%. The dependence of chemical composition on sputtering power could be attributed to a combined effect arising from sputtering yield and differential lateral diffusion as well as sticking coefficients related to mass differences.

Figure 4-19. Chemical composition of as-deposited Ni-Ti-Hf thin films as a function of the power applied on Hf target. The power of the $\text{Ni}_{50}\text{Ti}_{50}$ target was fixed at 200 W.

In this research, NiTiHf thin films with different compositions of $\text{Ni}_{45}\text{Ti}_{32}\text{Hf}_{23}$, $\text{Ni}_{47.9}\text{Ti}_{35.7}\text{Hf}_{16.4}$ and $\text{Ni}_{48}\text{Ti}_{37.7}\text{Hf}_{16.4}$ (at.%) were selected for further study because of the following reasons. The transformation temperature of Ni-Ti-Hf alloys has been found to increase with the Hf content. On the other hand, the transformation temperature of SMAs thin films is generally several tens of degree lower than that of bulk materials with the same composition. Thus, for the purpose of fabricating high temperature SMAs thin films, a thin film with a higher Hf content seems optimum. Another reason is related to the further work on mechanical properties. It has been found that Ti-rich Ni-Ti thin films annealed at low temperature display better mechanical properties than Ni-rich and near-equiatomic ones [139, 140]. Therefore, it is hopeful to demonstrate similar improvement for the present thin films.

4.2.2 Crystallization Behavior under Conventional Annealing

Figure 4-20 shows the room temperature XRD patterns of as-deposited thin films. All the patterns show a broad and low intensity peak appearing at 2θ value of about $39\text{--}41^\circ$, indicating that the as-deposited Ni-Ti-Hf thin films were completely amorphous. However, a slight difference among the 2θ values of three Ni-Ti-Hf thin films presents. The broad peak of $\text{Ni}_{45}\text{Ti}_{32}\text{Hf}_{23}$ occurred at 2θ value of 39.8° , whereas the peaks of $\text{Ni}_{47.9}\text{Ti}_{35.7}\text{Hf}_{16.4}$ and $\text{Ni}_{48}\text{Ti}_{37.7}\text{Hf}_{14.3}$ were at 40.4° and 40.9° , respectively. The peak position represented by the wavenumber $Q_p = 4\pi \sin\theta/\lambda$ is inversely proportional to the mean nearest-neighbor distance in the local cluster of amorphous alloy [172]. With increasing Hf content, the position of the broad peak shifts to lower angle, implying an increase in the mean distance of nearest-neighbor atoms.

Figure 4-20. XRD patterns of the as-deposited $\text{Ni}_{48}\text{Ti}_{37.7}\text{Hf}_{14.3}$ (a), $\text{Ni}_{47.9}\text{Ti}_{35.7}\text{Hf}_{16.4}$ (b) and $\text{Ni}_{45}\text{Ti}_{32}\text{Hf}_{23}$ (c) thin films at room temperature.

DSC curves of the as-deposited $\text{Ni}_{48}\text{Ti}_{37.7}\text{Hf}_{14.3}$ and $\text{Ni}_{45}\text{Ti}_{32}\text{Hf}_{23}$ samples at different heating rates are plotted in Figure 4-21. All the DSC curves exhibit a significant exothermic peak corresponding to the crystallization process. The two-stage crystallization in $\text{Ni}_{40}\text{Ti}_{60}$ amorphous ribbon [87] is not observed. The onset of crystallization (T_x), the crystallization peak temperature (T_p) are also marked in Figure 4-21. It is seen that the onset of crystallization and the crystallization peak temperature both shift to higher temperature with the increasing heating rates, implying the crystallization process is dependent on the heating rate. The crystallization temperature are close to the results reported by other researchers [173]. With the increasing heating rates, the height of DSC peaks increases. This means that the higher is the heating rate, the larger number of nucleation sites. The $\text{Ni}_{48}\text{Ti}_{37.7}\text{Hf}_{14.3}$ thin film shows the lower characteristic temperatures as compared to the $\text{Ni}_{45}\text{Ti}_{32}\text{Hf}_{23}$ thin film. It is also seen that the crystallization temperature interval of the $\text{Ni}_{48}\text{Ti}_{37.7}\text{Hf}_{14.3}$ sample is narrower than that of the $\text{Ni}_{45}\text{Ti}_{32}\text{Hf}_{23}$ sample under the same heating rates. The crystallization curves of the $\text{Ni}_{47.9}\text{Ti}_{35.7}\text{Hf}_{16.4}$ samples are not presented since they are similar to that of the $\text{Ni}_{48}\text{Ti}_{37.7}\text{Hf}_{14.3}$ sample. Instead, the characteristic temperatures of $\text{Ni}_{47.9}\text{Ti}_{35.7}\text{Hf}_{16.4}$ thin film upon heating are summarized in Table 4-2.

Figure 4-21. DSC curves with different heating rates from 673K to 873K for the as-deposited $\text{Ni}_{48}\text{Ti}_{37.7}\text{Hf}_{14.3}$ (a) and $\text{Ni}_{45}\text{Ti}_{32}\text{Hf}_{23}$ (b) thin films.

Table 4-2. The onset of crystallization (T_x) and the crystallization temperatures (T_p) of the as-deposited $\text{Ni}_{47.9}\text{Ti}_{35.7}\text{Hf}_{16.4}$ thin film under different heating rates.

	5 °C/min	10°C/min	15°C/min	20°C/min	40°C/min
T_x (°C)	491	498	500	504	511
T_p (°C)	495	501	506	509	515

The activation energy of Ni-Ti-Hf thin films is also determined by the Kissinger's method shown in equation (4.1). According to the data of Figure 4-21 and Table 4-2, $\ln(\alpha/T_p^2)$ is plotted as a function of $1/T_p$ in Figure 4-22. The crystallization activation energy estimated from the slope of the fitted linear regression line is 487 kJ/mol for $\text{Ni}_{48}\text{Ti}_{37.7}\text{Hf}_{14.3}$ sample, 496 kJ/mol for $\text{Ni}_{47.9}\text{Ti}_{35.7}\text{Hf}_{16.4}$ sample and 519 kJ/mol for $\text{Ni}_{45}\text{Ti}_{32}\text{Hf}_{23}$ sample, respectively, which are all higher than that of the amorphous Ni-Ti binary thin film [174].

Figure 4-22. Kissinger's plots for the DSC data of the as-deposited $\text{Ni}_{48}\text{Ti}_{37.7}\text{Hf}_{14.3}$, $\text{Ni}_{47.9}\text{Ti}_{35.7}\text{Hf}_{16.4}$ and $\text{Ni}_{45}\text{Ti}_{32}\text{Hf}_{23}$ thin films.

4.3 Effect of Alloying Element on Crystallization Behavior

Since it involves the atomic diffusion, crystallization behavior of amorphous NiTi-based alloys is influenced by the addition of the third element. It is generally accepted that the addition of Hf will substitute for Ti, rather than Ni because Hf has similar electron configuration in the outer shells to that of Ti. The Cu totally replaces the Ni sites in $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ alloy. Therefore, all Ni-Ti-Hf thin films and $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon

can be written as $\text{Ni}_x\text{Ti}_{1-x}$. Figure 4-23 compares the activation energy of Ni-Ti-Hf thin films and $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon with that of other amorphous NiTi-based alloys. It is seen that amorphous Ni-Ti-Hf thin films have higher activation energy than binary Ni-Ti alloys and Ti-Ni-Cu alloys. Furthermore, with increasing Ni content, the activation energy decreases. This is opposite to the Ni-content dependence of the activation energy when Ni content is in the range from 35 at.% to 55 at.% [86]. This indicates that the addition of Hf plays a dominant role in crystallization of amorphous Ni-Ti-Hf thin film. The addition of Cu reduces the activation energy, which is consistent with other reports in Ti-Ni-Cu thin films [89, 175]. In addition, the Ni-Ti-Hf thin films show higher crystallization temperature and $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon shows lower one than Ni-Ti alloys. Figure 4-23 clearly indicates that the addition of Hf makes the amorphous thin film thermodynamically more stable, and the addition of Cu is on the opposite side.

Figure 4-23. Comparison of the activation energy of Ni-Ti-Hf thin films and $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon with those of other NiTi-based ribbon and thin films.

The condition of Ni-Ti-Hf thin films and $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon are more close to the empirical rules proposed by Inoue [63] for thermal stability of amorphous alloys as compared to Ni-Ti binary alloys. The effect of alloying elements can be understood by taking into account of the atomic radius and the enthalpy of mixing. The atomic radius mismatch and binary enthalpy of mixing in Ni-Ti-Hf thin films and Ti-Ni-Cu alloy are summarized in Table 4-3. The atomic radius mismatches of Hf and Ti with Ni are about 25% and 15%, respectively. The increased atomic radius mismatch may cause the amorphous structure more dense and suppress the diffusion of the atoms. Thus, the significantly different atomic size mismatch kinetically inhibits the crystallization of Ni-Ti-Hf thin films. The broadened crystallization peaks of $\text{Ni}_{45}\text{Ti}_{32}\text{Hf}_{23}$ thin film as compared to $\text{Ni}_{48}\text{Ti}_{37.7}\text{Hf}_{14.3}$ thin film may also suggest the decreased atomic diffusivity. In the case of $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ alloy, the size of the Cu atom is very close to that of the Ni atom. So it is suggested that the atomic size mismatch does not take a dominant role in the crystallization of $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ alloy.

Next we consider the effect of the enthalpy of mixing between the binary constituent elements. The stability of the amorphous thin films is dominated by the strength of interaction between the constituent atoms [174]. The relative strength of this bonding can be represented by comparing the enthalpy of mixing. The constituent elements with larger negative enthalpy of mixing usually have stronger bonding. The enthalpy of mixing of Ni-Hf pair is -42 kJ/mol, larger than that of Ni-Ti pair (-35 kJ/mol). The enthalpy of mixing of Ti-Cu pair is -9KJ/mol, Ni-Cu pair even has a positive enthalpy of mixing [171]. Therefore, it is suggested that the average bonding strength in amorphous Ni-Ti-Hf thin film is larger than that of Ni-Ti thin film, and

furthermore, increases with increasing Hf content. The average bonding strength between unlike atoms in $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ alloy is statistically decreased. In the present case, the pre-existed crystalline particles in $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ alloy also provide some nucleation sites to reduce the nucleation energy. Based on the above discussions, one can see that the crystallization of Ni-Ti-Hf amorphous thin films requires more energy to structurally and chemically overcome the dense atomic configuration and the stronger bonding between the constituent elements than Ni-Ti binary thin films. The role of Cu in crystallization of Ti-Ni-Cu alloy is dominantly determined by the chemical bonding between the constituent elements, which favors reducing the activation energy.

Table 4-3. Atomic radius mismatch and binary mixing enthalpy of Ti, Ni, Cu and Hf.

	Atomic radius mismatch (%)			Enthalpy of mixing (kJ/mol)		
	Ni	Cu	Hf	Ni	Cu	Hf
Ti	15	13	7	-35	-9	0
Ni		3	25		+4	-42

4.4 Summary

1. The as-spun $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon mainly consists of amorphous and some crystalline particles on the free side. The initially amorphous ribbon can be fully crystallized under RTA at 400 °C for 30 s. However, under CTA, the ribbon remains amorphous even after annealed at 400 °C for 15 min. The crystallization at low temperature under rapid heating is possibly attributed to the release of the extra energy stored in the free-volume of amorphous state.
2. No B11 TiCu precipitates are found in the $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon annealed under

RTA at 400 °C for up to 300 s.

3. $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon and Ni-Ti-Hf thin films crystallize through single stage transformation. The addition of Cu reduces the crystallization temperature and activation energy, which is opposite to the role of Hf. This is ascribed to that the addition of Cu reduces the average bonding strength between the constituent elements. The addition of Hf increases not only the average bonding strength between the constituent elements but also atomic radius mismatch in NiTiHf alloys.
4. The crystallization process has significant influences on martensitic transformation of $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon. A two-stage martensitic transformation is found after heating the sample to 550 °C at different heating rates. For the transformation at high temperature side, no obvious change with the heating rate is observed. For the transformation at low temperature side, the transformation temperatures/ hysteresis first decrease/increases with decreasing heating rates and then quickly reaches to a stable value.

Chapter 5 Phase Transformation Characteristics and Microstructure

Most of the important properties of NiTi-based SMAs depend on microstructure, including precipitation and grain size, resulting from the annealing treatment. Although several reports have been published on the precipitation behavior of $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon, how the type, volume fraction and distribution of precipitates vary with the annealing temperature and time is unknown. In addition, no detailed report on the microstructural evolution of Ni-Ti-Hf thin films is available to date.

The annealing treatment may also lead to the development of texture in the initially amorphous materials. Different from precipitates and grain size, the texture does not influence martensitic transformation behavior without load, but strongly influences the shape recovery properties. Therefore, it is important to investigate the texture development in order to understand the subsequent shape recovery behavior.

In this chapter, microstructure and martensitic transformation behavior of $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon was first investigated. The effect of annealing condition on precipitation was revealed by XRD and TEM observations. The volume fraction of precipitates was quantitatively determined by Rietveld refinement. The pole figures of the ribbon annealed at different temperatures were obtained. The effect of annealing on martensitic transformation behavior was also studied by DSC method. Following the investigation on the $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon, microstructure and martensitic transformation of Ni-Ti-Hf thin films were also investigated. The emphasis was placed on the effect of grain size on martensitic transformation.

5.1 Microstructure of $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ Ribbon

5.1.1 Martensite Structure of $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon

Figure 5-1. TEM bright field image (a) and the SAED patterns (b), (c) of martensite in the ribbon annealed at 500 °C for 300 s under RTA. The SAED patterns (b), (c) correspond to the areas B, C in (a), respectively. The beam directions are parallel to the $[100]_{M,T}$ (b) and $[\bar{1}2\bar{1}]_{M,T}$ (c).

The microstructure of the rapidly annealed ribbon was first studied using TEM. Figure 5-1 shows the typical morphology and corresponding SAED patterns of martensite

observed in the sample annealed at 500 °C for 300 s. The SAED patterns (b) and (c) correspond to the area of B and C in Figure 5-1 (a), showing the variants are (011) compound (B) and (111) type I (C) twinned, respectively. It is seen that the martensite variants are self-accommodated by single-pair morphology, rather than the triangular morphology usually observed in Ni-Ti alloy.

When the annealing temperature was increased 600 °C, martensite variants are still characterized by single-pair morphology. With increasing annealing temperature to 700 °C, in addition to the single-pair morphology, the martensite variants are also observed self-accommodated with triangular morphology, as shown in Figure 5-2 (a). The SAED pattern in Figure 5-2 (b) shows that the martensite variants are (011) compound twinned. The martensite morphology and twin modes are same as those of the conventionally annealed ribbon [141]. The observation of single-pair variant suggests the existence of internal stresses particularly aligned in some of grains, favoring the single-pair variant morphology. Such internal stress may originate from the grain boundaries. With increasing annealing temperature, the internal stresses are released, causing that some of grains are characterized by the triangular morphology.

Figure 5-2. TEM bright field image (a) of martensite in the ribbon annealed at 700 °C for 300 s under RTA. The SAED pattern (b) shows the (011) compound twin. The incident beam direction is parallel to the $[100]_{M,T}$.

5.1.2 Precipitation of Rapidly Annealed $Ti_{50}Ni_{25}Cu_{25}$ Ribbon

Figure 5-3 shows the precipitation in the $Ti_{50}Ni_{25}Cu_{25}$ ribbon depends on both annealing temperature and duration under RTA. When annealed at 400 °C for up to 900 s, or 500 °C for up to 60 s, no precipitate was formed (Figure 5-3 (a), (b) and (c)). While after annealing at 400 °C for 1200 s or 500 °C for 300 s (Figure 5-3 (a), (b)), the tetragonal B11 TiCu precipitates started to appear. If the annealing temperature is increased to 600 °C, after holding for 600 s, a peak between (110)-B11 and (020)-B19 appears, as indicated by the arrow in Figure 5-3 (d). This indicates that a new phase presented in the sample, which is not observed in the same ribbon annealed below 750 °C for 15 min under conventionally processing [50, 146]. However, when further annealed at 800 °C for 300 s, B11 TiCu precipitates disappeared leaving only the unknown precipitates in the microstructure (Figure 5-3 (b)). Figure 5-3 clearly shows that B11 TiCu is metastable and it converts to the unknown phase at higher

temperature or longer holding time as a result of thermally activated diffusion process.

Figure 5-3. XRD patterns of the ribbons annealed at different conditions under RTA showing the formation of precipitates due to annealing.

In order to determine the unknown phase, the sample annealed at 800 °C for 300 s was investigated by TEM. The general morphology is shown in Figure 5-4. No thin-plate B11 TiCu precipitates are observed, consistent with the XRD results. It is seen that some precipitates formed in the grains (Figure 5-4(a)) and on the grain boundaries (Figure 5-4(b)). The diameters of these particles are approximately 80-100 nm.

Figure 5-4. TEM bright field images of the ribbon annealed at 800 °C for 300 s under RTA showing the morphology and distribution of precipitates.

EDX results show that the particles are a Ti-rich phase and Ti-content is about 16 at.% higher than that of the matrix. The EDX spectra were collected from the particles that locate at the edge of the hole in the samples in order to eliminate the contributions from the matrix. The unknown phase shown in Figure 5-3 can be indexed as a cubic structure by the following lattice parameter: $a = b = c = 1.137$ nm, which agrees well with that from X-ray powder diffraction data of a cubic Ti_2Ni phase having a space group of $Fd\bar{3}m$ [167]. Therefore, the precipitates are suggested to be $\text{Ti}_2(\text{Ni}, \text{Cu})$ phase with a solution of Cu into Ni lattice sites. In order to further confirm the identification,

SAED of these particles were carried out. Figure 5-5 shows a set of electron diffraction patterns of the particles and their corresponding indexing. All the electron diffraction patterns can be well indexed by assuming the structure to be cubic with the above lattice parameter.

Figure 5-5. SAED patterns from $\text{Ti}_2(\text{Ni}, \text{Cu})$ precipitates. The incident beam directions are parallel to $[100]_{\text{Ti}_2(\text{Ni}, \text{Cu})}$ (a), $[011]_{\text{Ti}_2(\text{Ni}, \text{Cu})}$ (b) and $[\bar{1}\bar{2}\bar{3}]_{\text{Ti}_2(\text{Ni}, \text{Cu})}$ (c), respectively.

Figure 5-6 shows the XRD patterns of the samples annealed at different temperatures for 1200 s under RTA and CTA, respectively. The sample rapidly

annealed at 700 °C for 1200 s consists of B19 martensite, B11 TiCu and $\text{Ti}_2(\text{Ni,Cu})$ precipitates at room temperature. Different from the rapidly annealed samples, the ribbon conventionally annealed at 700 °C for 1200 s consists of B19 martensite and B11 TiCu precipitates. TEM observations further confirm the inexistence of $\text{Ti}_2(\text{Ni,Cu})$ precipitates. Annealing at 800 °C under CTA results in the reduction of B11 TiCu precipitates and the presence of $\text{Ti}_2(\text{Ni,Cu})$.

Figure 5-6. XRD patterns of the ribbons rapidly annealed at 700 °C for 1200 s (a) and conventionally annealed at 700 °C and 800 °C for 1200 s (b), respectively.

Figure 5-7 summarizes the effect of annealing temperature and time on the microstructure evolution under RTA as revealed by the XRD results. There are four regions relating to the microstructural evolution. In Section 4.1.4, the present ribbon can be fully crystallized after rapid annealing at 400 °C for 30 s. When the initially amorphous ribbons are annealed, the microstructure changes in the sequence of B19 $\rightarrow$ B19 + B11 $\rightarrow$ B19 + B11 + $\text{Ti}_2(\text{Ni,Cu})$ $\rightarrow$ B19 + $\text{Ti}_2(\text{Ni,Cu})$ with the increasing annealing temperature and time.

Figure 5-7. Microstructure of the ribbon as a function of annealing temperature and time under RTA.

In order to further reveal change of B11 TiCu precipitates due to RTA, TEM observations of the samples annealed at different temperatures for 300 s were carried out, as shown in Figure 5-8. The electron beam directions of the bright field images are parallel to the [101] direction of B19 martensite. After annealing at 500 °C for 300 s,

a large amount of homogeneously and densely distributed B11 TiCu precipitates appeared. The precipitates are approximately 10 nm in length (Figure 5-8 (a)) and, after annealed at 600 °C, grow to around 25 nm, as shown in Figure 5-8 (b). The SAED pattern shown in Figure 5-8 (d) corresponds to the sample annealed at 600 °C shown in (b). The electron diffraction pattern of B11 TiCu overlaps with that of B19 martensite, as indexed in Figure 5-8 (d). The SAED pattern further reveals a certain crystallographic orientation relationship between B11 TiCu and B19 martensite, as has also been reported previously [50, 147]. Annealing at 700 °C leads to further growth of B11 TiCu precipitates to about 60 nm, as shown in Figure 5-8 (c). The image contrast due to the strain field around the B11 TiCu precipitates is clearly observed, indicating a lattice mismatch between B19 martensite and B11 TiCu. Comparing Figure 5-4 with Figure 5-8 clearly shows that B11 TiCu has a much higher distribution density than $\text{Ti}_2(\text{Ni,Cu})$. The strain contrast around B11 TiCu precipitates seems to be higher than that of $\text{Ti}_2(\text{Ni,Cu})$.

Figure 5-8. TEM bright field images of the ribbons annealed at 500 °C (a), 600 °C (b), and 700 °C (c) for 300 s, respectively. The SAED pattern in (d) was taken from (b).

The incident beam is parallel to $[101]_{\text{B19}}//[221]_{\text{B11}}$.

It is difficult to quantitatively determine the volume fraction from TEM images because of the strong strain-field around the precipitates. The volume fractions of B11 TiCu and $\text{Ti}_2(\text{Ni,Cu})$ precipitates in the ribbons annealed for 300 s were calculated through Rietveld refinement of the XRD results. Figure 5-9 shows that the volume fraction of B11 TiCu precipitates increased from 2% at 500 °C annealing temperature to about 11% at 600 °C, and then gradually decreased with further increasing annealing temperature. Along with the decrease of the volume fraction of B11 TiCu,

the volume fraction of $\text{Ti}_2(\text{Ni,Cu})$ precipitates increased up to about 11.2% at an annealing temperature of 800 °C.

Figure 5-9. Volume fractions of B11 TiCu and $\text{Ti}_2(\text{Ni,Cu})$ precipitates in the ribbons annealed for 300 s at different temperatures shown.

5.1.3 Discussion on the Precipitation Behavior

The chemical composition of the as-spun ribbon has been carefully checked by EDX and is found to be homogeneous and very close to the nominal composition. Based on the isothermal section of Ti-Ni-Cu ternary phase diagram developed by Van Loo et al. [176], $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ alloy only has a single phase at 800 °C. In addition, the pseudo-binary TiNi-TiCu phase diagram obtained from melt-spun ribbon also demonstrates a single phase structure at 800 °C or above and a two-phase region consisting of B2 parent phase and B11 TiCu at lower temperatures, as shown in Figure 2-7 [16, 108]. In the present study, however, $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon shows a different precipitation behavior during annealing. Two different precipitates present in the annealed ribbon,

namely, B11 TiCu and $\text{Ti}_2(\text{Ni,Cu})$. The $\text{Ti}_2(\text{Ni,Cu})$ phase unexpectedly presents after rapidly annealing at 600 °C for 600 s or conventionally annealing at 800 °C for 1200 s. It has been found by Nagarajan et al. [177] that the addition of a small amount of Si can promote the formation of Ti_2Ni precipitates in $\text{Ni}_{50}\text{Ti}_{50}$ alloy. Accordingly, it is suggested that the Si impurity introduced during melt-spinning process may play an import role in the precipitation of $\text{Ti}_2(\text{Ni,Cu})$. The samples heat-treated under RTA and CTA yield the same annealing products, but the temperature that leads to the formation of B11 TiCu and $\text{Ti}_2(\text{Ni,Cu})$ precipitates under RTA is lower than that under CTA. This may suggest that RTA can enhance the atomic diffusion.

5.2 Texture of $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ Ribbon

It is important to examine the texture when the ribbon is considered to use for a two-dimensionally shaped actuator. The texture development of $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon annealed at different temperatures for 300 s was investigated by pole figure measurements at room temperature. Figure 5-10 shows the typical pole figures of the samples annealed at different temperatures for 300 s. In the pole figures, RD is the spinning direction of the ribbon. TD is perpendicular to the spinning direction and ND the normal direction of the ribbon surface which corresponds to the center of the pole figure. It is seen that the $\{111\}$ pole figure shows a considerably uniform distribution of pole density. Other pole figures of the ribbons also show the random distribution of crystal orientations, indicating that no significant texture was formed during annealing under RTA. This is different from what has been observed in the same ribbon conventionally annealed that shows development of texture [50]. Such difference might be related to the diffusion process accompanied with the crystallization. In the

case of RTA, the short annealing duration seems not sufficient for the preferential growth of the crystals.

Figure 5-10. $\{111\}$ pole figures of the ribbons annealed for 300 s at 400 °C (a), 500 °C (b), 600 °C (c), 700 °C (d) and 800 °C (e) under RTA showing no significant texture.

5.3 Martensitic Transformation of $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ Ribbon

5.3.1 Effect of Annealing Temperature

Martensitic transformation behavior of the annealed $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ samples was measured by DSC tests. The results are shown in Figure 5-11. It is seen that all the samples show similar transformation behavior except for the one annealed at 700 °C for 300 s. Besides the weak shoulder appearing on the high temperature side, the DSC curves of the sample annealed at 700 °C are also characterized by the weak peaks on the low temperature side, as indicated by the arrows. Meanwhile, the sample annealed at 700 °C also shows larger transformation intervals as compared to others. The weak shoulders appearing on the high temperature side have been ascribed to the inhomogeneous microstructure resulting from the melt-spinning process in section 4.1.3 and will not be discussed.

Figure 5-11. DSC curves upon cooling (a) and heating (b) of the $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbons annealed at 500 °C, 600 °C, 700 °C and 800 °C for 300 s, respectively.

Figure 5-12(a) shows the annealing temperature dependence of the transformation temperatures. The transformation temperatures first remain stable with the increasing annealing temperature up to 550 °C, then increase until they reach the maximum values after annealing at 600 °C or 650 °C. Further increase in annealing temperature results in the decrease of the transformation temperatures. The sample annealed at 700 °C shows the lowest M_f temperature due to the widened transformation peak. Figure 5-12(b) plots the transformation hysteresis (ΔT) as a function of annealing temperature. The transformation hysteresis is about 6 °C and exhibits little dependence on the annealing temperature.

Figure 5-12. Effect of annealing temperature on the transformation temperatures (a) and ΔT (b) of the ribbons annealed for 300 s.

Taking into account the effect of annealing on the microstructure shown in Figure 5-7, the dependence of transformation temperature on annealing temperature can be directly attributed to the change of grain size of matrix, and presence of B11 TiCu and $Ti_2(Ni,Cu)$ precipitates. The increase of annealing temperature results in the increased

grain size. It is generally known that martensitic transformation temperature increases with increasing grain size. This is attributed to the decrease of the surface/volume ratio, which reduces the non-chemical energy terms when grain size increases [152]. Whereas, by annealing below 550 °C, the coherent B11 TiCu precipitates form and suppress martensitic transformation [147]. The net result is the insignificant change of the transformation behavior. At temperature above 550 °C, the increase in grain size becomes dominant, resulting in the increase in the transformation temperature. Annealing at 650 °C or above results in the precipitation of $Ti_2(Ni,Cu)$ phase and the reduction of B11 TiCu precipitates. The former reduces the transformation temperature by depleting Ti content in the matrix.

5.3.2 Effect of Thermal Cycling

Thermal cycling stability of SMAs is a critical issue on its commercial applications, because SMAs have to subject to many cycles by repeated cooling and heating process. It should be mentioned that all the samples show similar dependence on the thermal cycling, irrespective of the annealing temperature. As an example, Figure 5-13 shows the effect of thermal cycling on the transformation peak temperatures of the $Ti_{50}Ni_{25}Cu_{25}$ ribbon annealed at 800 °C for 300 s. The first twenty cycles were consecutively measured in the DSC instruments; afterwards, the sample was removed from the instrument and cycled between ice-water and an oven with a temperature of 100 °C much higher than A_f for up to 50 complete thermal cycles. The transformation peak temperatures have almost no change after 50 cycling, which is consistent with the results in $Ti_{50}Ni_{30}Cu_{20}$ alloys [178]. This suggests that the sample has perfect thermal cycling stability, which is comparable to that of R-phase transformation [179].

The effect of thermal cycling on martensitic transformation temperature of NiTi-based alloys has been ascribed to the introduction of dislocations during transformation [179]. The stress-fields created by the dislocations impede the movement of interface between martensite and parent phase, causing the decrease in the transformation temperatures. According to this mechanism, two factors should be responsible for the good thermal stability of $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon. One is the addition of Cu, which improves the critical stress for slip [180]. This favours suppressing the generation of dislocation during transformation. The other is related to the B2-B19 transformation whose lattice distortion is relatively smaller as compared to B2-B19' transformation. Smaller lattice distortion, less sensitivity of the transformation temperature to the stress-field [179].

It is emphasized that the transformation hysteresis of the B2-B19 martensitic transformation is comparable to that of the R-phase transformation besides the thermal cycling stability, but the shape recovery strain of the former is much larger than that of the latter. Therefore, $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon is likely a promising material for microactuators application which requires large recovery strain and high response frequency.

Figure 5-13. Transformation peak temperatures of the ribbon annealed at 800 °C for 300 s as a function of the number of thermal cycling.

5.4 Microstructure of Ni-Ti-Hf Thin Films

Similar to the as-spun $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon, the as-deposited Ni-Ti-Hf thin films are all in amorphous state. In order to investigate the microstructure and martensitic transformation, the as-deposited $\text{Ni}_{47.9}\text{Ti}_{35.7}\text{Hf}_{16.4}$ thin films were annealed at 550 °C, 600 °C, 650 °C, 700 °C and 750 °C for 25 s, respectively. Figure 5-14 shows the representative XRD pattern of $\text{Ni}_{47.9}\text{Ti}_{35.7}\text{Hf}_{16.4}$ sample annealed at 600 °C. It is seen that the sample was crystallized. The pattern could be indexed mainly by a monoclinic B19' martensite with the following lattice parameters: $a = 0.295$ nm, $b = 0.409$ nm, $c = 0.484$ nm and $\beta = 98.6^\circ$, which are consistent with other reports in bulk materials [40, 181]. It is seen that several peaks from about 37° to 41° overlap, which is due to the strongest peaks of all known equilibrium phases are situated within this region. This overlap produces a marked broadening in this region and causes the difficulty to index the diffraction peaks. All other thin films are also characterized by the same crystal structure, but slightly different lattice parameters.

Figure 5-14. XRD pattern of $\text{Ni}_{47.9}\text{Ti}_{35.7}\text{Hf}_{16.4}$ thin film annealed at 600 °C for 25 s under RTA.

Figure 5-15 shows the general features of the microstructure of the $\text{Ni}_{47.9}\text{Ti}_{35.7}\text{Hf}_{16.4}$ samples annealed by RTA at different temperatures for 25 s, respectively. The corresponding SAED patterns are also inserted in the up-corner of the TEM images. The microstructure of the annealed $\text{Ni}_{47.9}\text{Ti}_{35.7}\text{Hf}_{16.4}$ samples shows a strong dependence on the annealing temperature. When the sample was annealed at 550 °C for 25 s, the blurred contrast is observed in the TEM image and no well-defined grain boundary can be found from Figure 5-15 (a). The corresponding SAED pattern shows an unsharp or diffuse diffraction ring, which suggests that there are some volume fraction of amorphous materials in the samples. The occasional spots are attributed to the diffraction of the crystalline parts. When the annealing temperature was increased to 600 °C, as shown in Figure 5-15 (b), the grain boundaries are well delineated although there are still some blurred regions. The corresponding SAED

patterns show the polycrystalline features. As the annealing temperature increased to 700 °C, in addition to the larger grain size, some small equiaxed precipitates that are not visible when annealed at below 700 °C became visible, distributed mainly along the grain boundaries. Only a few scattered particles are scattered in the grain interiors. The particles with a diameter of about 15-20 nm might be $(\text{Ti,Hf})_2\text{Ni}$ type precipitates which are often observed in bulk NiTiHf alloys [182]. The Ti-rich $\text{Ni}_{49.6}\text{Ti}_{50.4}$ thin film annealed at low temperature also presents the Ti_2Ni precipitates with similar morphology and distribution [100]. It should be pointed out that the samples have been fully crystallized since no diffuse rings are observed when the annealing temperature was higher than 600 °C.

Figure 5-15. TEM bright field images and the corresponding SAED patterns of $\text{Ni}_{47.9}\text{Ti}_{35.7}\text{Hf}_{16.4}$ thin films annealed at 550 °C (a), 600 °C (b), 650 °C (c) 700 °C (d) and 750 °C (e) for 25 s, respectively.

Two-dimensional average grain size was determined from the TEM images. At least 300 different grains were measured for each sample except that annealed at 550 °C since no well-defined grain boundaries can be found. Figure 5-16 shows the size distributions of the grains for $\text{Ni}_{47.9}\text{Ti}_{35.7}\text{Hf}_{16.4}$ thin films annealed at different temperatures. The average grain size is also indicated in this figure. As expected, the grain size increases as the annealing temperature increases. The maximum average grain size is about 248 nm, much smaller than that in annealed NiTi films and in bulk Ni-Ti-Hf alloys whose grain sizes are typically several microns and several tens of microns, respectively [140, 182]. Thus, the finer grains are considered to be the characteristic of Ni-Ti-Hf thin films annealed by RTP. The distribution range also increases with the increasing annealing temperature. When the sample was annealed at 600 °C, the grains had a diameter of about 8-61 nm. When the annealing temperature was increased to 750 °C, the distribution range increased to 150-375 nm. The Gauss fitting curves were also plotted in dash line in Figure 5-16. It shows that the actual size

distributions agree well with the fitting curves, indicating a uniform growth of grains during annealing.

Figure 5-16. Histograms of the grain size distributions of $\text{Ni}_{47.9}\text{Ti}_{35.7}\text{Hf}_{16.4}$ thin film annealed at 600 °C (a), 650 °C (b), 700 °C (c), and 750 °C (d) for 25 s, respectively.

The dash lines present the corresponding Gauss fitting curves.

Martensite variants in Ni-Ti-Hf bulk alloys are usually self-accommodated by spear-like and mosaic-like morphology [39]. However, in the present case, martensite variants are found to be self-accommodated by single-pair morphology, as shown in Figure 5-17. This is same as the morphology in $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon. The

corresponding SAED pattern shows that the martensite variants are (011) twin-related, which agrees well with the results in bulk alloy [39, 183].

Figure 5-17. TEM bright field image (a) of $\text{Ni}_{47.9}\text{Ti}_{35.7}\text{Hf}_{16.4}$ thin film annealed at 700 °C for 25 s under RTA. The SAED pattern (b) corresponds to the region A in (a).

The incident electron beam in (b) is parallel to $[100]_M$.

A significant result regarding the microstructure of Ni-Ti-Hf thin films is the nanocrystalline structure. It is suggested that this fine microstructure results from the RTA process with a high heating rate. Crystallization of amorphous materials consists of a nucleation and growth process. In order to obtain a nanocrystalline structure, largest nucleation rate and slowest growth rate are necessary. In the sputtering deposited thin films, large number of structural defects resulting from the bombardment of the high energetic Ar ions onto the growing thin film exists and can act as the favorable nucleation site during heterogeneous crystallization. The atomic step and impurity also contribute to the nucleation. Another reason for higher nucleation rate comes from the high heating rate. Both the nucleation rate and growth rate are temperature dependent. However, since the dependence is more pronounced

for nucleation, higher heating rate will result in smaller grain size [101]. After embryo nuclei exceed the critical size for growth, grain growth takes place by diffusion when the temperature is high enough and the time is long enough and ceases when the interfaces of neighboring crystallites impinge on each other and consume all materials. In this case, the isothermal time after nucleation is short. As a result of the higher nucleation rate and shorter growth time, the fine grain is produced finally. The higher annealing temperature causes the larger growth rate since T_a/T_m (T_a : annealing temperature, T_m : melting temperature) increases. Consequently, the final grain size increases with the increasing annealing temperature.

A difference between the crystallization by CTA and RTA is worthy to be mentioned. In the case of CTA, heating begins at the surface of the thin film. Thus the nucleation begins at the surface and progresses into the depth of the layer. As a result, large grains form on the top layer of the thin films. The results on crystallization process of Ni-Ti thin films reported by Vestel et al. seems to support this idea [184]. They found that the crystalline grains always nucleate first at the surface and then grow inward to produce columnar grains. In the case of RTA, heating is applied on the whole thin film which does absorb IR radiations. As a result, the crystallization is uniform in depth of the thin film. This produces a homogeneous grain size distribution through the thickness, which has been observed in the sol-gel indium tin oxide thin films annealed by RTA [105].

5.5 Martensitic Transformation of Ni-Ti-Hf Thin Films

5.5.1 Effect of Composition

The martensitic transformation behavior of Ni-Ti-Hf thin films was first studied as a function of composition. Figure 5-18 shows the DSC curves of the $\text{Ni}_{48}\text{Ti}_{37.7}\text{Hf}_{14.3}$, $\text{Ni}_{47.9}\text{Ti}_{35.7}\text{Hf}_{16.4}$ and $\text{Ni}_{45}\text{Ti}_{32}\text{Hf}_{23}$ thin films annealed at 600 °C for 25 s, respectively. These curves have been normalized with respect to the mass of the samples. Both forward and reverse transformation curves show one-stage transformation. No R-phase transformation can be identified, which is different from the results reported by Gu et al. [19]. It is seen that the transformation temperatures shifted to high temperature with the increasing Hf content, being consistent with the trend in bulk materials [40]. The transformation temperatures are much higher than those of Ni-Ti thin films. The increase in the transformation temperatures is related to the addition of Hf since the transformation temperatures are independent of the Ni content when the Ni content is lower than 50 at.% [185]. Like other SMA thin films, the transformation temperatures are much lower than those of the Ni-Ti-Hf bulk materials with the same composition. The transformation hysteresis also increased with the increasing Hf content. Large transformation hysteresis usually results in the slow response frequency which is not desired by the microactuators.

Figure 5-18. DSC curves of the $\text{Ni}_{48}\text{Ti}_{37.7}\text{Hf}_{14.3}$, $\text{Ni}_{47.9}\text{Ti}_{35.7}\text{Hf}_{16.4}$ and $\text{Ni}_{45}\text{Ti}_{32}\text{Hf}_{23}$ thin films annealed at 600 °C for 25 s.

5.5.2 Effect of Annealing Temperature

Figure 5-19 shows M_s and A_s temperatures as a function of annealing temperature for $\text{Ni}_{47.9}\text{Ti}_{35.7}\text{Hf}_{16.4}$ thin film. All samples were taken from the same piece of silicon wafer. It is seen that when the annealing temperature was below 700 °C, both M_s and A_s increased as the annealing temperature increased. Similar dependence of M_s on the annealing temperature has been reported for $\text{Ti}_{35.0}\text{Ni}_{49.7}\text{Zr}_{15.4}$ thin film annealed from 500 °C to 700 °C [169]. For the sample annealed at 750 °C, M_s is slightly lower than that of the sample annealed at 700 °C; however, A_s shows an opposite trend and is much higher. The detailed transformation temperatures and the transformation enthalpy are also summarized in Table 5-1. It can be seen that for the samples annealed at 550 °C and 750 °C, the amount of latent heat is much lower than that of the samples annealed at 650 °C and 700 °C. This indicates that a considerable volume of materials in those samples does not participate in the transformation.

Figure 5-19. M_s and A_s temperatures of the $\text{Ni}_{47.9}\text{Ti}_{35.7}\text{Hf}_{16.4}$ thin film as a function of annealing temperature.

Table 5-1. Transformation temperatures and transformation enthalpy for $\text{Ni}_{47.9}\text{Ti}_{35.7}\text{Hf}_{16.3}$ thin film annealed at different temperatures for 25s.

Annealing temperature (°C)	M_f (°C)	M_s (°C)	A_s (°C)	A_f (°C)	$\Delta H^{A \rightarrow M}$ (J/g)	$\Delta H^{M \rightarrow A}$ (J/g)
550	96	122	153	197	12.45	-11.38
600	105	125	162	196	16.25	-14.28
650	120	162	175	225	20.05	-18.69
700	136	177	198	248	18.65	-17.10
750	153	171	213	234	14.07	-12.81

Based on the results of TEM observations and XRD results as well as the discussion on microstructure, the following significant results should be considered: the presence of precipitates and the difference in grain size. Therefore, it is suggested that the dependence of martensitic transformation temperature on the annealing temperature arises from a combined effect of precipitates and grain size, which will be discussed in detail in the following.

Precipitation at an intermediate temperature from a supersaturated matrix has two major effects on the martensitic transformation temperature. First, the matrix composition is changed. This generally drives the (Ti, Hf)-to-Ni ratio in the matrix towards a near-equiatomic composition, which may change the M_s temperature because martensitic transformation is strongly sensitive to the composition. Generally, martensitic transformation temperature of Ni-Ti-Hf alloys decreases as the content of Ni in matrix increases or the content of Hf decreases. In this case, the precipitates are considered to be (Ti,Hf)-rich $(\text{Ti,Hf})_2\text{Ni}$ phase. The precipitation will result in the depletion of (Ti,Hf) content and hence the enrichment of Ni content in the matrix. As a result, the martensitic transformation temperature will drop down. Second, the fine and widely dispersed second phase particles, which are often semi-coherent with the matrix, generate interface strains, and hence internal stresses and stress gradients which alter martensitic transformation characteristics. TEM in-situ observations on the $\text{Ni}_{49.6}\text{Ti}_{50.4}$ thin film demonstrates that the propagation of the martensitic plate is suppressed by Ti_2Ni phase [100]. This means that it will also cause the decrease in martensitic transformation temperature. However, both two effects are opposite to the trend observed in the samples annealed at the temperatures from 550 °C to 700 °C. Therefore, it is suggested that the observed increase in martensitic transformation temperature in the Ni-Ti-Hf thin films annealed in this range of temperature could be mainly attributed to the effect of another factor, such as change of grain size.

The martensitic transformation temperature shifts towards lower temperature as the grain size decreases when the annealing temperature is below 700 °C, suggesting that the martensitic transformation is suppressed. Similar results are also demonstrated

in a cold-rolled $\text{Ni}_{50.2}\text{Ti}_{49.8}$ alloy [186] and a $\text{Ni}_{49.7}\text{Ti}_{50.3}$ alloy prepared by heavy pressure torsion following annealing at low temperatures [187] that are both characterized by nanocrystalline structure. It has been theoretically proposed that in nano-crystals, the nucleation barrier opposing the martensitic transformation increases with the decreasing grain size [188]. This requires an increased chemical driving force to overcome the barrier, thus lowering M_s temperature. This is also in agreement with the calculation of non-chemical energy carried out for ZrO_2 nanoparticles containing martensite [189]. Similar to the present case, smaller particles are more stable against the martensitic transformation than larger ones.

Therefore, the dependence of martensitic transformation temperature on the annealing temperature results from a combined effect of the precipitates and change of grain size. When the annealing temperature is lower than 700 °C, the effect of the grain size plays a dominant role, the transformation temperature increases with the increasing grain size. When the sample is annealed at 750 °C, the effect of precipitates has to be taken into account. This effect lowers the transformation temperature.

5.5.3 Effect of Thermal Cycling

Thermal cycling stability of martensitic transformation in Ni-Ti-Hf thin films was also investigated by DSC. The first twenty cycles were consecutively measured in the DSC instrument. Afterwards the samples were removed from the instrument and cycled between ice-water and an oven with a temperature of 400 °C for up to 50 complete thermal cycles. Figure 5-20 plots the transformation peak temperatures as a function of the number of thermal cycling for Ni-Ti-Hf thin films annealed at 650 °C for 25 s. It is

clear that the transformation temperatures shifted to the lower temperature rapidly at the initial 10 cycles and drop down slowly in the following cycles.

Comparison the result with that of Figure 5-13 shows that martensitic transformation in Ni-Ti-Hf thin films has less thermal cycling stability than that of $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon. Martensite in Ni-Ti-Hf thin films has a B19' structure, as shown in Figure 5-14. This means that martensitic transformation in Ni-Ti-Hf thin films requires larger lattice deformation than that of $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon, being more sensitive to the introduction of dislocations according to Miyazaki et al. [179]. The substructure of B19' martensite in Ni-Ti-Hf alloys is dominantly characterized by (001) compound twin [183]. It has been reported that the (001) compound twin alone is unable to act as the lattice invariant shear necessary for martensitic transformation and some lattice defaults are introduced to complete the twinning deformation [190]. These factors suggest that martensitic transformation of Ni-Ti-Hf thin films may yield higher density of dislocation, hence, lowers the transformation temperature effectively.

Figure 5-20. Effect of thermal cycling on the transformation peak temperatures of Ni-Ti-Hf thin films annealed at 650 °C for 25 s under RTA.

It is seen from Figure 5-20 that the composition also influences the thermal stability of Ni-Ti-Hf thin films. The difference of the transformation peak temperatures between the 1st and the Nth cycle (ΔT_H) was used to further compare the thermal stability. The results are shown in Figure 5-21. After 50 cycles, the transformation temperatures of Ni₄₅Ti₃₂Hf₂₃ thin film reduced by less than 10 °C. The transformation temperatures of other thin films reduced by about 20-30 °C. This implies that Ni₄₅Ti₃₂Hf₂₃ thin film has a better thermal stability than other thin films.

Figure 5-21. The difference of the transformation peak temperatures between the 1st and the Nth cycles (ΔT_H) of Ni-Ti-Hf thin films annealed at 650 °C for 25 s under RTA.

5.6 Summary

1. A new precipitate forms when the Ti₅₀Ni₂₅Cu₂₅ ribbon is annealed at 600 °C for 600 s under RTA. The precipitate is identified as a cubic Ti₂(Ni,Cu) phase whose structure is close to that of Ti₂Ni. With increasing annealing temperature or time, the precipitation sequence in the ribbon is B11 TiCu → B11 TiCu + Ti₂(Ni,Cu) → Ti₂(Ni,Cu).
2. The rapidly annealed Ti₅₀Ni₂₅Cu₂₅ ribbons show different precipitation behavior from the conventionally annealed ribbons. With rapid thermal processing, the annealing temperature at which B11 TiCu or Ti₂(Ni,Cu) precipitates form is lower than that under CTA.
3. Phase transformation temperatures of Ti₅₀Ni₂₅Cu₂₅ ribbon are affected by the annealing temperature under RTA. They reach a maximum value at around 600 °C

and then decrease with further increasing annealing temperature. This can be attributed to the combined effect of the grain size change and the formation of B11 TiCu and $\text{Ti}_2(\text{Ni}, \text{Cu})$ precipitates.

4. Nanocrystalline structure is formed in RTA-processed $\text{Ni}_{47.9}\text{Ti}_{35.7}\text{Hf}_{16.3}$ thin films. The grain size increases with increasing annealing temperature. After annealing at 700 °C for 25 s, $(\text{Ti}, \text{Hf})_2\text{Ni}$ precipitates become visible.
5. The addition of Hf is effective in increasing the martensitic transformation temperatures. As the annealing temperature is increased, the transformation temperature (M_s) of $\text{Ni}_{47.9}\text{Ti}_{35.7}\text{Hf}_{16.3}$ thin films first increases and then slightly decreases, which possibly relates to a combined effect of grain size change and $(\text{Ti}, \text{Hf})_2\text{Ni}$ precipitate formation.

Chapter 6 Thermomechanical Properties

Thermomechanical behavior is the most important issue since it determines usefulness of SMAs as a stress-strain-temperature functional material. The properly annealed $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon can exhibit excellent superelasticity and good SME [159]. Previous research further identified two major influencing factors, namely precipitation and texture [50]. In Chapter 5, the type, volume fraction and distribution of B11 TiCu and $\text{Ti}_2(\text{Ni,Cu})$ precipitates have been found to be dependent on annealing conditions. However, up to now, a comprehensive understanding on the relation between precipitate and shape memory properties is missing. Our knowledge on how the type, volume fraction and distribution of the precipitates affect the shape memory properties is unsatisfactory.

In this chapter, the effect of annealing condition on the thermomechanical properties of $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon was studied. The properties include recovery strain, critical stress for slip and two-way memory strain etc. The effect of annealing condition was evaluated in terms of structural evolution and shape memory property to establish a structure-property relationship. This understanding is crucial for the design and application of $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon in MEMS devices. Following the results on the shape memory properties of the ribbon, a demonstration of SME in Ni-Ti-Hf thin films was given.

6.1 Thermomechanical Properties of $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ Ribbon

6.1.1 Deformation of B19 Martensite

The deformation behavior of the annealed ribbons was first investigated through tensile tests at room temperature (in martensite). Figure 6-1 shows the typical stress-strain curves of the samples annealed at different temperatures for 300 s. In each tensile test, the strain was increased from 1% to 5.5% subsequently with an interval of 0.5%. Following each unloading process, the sample was heated to recover the deformation and then cooled to room temperature at the rate of 2 °C/min. A same sample was used throughout the test. The tests were repeated on several samples for each annealing condition to confirm the reproducibility of the results.

Within the deformation range, the stress-strain curves could be divided into three or four stages depending on the annealing temperature. Only the stress-strain curves of the sample annealed at 800 °C consists of four stages, as schematically shown in Figure 6-1 (e). In the first stage, the stress increases rapidly, corresponding to the elastic deformation of self-accommodated martensite variants [191, 192]. In the second stage, the curves are characterized by a non-flat stress-plateau, the stress slowly increases until the strain reaches about 2.5%. The deformation is mainly related to the reorientation/detwinning of martensite variants [191, 192]. This process occurs at a relatively low stress (about 60 MPa), indicating that the martensite variants are easily reoriented by the external stress. In the third stage, the stress increases linearly with increasing the strain. The deformation mechanism corresponds to a further detwinning of martensite variants and generation of dislocations [191, 192]. In the fourth stage, a final plastic deformation leading to fracture occurs. The plastic

deformation of the reoriented martensite variants is responsible for the deformation in this stage [191, 192]. Such a yield is only visible in the sample annealed at 800 °C, implying that the reoriented martensite variants may have lower yield stress than those of other samples.

Figure 6-1. Stress-strain curves of the ribbons annealed at 400 °C (a), 500 °C (b), 600 °C (d), 700 °C (d) and 800 °C (e) for 300 s under RTA, respectively (tests performed at room temperature).

A general feature of the stress-strain curves is the non-flat stress plateau, which implies that the detwinning process of the ribbon requires continuous increase in stress to provide the driving force. This may be related to grain size effect. Most of the grains in the ribbon are much smaller than that of conventional prepared alloys. It is known that the detwinning process proceeds unevenly within the plateau region [192]. The localized internal stress is unable to trigger the detwinning of the neighboring martensite twins of less favorably oriented because of the constraint from the grain boundaries. This is also supported by the deformation behavior in Ni-Ti thin films with ultrafine grains [140].

Figure 6-2 shows the strain-temperature curve of the ribbon annealed at 400 °C after 5.5% deformation. It is seen that the sample shrank slowly at the beginning of the heating. When the temperature is higher than A_s , the shape recovery proceeded rapidly. An obvious TWME was induced upon cooling.

Figure 6-2. Strain-temperature curve of the ribbon annealed at 400 °C for 300 s after 5.5% deformation at room temperature.

Following Figure 3-5, several characteristic parameters, spring-back strain (ε_{EL}), one-way memory strain (ε_{RE}), recovery strain (ε_A) and irreversible strain (ε_{IR}), are determined from the strain-temperature curves. For the sample annealed at 400 °C for 300 s, the results are shown in Figure 6-3 as a function of tensile strain. The recovery ratio (η) is also plotted. The contribution of thermal expansion has been removed. When the tensile strain was less than 2%, the ribbon fully recovers its deformation after heating. With further increasing the tensile strain, an irreversible strain presented because of the introduction of dislocations. Correspondingly, η decreased with the increasing tensile strain. ε_{EL} increased slowly at the initial stage and then progressed rapidly, which is different from the trend of ε_{RE} . The dashed line plots the linear elasticity evolution with the tensile strain. The deviation of ε_{EL} from linearity is due to the dislocation formation.

Figure 6-3. Effect of tensile strain on ε_{EL} , ε_{RE} , ε_{IR} , ε_A and η . The sample was annealed under RTA at 400 °C for 300 s.

The effect of annealing temperature on ε_{EL} , ε_{RE} , ε_A , ε_{IR} and η is shown in Figure 6-4. The tensile strain is 4.5%. It is seen that ε_A of the sample annealed at 500 °C is about 4.34% which is the highest recovery strain achievable among the tests on the samples annealed at different temperatures, due to the lowest ε_{IR} (Figure 6-4 (b)). This further indicates that the sample has the strongest resistance to dislocation movements. These figures clearly show that the shape recovery strain may be optimized by annealing at 500 °C.

Figure 6-4. Effect of annealing temperature on ε_{EL} , ε_{RE} , ε_A (a), ε_{IR} and η (b). The deformation strain is 4.5%.

6.1.2 Two-way Memory Effect Developed by Martensite Deformation

From Figure 6-2, it is seen that the TWME is developed during cooling by the deformation of B19 martensite. The TWME results from the specially arranged dislocations produced during martensite deformation [191]. The dislocations create the directional internal stress fields and cause preferential growth of martensite variants. The determination of two-way memory strain (ε_{TW}) has been shown in Figure 3-5.

The dependence of ε_{TW} on the tensile strain is shown in Figure 6-5. Within the present deformation range, ε_{TW} monotonously increases with the increasing tensile strain. The sample annealed at 800 °C shows much larger ε_{TW} than other samples. The maximum ε_{TW} of 1.25% is obtained in this sample after 5.5% deformation. This value is comparable to that of the equiatomic Ni₅₀Ti₅₀ alloy [191] and higher than that of the Ni₄₉Ti₃₆Hf₁₅ alloy [193] induced by the same deformation strain. However, it does not mean that the maximum obtainable ε_{TW} in the Ti₅₀Ni₂₅Cu₂₅ alloy is comparable to that in equiatomic Ni-Ti alloy. Miyazaki et al. [194] reported that the maximum obtainable ε_{TW} decreases with the increasing Cu content. For the Ti₅₀Ni₄₀Cu₁₀ alloy, the maximum obtainable ε_{TW} is about 3.5% when the sample is deformed in B19 martensite [195]. This value is smaller than that obtained in the Ti₅₀Ni₅₀ alloy (4.1%) [191]. For the sample annealed at 500 °C, the tensile strain where TWME first appears is 4% which is higher than that of other samples.

Figure 6-5. Effect of tensile strain on ε_{TW} of the ribbons annealed for 300 s at different temperatures.

Figure 6-6 illustrates a plot of ε_{TW} as a function of annealing temperature under the tensile strains of 4% and 4.5%, respectively. ε_{TW} initially decreased and reached a minimum in the sample annealed at 500 °C, and subsequently increased at higher annealing temperatures, implying that annealing at higher temperature is favorable to induce TWME through martensite deformation.

Figure 6-6. Effect of annealing temperature on ε_{TW} . The ribbons were deformed to 4% and 4.5%, respectively.

In order to investigate the thermal stability of TWME, the sample annealed at 800 °C was deformed to 4.5% strain and thermally cycled between 30 and 110 °C. The strain-temperature curves and the variation of ε_{TW} with the number of thermal cycling are shown in Figure 6-7. After ten cycles, ε_{TW} is reduced by about 0.06% and becomes stable.

Figure 6-7. Strain-temperature curves of the ribbon annealed at 800 °C for 300 s after 4.5% deformation under thermal cycling (a) and ε_{TW} as a function of number of thermal cycling (b).

6.1.3 Martensite Stabilization

Martensite in SMAs is usually stabilized by martensite deformation. Figure 6-8 shows the transformation behavior of the samples annealed at different temperatures. The samples have been deformed to 4.5% at room temperature and unloaded prior to DSC tests. The transformation behavior of the deformed samples is characterized by a much smaller transformation interval upon the first heating as compared to the second heating. The reverse transformation temperatures upon first heating are slightly higher than that upon second heating, indicating that the martensite is stabilized by deformation. The difference between the reverse transformation temperatures (about 5 °C) is much lower than that for equiatomic $\text{Ni}_{50}\text{Ti}_{50}$ (about 20 °C) [191] and $\text{Ni}_{49}\text{Ti}_{36}\text{Hf}_{15}$ alloys (about 13 °C) [196] with the same deformation strain. The martensite stabilization is a one-time effect and disappears during the second heating.

The stabilization behavior of the deformed samples is also strongly influenced by the annealing temperature. For the sample annealed at 400 °C, the reverse transformation occurs in one-stage upon first heating. However, annealing at higher temperature leads to the reverse transformation proceeding in a multiple-stage manner during first heating. The multiple-stage transformation is unstable and reduces the amount of stages (Figure 6-8 (b)-(e)) during the second heating depending on the annealing temperature. After the second heating, the transformation behavior progresses in a stable way. In comparison to Figure 5-11, the transformation behavior of the deformed samples changes to the similar way as that of undeformed samples except that annealed at 500 °C.

Figure 6-8. DSC curves of the deformed ribbons annealed at 400 °C (a), 500 °C (b), 600 °C (c), 700 °C (d) and 800 °C (e) for 300 s, respectively. The tensile strain is 4.5%.

The A_s temperature upon first heating is shown in Figure 6-9 as a function of tensile strain. The transformation temperature was determined from the strain-

temperature curves shown in Figure 6-2 by using cross-tangential line method. The A_s temperature continuously increases with increasing tensile strain due to the stabilization effect.

Figure 6-9. Effect of tensile strain on the reverse transformation temperature (A_s) upon first heating. The ribbon annealed at different temperatures for 300 s under RTA.

6.1.4 Constraint Shape Recovery Property

In order to further understand the effect of annealing on shape memory properties, the ribbons annealed at different conditions were investigated by thermal cycling tests subjected to different constraint stresses. The constraint stress was increased step-by-step from 30 to 300 MPa, and a same sample was used throughout the test. Figure 6-10 shows the strain-temperature curves of the samples annealed at different temperatures under a stress of 30 MPa. The elongation upon cooling and the contraction upon heating indicate that the annealed ribbons have well-defined SME. The strain (ϵ_M) during cooling is related to stress-assisted transformation from B2 parent phase to B19 martensite. While, the recovery strain (ϵ_R) upon heating is due to the reverse transformation from B19 martensite to B2 parent phase. The deformation is fully

recovered under a stress of 30 MPa. All samples clearly show one-stage transformation under load. The transformation temperatures are indicated by the arrows in Figure 6-10 (a). The transformation hysteresis (ΔT) defined as the difference between A_f and M_s temperatures is between 6 and 8 °C.

Figure 6-10. Strain-temperature curves of the samples annealed for 300 s at 400 °C (a), 500 °C (b), 600 °C (c), 700 °C (d) and 800 °C (e), respectively. The constraint stress is 30 MPa.

Figure 6-11 shows ε_M as functions of annealing temperature and constraint stress. The overall trend is that when annealed below 600 °C, ε_M decreases with increasing annealing temperature. Whereas, ε_M did not change significantly in temperature range between 600 and 700 °C. A further increase to 800 °C leads to a more significant increases of ε_M . It is further noted that ε_M gradually becomes less sensitive to the annealing temperature with increasing constraint stress. The overall increase of ε_M with increasing constraint stress indicates a stress-assisted preferential growth of martensite variants during forward transformation. In the present case, the maximum ε_M has reached up to about 3% under 300 MPa.

Figure 6-11. Effect of annealing temperature and constraint stress on ε_M .

Figure 6-12 shows the strain-temperature curves of the differently annealed samples under a constraint stress of 300 MPa. The irreversible strain (ε_p) is mainly due to the plastic deformation introduced during a full cycle of forward and reverse transformation. The ribbon annealed at 500 °C shows higher resistance to the plastic deformation, as reflected by the small ε_p . This is same as the results shown in Figure

6-4. As compared to the results in Figure 6-10, the transformation temperatures and hysteresis (ΔT) increase with the increasing constraint stress. As an example, M_s temperature of the sample annealed at 800 °C increases from 71.8 °C under 30 MPa to 118.3 °C under 300 MPa and ΔT from 7.9 to 19.7 °C. The increase in the transformation temperatures follows the Clausius-Clapeyron equation, as shown in Figure 6-13 (a). The slope of the stress- M_s temperature changes from 5 to 7.3 MPa/°C and falls in the reported range of 4-20 MPa/°C [58]. Figure 6-13 (b) shows the effect of constraint stress on ΔT . It is seen that ΔT initially remains almost constant irrespective of the constraint stress. This agrees well with the results previously reported [153] showing a constant hysteresis with the increasing constraint stress from 6.3 to 45 MPa for the same ribbon under conventionally annealing treatment. Once the constraint stress is increased to some critical values, ΔT increases. The increase in hysteresis is likely related to the plastic deformation that increases the frictional work against interfacial movement during phase transformation.

Figure 6-12. Strain-temperature curves of the samples annealed for 300 s at 400 °C (a), 500 °C (b), 600 °C (c), 700 °C (d) and 800 °C (e) for 300 s, respectively. The constraint stress is 300 MPa.

Figure 6-13. Effect of stress on M_s temperature (a) and ΔT (b) for the samples annealed at different temperatures. The slope of the stress- M_s temperature as a function of annealing temperature is plotted in the insert of (a).

Figure 6-14 shows that the ε_p increases with the increasing constraint stress once it appears. For the ribbons annealed at 700 °C and below, ε_p appeared at a stress of 200 MPa. For the sample annealed at 800 °C, the stress was 150 MPa, and ε_p has reached to 0.52% under a stress of 300 MPa. As compared to the results in Figure 6-13, it is seen

that the stresses levels at which ε_P appeared are the same as that at which ΔT starts to increase. This further confirms that the increase in ΔT is due to plastic deformation.

Figure 6-14. Effect of constraint stress on ε_P in the samples annealed at different temperatures for 300 s.

During thermal cycling, plastic deformation occurs when the constraint stress reaches a critical value and is regarded as the critical stress for slip (σ_s). In this study, σ_s is defined as the stress where ε_P of 0.1% is detected, as indicated in Figure 6-14. The effect of annealing temperature on the σ_s is shown in Figure 6-15. It is seen that the sample annealed at 500 °C has the highest critical stress of 256 MPa, indicating that annealing at 500 °C is effective in improving the resistance to dislocation movements. In the samples annealed from 600 to 700 °C, σ_s is almost independent of the annealing temperature. A general decreasing trend is seen with further increasing the annealing temperature.

Figure 6-15. Critical stress (σ_s) for plastic deformation of 0.1% strain for the samples annealed for 300s at various temperatures shown.

Figure 6-16 shows that for nearly all the samples, ε_R increases with increasing stress below 200 MPa and it slightly decreases when above this stress level with exception of the sample annealed at 500 °C. For the sample annealed at 500 °C, its ε_R increases continuously with the constraint stress raised to 350 MPa. The maximum recovery strain ($\varepsilon_R^{\max}$) can be extracted from Figure 6-16, as indicated by the arrow. The variation of $\varepsilon_R^{\max}$ as a function of annealing temperature is shown in Figure 6-17. The constraint stresses corresponding to $\varepsilon_R^{\max}$ are also shown. The results show that annealing at 500 °C yields the highest recovery strain of 2.91 %. Further increasing the annealing temperature to 650 °C results in a continuous decrease of $\varepsilon_R^{\max}$. While, a slightly increasing trend is seen if the annealing temperature is further raised to 800 °C. The results in Figure 6-15 and Figure 6-17 suggest that the optimized shape memory properties of the ribbon can be obtained by annealing at 500 °C. This observation is

similar to the previous studies on superelasticity of $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon [159, 197] which show that the superelasticity can be optimized by annealing at 500 °C.

Figure 6-16. Effect of constraint stress on ε_R of the ribbons annealed for 300 s at different temperatures.

Figure 6-17. Effect of annealing temperature on $\varepsilon_R^{\max}$ of the ribbons annealed for 300 s at different temperatures. The corresponding constraint stresses are also shown.

6.1.5 Explanation on the Structure-Property Relation

6.1.5.1 Constraint Shape Recovery

The influencing factors

Table 6-1 summarizes the major observation in present work (Chapter 5 and Section 6.1.4) and reported earlier that help to gain an overall picture of the factors affecting the properties of $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ melt-spun ribbons. In the table, ε_M , ε_P and $\varepsilon_R^{\max}$ are listed and the corresponding constraint stresses are also indicated. It should be noted that all the previous results were obtained in the fully crystallized ribbons except for that reported in reference [154]. In reference [154], the $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbons were found to be not fully crystallized even after annealing at 500 °C for 60 mins. During the progress of crystallization, the Cu content in the crystallized grains was found to increase with the increasing annealing time, resulting in the decrease in ε_M [154]. For the fully crystallized ribbon, this table highlights the effect of the precipitation and texture development on the shape memory properties. The overall tendency of the results is consistent, i.e., ε_M upon cooling reaches maximum values in the annealing temperature range between 400 and 500 °C. However, the absolute values are different. The RTA annealed samples have overall higher values than those annealed under CTA. This might be result of different microstructure evolutions due to different heating rate and annealing duration or possible effect of oxidation of the samples (under CTA).

Table 6-1. Summary of the present observations and major results reported in the literature.

Annealing Conditions °C / second	Precipitates	Textures	ε_M , % (MPa*)	ε_P , % (MPa*)	$\varepsilon_R^{\max}$, %	Sources
400 / 300	None	None	2.99 (300) 2.16 (50)	0.27 (300) 0 (50)	2.81	RTA (present work)
500 / 300	B11	None	2.97 (300) 2 (50)	0.15 (300) 0 (50)	2.91	
600 / 300	B11	None	2.89 (300) 1.84 (50)	0.36 (300) 0 (50)	2.66	
700 / 300	B11+ Ti ₂ (Ni,Cu)	None	2.87 (300) 1.91 (50)	0.39 (300) 0 (50)	2.67	
800 / 300	Ti ₂ (Ni,Cu)	None	2.95 (300) 2.17 (50)	0.52 (300) 0 (50)	2.74	
500 / 10	None	-	290 (200) 2.5 (50)	0 (200) 0 (50)	2.90	RTA [197]
450 / 900	None	[211] _{B19}	1.51 (45)	0 (45)	-	CTA [50, 153, 157]
500 / 900	B11	[211] _{B19} + (111)[$\bar{7}15$] _{B19}	1.44 (45)	0 (45)	-	
600 / 900	B11	(111)[$\bar{7}15$] _{B19} + (011)[$2\bar{1}1$] _{B19}	0.41 (45)	0 (45)	-	
700 / 900	B11	(111)[$\bar{7}15$] _{B19} + (011)[$2\bar{1}1$] _{B19}	0.26 (45)	0 (45)	-	
500 / 180	None	-	2 (90)	0 (45)	-	CTA [154]
500 / 300	None	-	1.94 (90)	0 (45)	-	
500 / 900	None	-	1.8 (90)	0 (45)	-	
500 / 3600	None	-	1.3 (90)	0 (45)	-	
465 / 600	None	-	2.6 (231)	0 (231)	-	CTA [60, 62, 198]
612 / 210	B11	[011] _{B2}	2.8 (150)	0.3 (150)	-	
500 / 1800	-	[011] _{B2} + (001)[100] _{B2} + (001)[110] _{B2}	1.5 (55)	0 (55)	-	

* the corresponding constraint stress - unavailable

Precipitation effect

In the RTA annealed ribbons, since no significant texture is found (Section 5.2), the dependence of shape memory properties on annealing temperature will be discussed on the basis of the precipitation evolution shown in Section 5.1. It is envisaged that precipitates can influence ε_R in the following ways: (1) changing the composition of matrix; (2) reducing the volume fraction of matrix and (3) influencing the formation and growth of martensite variants.

The composition of the as-spun ribbon has been found to be homogeneous and close to the nominal value before annealing. After annealing, the composition of the matrix has changed due to the precipitation of B11 TiCu and Ti₂(Ni,Cu), which may affect ε_R by changing the lattice parameters of martensite and parent phase. Table 6-2 shows the lattice parameters of B19 martensite determined by Rietveld refinements from XRD results. It is confirmed that the lattice parameters did not change significantly with annealing temperature. The same tendency is believed to be valid for parent phase because of lattice correspondence. Therefore, effect of compositional change on ε_R is excluded.

Table 6-2. Lattice parameters of B19 martensite of the Ti₅₀Ni₂₅Cu₂₅ ribbons annealed for 300 s at different temperatures.

Annealing (°C)	<i>a</i> (nm)	<i>b</i> (nm)	<i>c</i> (nm)
400	0.29128	0.42944	0.45310
500	0.29122	0.42942	0.45252
600	0.29091	0.42941	0.45295
700	0.29068	0.42932	0.45278
800	0.29051	0.42963	0.45277

It is also expected that the volume fraction of matrix is changed due to formation of precipitates and, consequently, ε_R is affected. In order to verify the effect of precipitation, we use the following equation to estimate the recovery strain resulting from the reduction of matrix volume fraction and compare with the experimental observations:

$$\varepsilon_R' = \varepsilon_R^{\text{exp}}(100 - V_p)\% \quad (6.1)$$

where ε_R' is the estimated recovery strain by taking into account the reduction of matrix volume fraction, $\varepsilon_R^{\text{exp}}$ is the experimental value of the precipitate-free sample, and V_p is the volume fraction of the precipitates. In this work, this estimation has been divided into two groups: (1) the results obtained under low constraint stress; and (2) the maximum recovery strain achievable under high constraint stress. For group (1), the recovery strain of the sample annealed at 400 °C is taken as $\varepsilon_R^{\text{exp}}$. For group (2), the $\varepsilon_R^{\text{exp}}$ is estimated by $2.91/(1-2\%)=2.97$, in which 2.91 corresponds to the maximum recovery strain of the sample annealed at 500 °C which is the highest value among the samples (Figure 6-17 and Table 6-1), and its corresponding volume fraction of precipitate is 2% (Figure 5-9). Based on the results of Figure 5-9, Figure 6-16 and Figure 6-17, the estimated recovery strains as a function of annealing temperature are plotted in Figure 6-18 in comparison with the experimental results. When the constraint stress is low (30 MPa), the estimated recovery strains show large difference with the experimental values (Figure 6-18 (a)). With increase in the constraint stress, the difference between the estimated and experimental values gradually decreases (Figure 6-18 (b), (c) and (d)).

Figure 6-18. Comparison of the experimentally determined values of shape recovery strains and estimated values based on the volume fraction of precipitate. The samples were annealed for 300 s at different temperatures shown. The constraint stresses are 30 MPa (a), 50 MPa (b) and 150 MPa (c), respectively. The maximum recovery strain is shown in (d).

Figure 6-18 shows that the effect of annealing temperature on ε_R is stress-dependent. We will discuss the annealing temperature difference of ε_R under low constraint stress and high constraint stress separately.

1. Shape recovery under low constraint stress

Under low constraint stress, ε_R is equal to ε_M since no plastic deformation is introduced. The effect of annealing temperature on ε_M agrees well with that previously reported [153, 157]. Figure 6-18 (a) indicates that, under low constraint stress, the reduction of matrix volume fraction does not take a dominant role in determining the shape recovery strain. In this case, the resistance of B11 TiCu precipitates to the

growth of martensite variants is predominant, thus reducing the ε_M . The dependence of ε_M on annealing temperature correlates well with the change of volume fraction of B11 TiCu shown in Figure 5-9. With increasing annealing temperature from 400 to 600 °C, the volume fraction of B11 TiCu increases, resulting in the decrease in ε_M . When the ribbons are annealed at the temperature from 600 to 700 °C, the volume fraction of B11 TiCu did not change significantly. Accordingly, ε_M remains almost constant in this temperature range. When annealed at higher temperatures, B11 TiCu greatly converts into $\text{Ti}_2(\text{Ni,Cu})$. The effect of $\text{Ti}_2(\text{Ni,Cu})$ on ε_M is weaker than that of B11 TiCu due to a much lower density (Figure 5-4 and Figure 5-8). This is likely responsible for the increase in ε_M . Figure 6-18 (a) shows that the estimated and experimental recovery strains of the sample annealed at 800 °C are almost the same. This also supports the weaker effect of $\text{Ti}_2(\text{Ni,Cu})$ on the growth of martensite variants.

2. Shape recovery under high constraint stress

With increasing constraint stress, ε_M shows a gradually decreased sensitivity to the annealing temperature (Figure 6-11). This is due to the increased interfacial movement that overcomes the resistance of thin plate B11 TiCu precipitates. The comparisons between the experimental and estimated recovery strains shown in Figure 6-18 (c) and (d) support this reasoning. Similar effect of thin plate precipitates on martensitic transformation was also observed in Ti-rich Ni-Ti thin films [92, 199] and $\text{Ni}_{52}\text{Ti}_{42}\text{Zr}_6$ alloy [200], respectively.

For the case of group (2) under high constraint stress, $\varepsilon_R^{\text{exp}}$ represents the recovery strain of the precipitate-free sample that reaches its full potential. In Figure 6-18 (d), the considerable consistency between the experimental and estimated $\varepsilon_R^{\text{max}}$ indicates

that the reduction of matrix volume fraction due to precipitation plays an important role. It is reasonable since the precipitates do not participate in phase transformation, hence do not contribute to SME. As ε_R is the difference between ε_M and ε_P , the effect of annealing temperature on $\varepsilon_R^{\max}$ can be elucidated by considering the evolutions of ε_M and ε_P together with the volume fraction of matrix. As shown in Figure 6-11, ε_M of the sample annealed at 400 °C is almost equal to that of the sample annealed at 500 °C, for example, under the stress of 300 MPa, the former is 2.99% and the latter is 2.97%. While, ε_P of the former is larger than that of the latter (Figure 6-14), due to the fact that the densely distributed B11 TiCu in the latter suppresses the dislocation movements. This results in the increase in $\varepsilon_R^{\max}$ with increasing the annealing temperature from 400 to 500 °C. With increasing annealing temperature from 500 to 650 °C, the volume fraction of matrix decreases (Figure 5-9). This is accompanied by the slight decrease in ε_M (Figure 6-11) and increase in ε_P (Figure 6-14). Therefore, $\varepsilon_R^{\max}$ decreases in this temperature range. With further increasing the annealing temperature to 800 °C, ε_M increases more rapidly than does ε_P . Simultaneously, the volume fraction of matrix increases (Figure 5-9). The net effect is the increase of $\varepsilon_R^{\max}$ with annealing temperature increased from 650 to 800 °C (Figure 6-17).

3. Critical stress for slip

The relation between σ_s and annealing temperature (Figure 6-15) can be rationalized as follows. When annealing at 500 °C for 300 s, the densely distributed B11 TiCu precipitates (Figure 5-8(a)) are responsible for the improved σ_s due to precipitation hardening. In the case of annealing at higher temperature, since the

atomic diffusion increases with increasing annealing temperature, diffusion of atoms more easily occurs resulting in the coarsening of B11 TiCu precipitates (Figure 5-8 (b) and (c)). Thus, the spacing between B11 TiCu is increased, resulting in the reduction of the number of pinning point and dislocations becoming easier to move. The sample annealed at 800 °C (Figure 5-4) shows the minimum σ_s , suggesting that $\text{Ti}_2(\text{Ni,Cu})$ precipitates cannot effectively suppress the dislocation movements. This is due to the lack of coherency with the matrix and low distribution density.

6.1.5.2 Transformation Hysteresis under Constraint Stress

In the thermoelastic martensitic transformation, the transformation hysteresis is naturally related to the frictional work dissipated due to overcoming the barrier opposing the interfacial movement [55, 201]. Comparison of Figure 6-13(b) and Figure 6-14 indicates that the evolution of transformation hysteresis with constraint stress correlates well with that of ε_P . Before the presence of ε_P , two features in Figure 6-13 (b) can be noted. The first one is that the sample annealed at 400 °C has the lowest hysteresis as compared to other samples. This is related to the absence of precipitates. The second one is the insignificant change of hysteresis with increasing the constraint stress, indicating that no extra energy-dissipating mechanism is involved. This is due to absence of plastic deformation, since the dislocations produced by plastic deformation is the main cause to introduce the extra energy dissipation [202]. After occurrence of ε_P , the introduced dislocations substantially increase the interfacial friction, thus contributing to the increase in the hysteresis. The dislocation density increases with further increasing constraint stress. The sample annealed at 500 °C shows the lowest ε_P as compared to other samples (Figure 6-14), hence, the hysteresis

of this sample increases less significantly with increasing constraint stress than other samples (Figure 6-13 (b))

6.1.5.3 Two-way Memory Effect

In the present study, the TWME induced by martensite deformation is directly associated with the development of the stress-field created by the dislocations generated during this process [191]. Figure 6-6 indicates that TWME is suppressed by annealing at 500 °C for 300 s. This may be ascribed to the precipitation hardening of B11 TiCu since the precipitates effectively hinder the movement of dislocations. Santamarta et al. [62] reported that $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon containing dense B11 TiCu precipitates does not show TWME after thermomechanical training, which partially conforms to the present results. With increasing or decreasing annealing temperature from 500 °C, the resistance to dislocation movements is reduced. Therefore, more preferentially reoriented martensite variants are selected during cooling, resulting in larger ε_{TW} .

6.1.5.4 Martensite Stabilization

The multiple-stage transformation is likely induced in equiatomic Ni-Ti alloy after martensite deformation due to the high density of dislocations introduced [191]. However, in the present work, it seems that the multiple-stage transformation cannot be simply rationalized by the same reason. This is supported by the fact that the transformation path of the sample annealed at 400 °C (Figure 6-8 (a)) did not change after martensite deformation although it had larger plastic deformation than the sample annealed at 500 °C (Figure 6-4 (b)).

Similar effect of deformation on the martensitic transformation was also reported in the Ti-rich Ni-Ti alloys containing densely distributed Ti_3Ni_4 precipitate [203, 204]. It was suggested that the sample volume can be divided into areas that differ in the dislocation density [203, 204]. Following the argument of reference [204], the inhomogeneous dislocation distribution is considered to be responsible for this complex transformation behavior. The precipitates interact with the dislocations in such a way that the former prevent the latter from moving. This likely causes the inhomogeneous distribution of dislocations in the interior of the grains. The volume with higher dislocation density requires more energy to trigger the transformation. The volume with lower dislocation density need less energy to transform as the movement of the interface between parent phase and martensite is easier. The sample annealed at 400 °C does not contain any precipitates (Figure 4-12), resulting in uniform distribution of the dislocations in the interior of the grains. Therefore, the transformation path does not change.

6.2 Shape Recovery of Ni-Ti-Hf Thin Films

The conventional tensile testing is not applicable to the Ni-Ti-Hf thin films because of the following reasons. One is related to that it is difficult to peel off the deposited thin films from silicon substrate. In addition, it is not easy to install the free standing Ni-Ti-Hf thin films to the clamps because it is very thin and brittle as compared to Ni-Ti binary thin films. Instead, a demonstration of SME in Ni-Ti-Hf thin films is given.

All the Ni-Ti-Hf thin films show SME upon heating. Figure 6-19 shows the SME of the $\text{Ni}_{47.9}\text{Ti}_{35.7}\text{Hf}_{16.4}$ thin film annealed at 600 °C for 25 s. At room temperature, the free-standing thin film is in martensite and shows a flat shape, as shown in Figure 6-19

(a). After deformed at room temperature (b), the thin film is heated up to about 160 °C, close to A_s temperature. With further increase in the temperature, the thin film gradually recovers to the original shape due to the reverse transformation, as shown in Figure 6-19 (c)-(f).

Figure 6-19. Photographs showing SME in the $\text{Ni}_{47.9}\text{Ti}_{35.7}\text{Hf}_{16.4}$ thin film annealed at 600 °C for 25s, (a) original shape (b) deformed shape (c)-(f) shape recovery upon heating.

6.3 Summary

1. The shape recovery strain depends on annealing temperature and constraint stress. With increasing constraint stress, the shape recovery strain shows decreased sensitivity to annealing temperature. Under low constraint stress thermal cycling, the B11 TiCu precipitates act as effective obstacles to the interfacial movement. Whereas, under high constraint stress, the interfacial movement overcomes the resistance of precipitates, leading to the decreased sensitivity.

2. The differently formed precipitates affect the shape recovery strain through either strengthening the matrix or changing the volume fraction of matrix. Under low constraint stress, precipitation strengthening is a predominant factor that reduces the martensite strain thus the shape recovery strain. Under high constraint stress, the volume fraction of precipitate becomes a dominating factor in determining the shape recovery strain through affecting the volume fraction of the material participating phase transformation.
3. The optimized shape recovery strain can be obtained through annealing at 500 °C for 300 s that produces fine dispersed precipitates to strengthen the matrix and yet to have low volume fraction.
4. The martensite deformation is an effective way to introduce the TWME in the $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon. The two-way memory strain increases with increasing deformation strain. An optimized TWME with large two-way memory strain and good thermal cycling stability can be obtained by annealing at 800 °C for 300 s that does not yield B11 TiCu to suppress the development of TWME.
5. The martensite deformation causes a thermal stabilization to the deformed B19 martensite. The reverse transformation of the deformed samples progresses in the multiple-stage manner upon first heating expect for that of the sample annealed at 400 °C.
6. All the Ni-Ti-Hf thin films demonstrate SME.

Chapter 7 Conclusions and Recommendations

7.1 Conclusions

In this work, $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ melt-spun ribbon and Ni-Ti-Hf thin films have been studied as potential actuation materials for MEMS and other applications. The aims of this investigation are to develop and characterize both $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon and Ni-Ti-Hf thin films and to establish the processing-microstructure-property relationship with a focus on the rapid thermal annealing of the initially amorphous materials and resulted properties. Based on the results, the mechanisms behind the properties are established. In view of applications, the present work provides an in-depth understanding on the relation between microstructure and properties and guidelines on optimization of the properties. The major conclusions are summarized as follows.

1. Crystallization behavior of NiTi-based thin films

The crystallization behavior of NiTi-based thin films is characterized by single-stage transformation. The addition of Cu reduces the crystallization temperature and activation energy. This is opposite to the addition of Hf. Based on the empirical rules for thermal stability of amorphous alloys, the effect of alloying elements is understood by taking into account the atomic radius mismatch and the chemical bonding among the constituent elements.

Crystallization of $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon at low temperature is achieved by rapid thermal annealing. Under a heating rate of 3000 °C/min, the initially amorphous ribbon can be fully crystallized after annealing at 400 °C for 30 s which is about 56 °C lower than the crystallization temperature under low heating rate (10 °C/min). Under

conventional thermal annealing of 10 °C/min, the ribbon remains amorphous even after annealed at 400 °C for 15 min. It is proposed that the structural relaxation can assist the crystallization under rapid thermal annealing by providing an extra energy resulting from the higher internal stress field associated with free volume in amorphous state.

2. Precipitation behavior of $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon

When the ribbon is rapidly annealed at 600 °C for 600 s, in addition to B11 TiCu, a new precipitate presents. The precipitate is identified as cubic $\text{Ti}_2(\text{Ni,Cu})$ whose structure is close to that of Ti_2Ni . The results show that B11 TiCu is metastable and it converts to $\text{Ti}_2(\text{Ni,Cu})$ at higher temperature or longer holding time due to the thermally activated diffusion process. As a result, with increasing annealing temperature or duration, the microstructure changes in the sequence of $\text{B19} \rightarrow \text{B19} + \text{B11} \rightarrow \text{B19} + \text{B11} + \text{Ti}_2(\text{Ni,Cu}) \rightarrow \text{B19} + \text{Ti}_2(\text{Ni,Cu})$. The distribution, morphology and volume fraction of the precipitates were studied as a function of annealing temperature. With rapid thermal processing, the annealing temperature at which B11 TiCu or $\text{Ti}_2(\text{Ni,Cu})$ precipitates form is lower than that under conventional thermal annealing.

3. Shape memory effect of $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon

The effect of annealing condition on the constraint shape recovery properties of $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon was investigated. It is found that the annealing temperature affects the shape recovery strain through precipitate evolution. Since the precipitates do not participate in phase transformation, the shape recovery strain resulting from the reduction of matrix volume fraction was estimated and compared with the

experimental observations. By considering this comparison together with the distribution of precipitates, it is found that the precipitates affect the shape recovery strain through either strengthening the matrix or changing the volume fraction of matrix. Under low constraint stress, the precipitation strengthening is a predominant factor that reduces the martensite strain thus the shape recovery strain. Under high constraint stress, the volume fraction of precipitate becomes a dominating factor in determining the shape recovery strain through affecting the volume fraction of the material participating in phase transformation. Properly formed precipitates, on the other hand, effectively suppress the dislocation movements, thus reducing the irreversible strain and improving the shape recovery strain.

An optimized shape memory behavior with 2.91% recovery strain has been obtained by annealing at 500 °C for 300 s that produces fine dispersed B11 TiCu precipitates to strengthen the matrix and yet to have low volume fraction.

Martensite deformation is an effective way to develop two-way memory effect in $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon. The relationship between annealing temperature and two-way memory strain has been established. An optimized two-way memory behavior with 1.25% two-way memory strain and good thermal cycling stability has been obtained by annealing at 800 °C for 300 s that does not yield B11 TiCu precipitates to suppress the development of two-way memory effect.

7.2 Recommendations

Although a great deal of research has been conducted in processing and characterization of NiTi-based thin films for MEMS and other applications, a number

of other interesting areas are needed to be explored and improved. Some of these are described below.

1. Precipitation mechanism of $\text{Ti}_2(\text{Ni,Cu})$ phase

According to the present study, a new precipitate of $\text{Ti}_2(\text{Ni,Cu})$ phase forms after proper annealing. However, this precipitation behavior is not expected based on the phase diagram and requires further understanding which is not established to date. If this precipitation mechanism is fully understood, it will be helpful to precisely control the microstructure through annealing, thus realizing the further optimization of properties.

2. Superelasticity of $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon

In addition to shape memory effect, superelasticity is another important issue for engineering applications. Previous results have reported that the $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon has a perfect superelasticity characterized by a small stress hysteresis, which is possibly related to the existence of single-pair martensite variants [60]. However, the comprehensive and systematic study of this relation is absent yet. It is known that the hysteresis during martensitic transformation originates from the irreversible friction energy dissipated due to overcoming the barrier opposing the interfacial movement [55]. Therefore, it is suggested that an understanding based on the thermodynamic theory of martensitic transformation is the most possible way.

3. Thermomechanical properties of NiTiHf thin films

Thermomechanical behavior of NiTiHf thin films determines their usefulness as the stress-strain-temperature functional materials, which is crucial to the development of potential applications in MEMS field. However, in the present study, due to the

limitation of experimental methods, the thermomechanical properties of NiTiHf thin films are not investigated. Since it is difficult to peel off the as-deposited thin films from substrate, the conventional tensile testing is not applicable. As an alternative method, a nano mechanical test instrument equipped with a heating/cooling system may be used to characterize the thermomechanical properties of NiTiHf thin films.

References

- [1] C. M. Wayman. Progress in Materials Science. 36 (1992) 203.
- [2] T. Tadaki, K. Otsuka, K. Shimizu. Annual Review of Materials Science. 18 (1988) 25.
- [3] K. Otsuka, X. Ren. Intermetallics. 7 (1999) 511.
- [4] K. Otsuka, K. Shimizu. International Metals Reviews. 31 (1986) 93.
- [5] W. J. Buehler, J. W. Gilfrich, R. C. Wiley. Journal of Applied Physics. 34 (1963) 1475.
- [6] K. Otsuka, C. M. Wayman, K. Nakai, H. Sakamoto, K. Shimizu. Acta Metallurgica. 24 (1976) 207.
- [7] D. P. Dunne, N. F. Kennon. Scripta Metallurgica. 16 (1982) 729.
- [8] A. Sato, E. Chishima, K. Soma, T. Mori. Acta Metallurgica. 30 (1982) 1177.
- [9] S. Nourbakhsh, P. Chen. Acta Metallurgica. 37 (1989) 1573.
- [10] Y. D. Kim, C. M. Wayman. Scripta Metallurgica et Materialia. 24 (1990) 245.
- [11] J. Van Humbeeck. Materials Science and Engineering A. 273-275 (1999) 134.
- [12] T. Duerig, A. Pelton, D. Stöckel. Materials Science and Engineering A. 273-275 (1999) 149.
- [13] K. Bhattacharya, R. D. James. Materials Research Society Symposium Proceeding. 489 (1999) 311.
- [14] Chen Zhang, Ralph H.Zee, Paul E.Thoma. IEEE. (1996) 239.
- [15] A. Ishida, V. Martynov. MRS bulletin. 27 (2002) 111.
- [16] W.J. Moberly, K.N. Melton, in: Engineering Aspects of Shape Memory Alloys. T. W. Duerig, K. N. Melton, D. Stökel, C. M. Wayman (Eds). Butterworth-Heinemann Ltd. London, U.K., 1990. p. 46.
- [17] T. H. Nam, T. Saburi, K. Shimizu. Materials Transactions JIM. 31 (1990) 959.
- [18] J. Van Humbeeck. Transactions of the ASME. 121 (1999) 98.
- [19] 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.
- [20] P. Schlobmacher. Materials Letters. 31 (1997) 119.

- [21] T. H. Nam, T. Saburi, Y. Nakata, K. Shimizu. *Materials Transactions JIM*. 31 (1990) 1050
- [22] M. Kohl, E. Just, W. Pfleging, S. Miyazaki. *Sensors and Actuators A-Physical*. 83 (2000) 208.
- [23] K.D. Skrobanek, M. Kohl, S. Miyazaki. *Proceeding of the 3rd International Conference on Intelligent Materials*. Lyon, France. 1996. 499.
- [24] C. M. Wayman, T. W. Duerig, in: *Engineering Aspects of Shape Memory Alloys*. T. W. Duerig, K. N. Melton, D. Stöckel, C. M. Wayman (Eds). Butterworth-Heinemann. London, U. K., 1990. p. 3.
- [25] K. Otsuka, C. M. Wayman, in: *Shape Memory Materials*. K. Otsuka, C. M. Wayman (Eds). Cambridge University Press. Cambridge, U.S.A, 1998. p. 37.
- [26] K. Otsuka, K. Shimizu. *International Metals Reviews*. 31 (1986) 93.
- [27] K. Otsuka, C. M. Wayman, in: *Shape Memory Materials*. K. Otsuka, C. M. Wayman (Eds). Cambridge University Press. Cambridge U.S.A, 1998. p. 41.
- [28] T. Saburi, S. Nenno. *Scripta Metallurgica*. 8 (1974) 1363.
- [29] T. Takezawa, S. Sato. *Supplement Materials Transaction JIM*. 17 (1976) 223.
- [30] T. A. Schroeder, C. M. Wayman. *Scripta Metallurgica*. 11 (1977) 225.
- [31] T. Fukuda, A. Deguchi, T. Kakeshita, T. Saburi. *Materials Transaction JIM*. 38 (1997) 514.
- [32] G. R. Purdy, J. G. Parr. *Transactions of the AIME*. 221 (1961) 636.
- [33] D. P. Dautovich, G. R. Purdy. *Canadian Metallurgical Quarterly*. 4 (1965) 129.
- [34] K. Otsuka, T. Sawamura, K. Shimizu. *Physical Status Solidi A*. 5 (1971) 457.
- [35] R. F. Hehemann, G. D. Sandrock. *Scripta Metallurgica*. 5 (1971) 801.
- [36] Y. Kudoh, M. Tokonami, S. Miyazaki, K. Otsuka. *Acta Metallurgica*. 33 (1985) 2049.
- [37] G. M. Michal, R. Sinclair. *Acta Crystallographica*. B37 (1981) 1803.
- [38] X. D. Han, W. H. Zou, R. Wang, Z. Zhang, D. Z. Yang, K. H. Wu. *Journal de Physique IV*. C8 (1995) 753.
- [39] X. D. Han, W. H. Zou, R. Wang, Z. Zhang, D. Z. Yang. *Acta Materialia*. 44 (1996) 3711.

- [40] P. L. Potapov, A. V. Shelyakov, A. A. Gulyaev, E. L. Svistunova, N. M. Matveeva, D. Hodgson. *Materials Letters*. 32 (1997) 247.
- [41] T. Tadaki, C. M. Wayman. *Metallography*. 15 (1982) 247.
- [42] T. Saburi, Y. Watanabe, S. Nenno. *ISIJ International*. 29 (1989) 405.
- [43] P. L. Potapov, A. V. Shelyakov, D. Schryvers. *Scripta Materialia*. 44 (2001) 1.
- [44] Ya Xu, S. Shimizu, Y. Suzuki, K. Otsuka, T. Ueki, K. Mitose. *Acta Materialia*. 45 (1997) 1503.
- [45] M. S. Wechsler, D. S. Lieberman, T. A. Read. *Transactions of the AIME*. 197 (1953) 1503.
- [46] D. S. Lieberman, M. S. Wechsler, T. A. Read. *Journal of Applied Physics*. 26 (1955) 473.
- [47] J. S. Bowles, J. K. Mackenzie. *Acta Metallurgica*. 2 (1954) 129.
- [48] O. Matsumoto, S. Miyazaki, K. Otsuka, H. Tamura. *Acta Metallurgica*. 35 (1987) 2137.
- [49] K. M. Knowles, D. A. Smith. *Acta Metallurgica*. 29 (1981) 101.
- [50] Z. L. Xie, G. P. Cheng, Y. Liu. *Acta Materialia*. 55 (2007) 361.
- [51] H. C. Tong, C. M. Wayman. *Acta Metallurgica*. 22 (1974) 887.
- [52] E. Hornbogen. *Acta Metallurgica*. 33 (1985) 595.
- [53] J. Ortin, A. Planes. *Acta Metallurgica*. 37 (1989) 1433.
- [54] J. Ortin, A. Planes. *Acta Metallurgica*. 36 (1988) 1873.
- [55] G. B. Olson, M. Cohen. *Scripta Metallurgica*. 9 (1975) 1247.
- [56] H. Warlimont, L. Delaey. *Progress in Materials Science*. 18 (1974) 1.
- [57] J. R. Patel, M. Cohen. *Acta Metallurgica*. 1 (1953) 531.
- [58] J. L. Proft, T. W. Duerig, in: *Engineering Aspects of Shape Memory Alloys*. T. W. Duerig, K. N. Melton, D. Stöckel, C. M. Wayman (Eds). Butterworth-Heinemann. London, U.K., 1990. p. 115.
- [59] Y. Furuya, M. Matsumoto, H. Kimura, K. Aoki, M. Masumoto. *Materials Transactions JIM*. 31 (1990) 504.
- [60] T. H. Nam, S. M. Park, T. Y. Kim, Y. W. Kim. *Smart Materials and Structures*. 14 (2005) S239.
- [61] Y. W. Kim, T. H. Nam. *Scripta Materialia*. 51 (2004) 653.

- [62] R. Santamarta, E. Cesari, J. Pons, T. Goryczka. Metallurgical and Materials Transactions A. 35A (2004) 761.
- [63] A. Inoue. Acta Materialia. 48 (2000) 279.
- [64] M. Liu, M. J. Tu, X. M. Zhang, Y. Y. Li, A. V. Shelyakov. Journal of Materials Science Letters. 20 (2001) 827.
- [65] E. Cesari, P. Ochin, R. Portier, V. Kolomytsev, Yu. Koval, A. Pasko, V. Soolshenko. Materials Science and Engineering A. 273-275 (1999) 738.
- [66] F. Dalle, A. Pasko, P. Vermaut, V. Kolomytsev, P. Ochin, R. Portier. Scripta Materialia. 43 (2000) 331.
- [67] F. Dalle, V. Kolomytsev, P. Ochin, R. Portier. Scripta Materialia. 44 (2001) 929.
- [68] P. Vermaut, L. Lityńska, R. Portier, P. Ochin, J. Dutkiewicz. Materials Chemistry and Physics. 81 (2003) 380.
- [69] M. Kohl, D. Dittmann, E. Quandt, B. Winzek, S. Miyazaki, D. M. Allen. Materials Science and Engineering A. 273-275 (1999) 784.
- [70] J. P. Chu, Y.W. Lai, T.N. Lin, S.F.Wang. Materials Science and Engineering A. 277 (2000) 11.
- [71] E. Makino, M. Uenoyama, T. Shibata. Sensors and Actuators A. 71 (1998) 187.
- [72] X. Y. Chen, Y. F. Lu, Z. M. Ren, S. Zhu. Journal of Material Research. 17 (2002) 279.
- [73] J. H. Le, K. W. Won, J. T. Chang. Thin Solid Films. 359 (2000) 46.
- [74] Donald M. Mattox, Handbook of Physical Vapor Deposition Processing Film Formation, Adhesion, Surface Preparation and Contamination Control., Westwood, New Jersey, U.S.A., Noyes Publications; 1998.
- [75] C. Craciunescu, J. Li, M. Wuttig. Scripta Materialia. 48 (2003) 65.
- [76] T. Saburi, in: Shape Memory Materials. K. Otsuka, C. M. Wayman (Eds). Cambridge University Press. Cambridge, U.S.A., 1998. p. 49.
- [77] S. Miyazaki, A. Ishida. Materials Science and Engineering A. 273-275 (1999) 106.
- [78] Ken K. Ho, Gregory P. Carman. Thin Solid Films. 370 (2000) 18.
- [79] Ken K. Ho, K. P. Mohanchandra, Gregory P. Carman. Thin Solid Films. 413 (2002) 1.

-
- [80] T. Lehnert, S. Tixier, P. Böni, R. Gotthardt. *Materials Science and Engineering A*. 273-275 (1999) 713.
- [81] A. Ohta, S. Bhansali, I. Kishimoto, A. Umeda. *Sensors and Actuators*. 86 (2000) 165.
- [82] P. Schloßmacher, N. Boucharat, H. Rösner, G. Wilde, A. V. Shelyakov. *Journal de Physique IV France*. 112 (2003) 731.
- [83] Hai Ni, Hoo-Jeong Lee, Ainissa G. Ramirez. *Journal of Material Research*. 20 (2005) 1728.
- [84] Hoo-Jeong Lee, Ainissa G. Ramirez. *Applied Physics Letters*. 85 (2004) 1146.
- [85] L. W. Chang, David S. Grummon. *Philosophical Magazine A*. 76 (1997) 191.
- [86] K. H. J. Buschow. *Journal of Physics F: Metallurgical Physics*. 13 (1983) 563.
- [87] C. Segger, P. L. Ryder. *Materials Science and Engineering A*. 179-180 (1994) 641.
- [88] D. V. Lougzuine, A. Inoue. *Journal of Materials Science*. 35 (2000) 4159.
- [89] J. Z. Chen, S. K. Wu. *Journal of Non-Crystalline Solids*. 288 (2001) 159.
- [90] Michael J. Vestel, David S. Grummon, Ronald Gronsky, Albert P. Pisano. *Acta Materialia*. 51 (2003) 5309.
- [91] T. Kikuchi, K. Ogawa, S. Kajiwara, T. Matsunaga, S. Miyazaki, Y. Tomota. *Philosophical Magazine A*. 78 (1998) 467.
- [92] J. X. Zhang, M. Sato, A. Ishida. *Acta Materialia*. 51 (2003) 3121.
- [93] J. W. Martin, R. D. Doherty, B. Cantor, *Stability of Microstructure in Metallic Systems* (Second edition), United Kingdom, Cambridge University Press; 1997.
- [94] Vincent H. Hammond, Marlene D. Houtz, James M. O'reilly. *Journal of Non-Crystalline Solids*. 325 (2003) 179.
- [95] T. Komatsu, K. Matusita, R. Yokota. *Journal of Materials Science*. 20 (1985) 3271.
- [96] K. Russew, F. Sommer. *Journal of Non-Crystalline Solids*. 319 (2003) 289.
- [97] J. M. Riveiro. *Journal of Physics: Condensed Matter* 1(1989) 459.
- [98] Y. Terunuma, M. Nagumo. *Materials Transaction JIM*. 36 (1995) 842.
- [99] Y. Makifuchi, Y. Terunuma, M. Nagumo. *Materials Science and Engineering A*. 226-228 (1997) 312.

- [100] T. Lehnert, S. Crevoiserat, R. Gotthardt. *Journal of Materials Science*. 37 (2002) 1523.
- [101] O. M. Ivasishin, R. V. Teliovich. *Materials Science and Engineering A*. 263 (1999) 142.
- [102] R. Kakkad, J. Smith, W. S. Lau, S. J. Fonash, R. Kerns. *Journal of Applied Physics*. 65 (1989) 2069.
- [103] X. L. Liu H. Y. Wei H. B. Fan Z. M. Liang P. Jin S. Y. Yang C. M. Jiao Q. S. Zhu P F Zhang, Z. G. Wang. *Journal of Physics D: Applied Physics*. 40 (2007) 6010.
- [104] Q. D. Zhuang, J. M. Li, Y. P. Zeng, S. F. Yoon, H. Q. Zheng, M. Y. Kong, L. Y. Lin. *Journal of Crystal Growth*. 212 (2000) 352.
- [105] K. Daovdi, C. S. Sandu, V. S. Teodorescu, C. Ghica, B. Canut. *Crystal Engineering*. 5 (2002) 187.
- [106] K. Otsuka, T. Kakeshita. *MRS bulletin*. 27 (2002) 91.
- [107] M. Nishida, C. M. Wayman, T. Honma. *Metallurgical Transactions*. 17A (1986) 1505.
- [108] S. P. Alisova, N. V. Volynskaya, P. B. Budberg, A. N. Kobylkin. *Izvestiya Akademii Nauk. SSSR. Metally*. 5 (1986) 210.
- [109] T. Matsunaga, S. Kajiwara, K. Ogawa, T. Kikuchi, S. Miyazaki. *Materials Science and Engineering A*. 273-275 (1999) 745.
- [110] T. H. Nam, J. H. Kim, M. S. Choi, H. W. Lee, Y. W. Kim, H. J. Im, J. S. Ahn, T. Mitani. *Journal of Materials Science Letters*. 21 (2002) 799.
- [111] T. H. Nam, J. H. Lee, D. W. Jung, C. A. Yu, Y. N. Liu, Y. W. Kim. *Materials Science and Engineering A*. 449-451 (2006) 1041.
- [112] A. Khantachawana, H. Mizubayashi, S. Miyazaki. *Materials Transaction JIM*. 45 (2004) 214.
- [113] W. Tang. *Metallurgical Transactions*. 28A (1997) 537.
- [114] X. Ren, K. Otsuka. *Materials Science Forum*. 327-328 (2000) 429.
- [115] K. H. Eckelmeyer. *Scripta Metallurgica*. 10 (1976) 667.
- [116] T. Honma, in: *Shape Memory Materials*. H. Funakubo (Eds). Gordon and Breach Scientific Publishers. New York, U.S.A, 1987. p. 83.
- [117] K. Otsuka, X. Ren. *Progress in Materials Science*. 50 (2005) 511.

- [118] C. M. Hwang, M. Meichle, M. B. Salamon, C. M. Wayman. *Philosophical Magazine A*. 47 (1983) 9.
- [119] C. M. Hwang, M. Meichle, M. B. Salamon, C. M. Wayman. *Philosophical Magazine A*. 47 (1983) 31.
- [120] C. M. Hwang, M. Meichle, M. B. Salamon, C. M. Wayman. *Philosophical Magazine A*. 47 (1983) 177.
- [121] Y. Nakata, T. Tadaki, K. Shimizu. *Materials Transactions JIM*. 32 (1991) 580.
- [122] H. Miyamoto, T. Taniwaki, T. Ohba, K. Otsuka, S. Nishigori, K. Kato. *Scripta Materialia*. 53 (2005) 171.
- [123] O. Mercier, K. N. Melton. *Metallurgical Transactions*. 10A (1979) 387.
- [124] J. L. Proft, K. N. Melton, T. W. Duerig. *Proceeding of the International Materials Research Society Conference*. Tokyo, Japan. 1987.
- [125] X. Huang, Y. Liu, S. F. Ling, H. H. Zhang, W. M. Huang. *Surface and Coatings Technology*. 167 (2003) 148.
- [126] F. Khelfaoui, M. Weller, R. Gotthardt. *Materials Science and Engineering A*. 378 (2004) 434.
- [127] C. M. Craciunescu, J. Li, M. Wuttig. *Thin Solid Films*. 434 (2003) 271.
- [128] P. Surbled, C. Clerc, B. Le Pioufle, M. Ataka, H. Fujita. *Thin Solid Films*. 41 (2001) 52.
- [129] H. B. Luo, F. L. Shan, Y. L. Huo, Y. M. Wang. *Thin Solid Films*. 339 (1999) 305.
- [130] A. Gyobu, Y. Kawamura, H. Horikawa, T. Saburi. *Materials Science and Engineering A*. 273-275 (1999) 749.
- [131] S. Miyazaki, K. Nomura. *IEEE*. (1994) 176.
- [132] A. Ishida, A. Takei, M. Sato, S. Miyazaki. *Thin Solid Films*. 281/282 (1996) 337.
- [133] T. Matsunaga, S. Kajiwarra, K. Ogawa, T. Kikuchi, S. Miyazaki. *Materials Science Forum*. 327-328 (2000) 175.
- [134] A. Ishida, M. Sato. *Acta Materialia*. 51 (2003) 5571.
- [135] M. Sato, A. Ishida, S. Miyazaki. *Thin Solid Films*. 315 (1998) 305.
- [136] T. Lehnert, H. Grimmer, P. Böni, M. Horisberger, R. Gotthardt. *Acta Materialia*. 48 (2000) 4065.

- [137] A. Gyobu, Y. Kawamura, T. Saburi, M. Asia. *Materials Science and Engineering A*. 312 (2001) 227.
- [138] K. P. Mohanchandra, D. Shin, G. P. Carman. *Smart Materials and Structures*. 14 (2005) S312.
- [139] A. Ishida, M. Sato, S. Miyazaki. *Materials Science and Engineering A*. 273-275 (1999) 754.
- [140] A. Ishida, M. Sato, T. Kimura, S. Miyazaki. *Philosophical Magazine A*. 80 (2000) 967.
- [141] Z. L. Xie, J. Van Humbeeck, Y. Liu, L. Dalaey. *Scripta Materialia*. 37 (1997) 363.
- [142] R. Santamarta, D. Schryvers. *Materials Transactions*. 44 (2003) 1760.
- [143] R. Santamarta, D. Schryvers. *Materials Science and Engineering A*. 378 (2004) 143.
- [144] R. Santamarta, D. Schryvers. *Intermetallics*. 12 (2004) 341.
- [145] H. Rösner, P. Schloßmacher, A. V. Shelyakov, A. M. Glezer. *Scripta Materialia*. 43 (2000) 871.
- [146] G. P. Cheng, Z. L. Xie, Y. Liu. *Journal of Alloys and Compounds*. 415 (2006) 182.
- [147] H. Rösner, P. Schloßmacher, A. V. Shelyakov, A. M. Glezer. *Acta Mater*. 49 (2001) 1541.
- [148] H. Rösner, P. Schloßmacher, A. V. Shelyakov, A. M. Glezer. *Materials Transactions*. 42 (2001) 1758.
- [149] H. Rösner, A. V. Shelyakov, A. M. Glezer, K. Feit, P. Schloßmacher. *Materials Science and Engineering A*. 273-275 (1999) 733.
- [150] H. Rösner, A. V. Shelyakov, A. M. Glezer, P. Schloßmacher. *Materials Science and Engineering A*. 307 (2001) 188.
- [151] J. Morgiel, E. Cesari, J. Pons, A. Pasko, J. Dutkiewicz. *Journal of Materials Science*. 37 (2002) 5319.
- [152] R. Santamarta, D. Schryvers. *Scripta Materialia*. 50 (2004) 1423.
- [153] G. P. Cheng, Z. L. Xie. *Journal of Alloys and Compounds*. 396 (2005) 128.
- [154] S. H. Chang, S. K. Wu, H. Kimura. *Intermetallics*. 15 (2007) 233.

- [155] Y. Furuya, M. Matsumoto, H. S. Kimura, T. Masumoto. *Materials science and Engineering A*. 147 (1991) L7.
- [156] G. B. Cho, C. I. Yu, J. H. Lee, Y. W. Kim, T. H. Nam. *Scripta Materialia*. 55 (2006) 597.
- [157] G. P. Cheng, Z. L. Xie, Y. Liu. *Materials Science and Engineering A*. 425 (2006) 268.
- [158] T. H. Nam, J. H. Kim, T. Y. Kim, Y. K. Lee, Y. W. Kim. *Journal of Materials Science Letters*. 21 (2002) 1851.
- [159] Y. Liu. *Materials Science and Engineering A*. 354 (2003) 286.
- [160] C. Zhang, Paul E. Thoma, Ralph Zee. *Materials Research Society Symposium Proceeding*. 64 (2000) 129.
- [161] H. D. Gu, K. M. Leung, C. Y. Chung. *Journal of Vacuum Science and Technology A*. 16 (1998) 3420.
- [162] P. Krulevitch, A. P. Lee, P. B. Ramsey, J. C. Trevino, J. Hamilton, M. Allen Northrup. *Journal of Microelectromechanical System*. 5 (1996) 270.
- [163] E. Makino, T. Mitsuya, T. Shibata. *Sensors and Actuators A*. 88 (2001) 256.
- [164] J. J. Gill, D. T. Chang, L. A. Momoda, G. P. Carman. *Sensors and Actuators A*. 93 (2001) 148.
- [165] R. W. Cheary, A. Coelho. *Journal of Applied Crystallography*. 25 (1992) 109.
- [166] N. Karlsson. *Journal of the Institute of Metals*. 79 (1951) 391.
- [167] M. H. Mueller, H. W. Knott. *Transactions of the AIME*. 227 (1963) 674.
- [168] Homer E. Kissinger. *Analytical Chemistry*. 29 (1957) 1702.
- [169] T. Sawaguchi, M. Sato, A. Ishida. *Metallurgical and Materials Transactions A*. 35A (2004) 111.
- [170] S. R. Elliott, *Physics of Amorphous Materials*(Second edition), England, Longman Scientific & Technical; 1990.
- [171] F. R. De Boer, R. Boom, W. C. M. Mattens, A. R. Middema, A. K. Niessen, *Cohesion in Metals*, Amsterdam, The Netherlands, North-Holland; 1988.
- [172] J. Eckert, L. Schultz, K. Urban. *Journal of Non-Crystalline Solids*. 127 (1991) 90.

- [173] 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.
- [174] J.Z.Chen, S.K.Wu. *Journal of Non-crystalline solids*. 288 (2001) 159.
- [175] Liuwen Chang, David S.Grummon. *Philosophical Magazine A*. 76 (1997) 163.
- [176] F. J. J. Van Loo, G. F. Bastin, A. J. H. Leenen. *Journal of the Less-common Metals*. 57 (1978) 111.
- [177] R. Nagarajan, K. Chattopadhyay. *Acta Materialia*. 42 (1994) 947.
- [178] T. H. Nam, G. S. Ha, H. W. Lee, S. G. Hur. *Materials Science and Technology*. 16 (2000) 1017.
- [179] S. Miyazaki, Y. Igo, K. Otsuka. *Acta Metallurgica*. 34 (1986) 2045.
- [180] T. Hashinaga, S. Miyazaki, T. Ueki, H. Horikawa. *Journal de Physique IV. Colloque C8* (1995) 689.
- [181] X. L. Meng, Y. F. Zheng, Z. Wang, L. C. Zhao. *Materials Letters*. 45 (2000) 128.
- [182] X. L. Meng, Y. F. Zheng, Z. Wang, L. C. Zhao. *Scripta Materialia*. 42 (2000) 341.
- [183] X. L. Meng, W. Cai, L. M. Wang, Y. F. Zheng, L. C. Zhao, L. M. Zhou. *Scripta Materialia*. 45 (2001) 1177.
- [184] M. J. Vestel, D. S. Grummon. *Materials Science and Engineering A*. 378 (2004) 437.
- [185] P. E. Thoma, J. J. Boehm. *Materials Science and Engineering A*. 273-275 (1999) 385.
- [186] H. Nakayama, K. Tsuchiya, M. Umemoto. *Scripta Materialia*. 44 (2001) 1781.
- [187] T. Waitz, V. Kazykhanov, H. P. Karnthaler. *Acta Materialia*. 52 (2004) 137.
- [188] Q. P. Meng, Y. H. Rong, T. Y. Hsu. *Physcial Review B*. 65 (2002) 174118.
- [189] W. Y. Yan, G. Reisner, F. D. Fischer. *Acta Materialia*. 45 (1997) 1969.
- [190] Y. F. Zheng, W. Cai, J. X. Zhang, Y. Q. Wang, L. C. Zhao, H. Q. Ye. *Materials Letters*. 36 (1998) 142.
- [191] Y. N. Liu, Y. Liu, J. Van Humbeeck. *Acta Materialia*. 47 (1999) 199.
- [192] Y. Liu, Z. L. Xie, J. Van Humbeeck, L. Delaey, Y. N. Liu. *Philosophical Magazine A*. 80 (2000) 1935.

- [193] X. L. Meng, Y. F. Zheng, W. Cai, L. C. Zhao. *Journal of Alloys and Compounds*. 372 (2004) 180.
- [194] S. Miyazaki, S. Chujo. *The First International Conference on Shape Memory and Superelastic Technologies*. California, U.S.A. 1994. p.73.
- [195] G. Airoldi, T. Ranucci, G. Riva, A. Sciacca. *Scripta Materialia*. 34 (1996) 287.
- [196] X. L. Meng, W. Cai, Y. F. Zheng, Y. B. Rao, L. C. Zhao. *Materials Letters*. 57 (2003) 4206.
- [197] Y. Liu, Z. L. Xie, Y. X. Tong, C. W. Lim. *Journal of Alloys and Compounds*. 416 (2006) 188.
- [198] T. Goryczka, P. Ochinnikov. *Materials Science and Engineering: A*. 438-440 (2006) 714.
- [199] S. Kajiwar, T. Kikuchi, K. Ogawa, T. Matsunaga, S. Miyazaki. *Philosophical Magazine Letter*. 74 (1996) 137.
- [200] A. M. Sandu, K. Tsuchiya, S. Yamamoto, Y. Todaka, M. Umemoto. *Scripta Materialia*. 55 (2006) 1079.
- [201] R.J. Salzbrenner, M. Cohen. *Acta Metallurgica*. 27 (1979) 739.
- [202] R. F. Hamilton, H. Sehitoglu, Y. Chumlyakov, H. J. Maier. *Acta Materialia*. 52 (2004) 3383.
- [203] D. Chrobak, D. Stróž, H. Morawiec. *Scripta Materialia*. 48 (2003) 571.
- [204] P. C. Su, S. K. Wu. *Acta Materialia*. 52 (2004) 1117.