Indentation and laser annealing of NiTi shape memory alloys

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Indentation and Laser Annealing of NiTi Shape Memory Alloys

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Abstract

A shape memory alloy (SMA) is able to memorize and recover its original shape, after it has been deformed, by heating it over its transformation temperature. The recoverable strain can be as much as around 7% and actuation stress up to 500 MPa in NiTi SMAs. Because of this unique thermomechanical characteristic, SMAs, in particular, NiTi, have been used in a variety of applications, from medical equipment to Micro-Electro-Mechanical Systems (MEMS). This thesis includes two independent parts: one is on small scale shape memory behavior of NiTi using instrumented indentation technique; the other is about laser annealing of NiTi thin films for MEMS applications.

For a better design of SMA based MEMS, a good understanding of small-scale mechanical properties and shape memory behavior of SMAs is necessary. At present, this is still under investigation. In this thesis, the microscopic shape memory effect and microindentation behavior of a NiTi alloy are studied by instrumented indentation technique and temperature controllable atomic force microscopy/3-D surface interferometer. Two-way shape memory effect (TWSME) induced by indentation is investigated at micro-scale. The TWSME produced by indentation may provide an alternative as a new actuation mechanism in micro actuators. A schematic explanation of the pile-up/sink-in phenomenon in SMAs upon indentation is presented. Some interesting findings include: 1) all indentations are pile-up type after thermal cycling; 2) the size of indentation is seemingly independent on the indentation temperature after one thermal cycle, but almost linearly proportional to the indentation load.

CO₂ laser annealing of NiTi thin films from Si wafer side has been developed in our group by He (2004). The films are locally re-crystallized and with shape memory function. However, this technique is not repeatable every time, so that the reliability is a problem to be solved. Previous theoretical investigation in He (2004) is not fruitful. In this thesis, a further study on annealing temperature is presented. First, laser energy absorption ratio is determined and the exact thickness of Si wafer is found to be a dominant factor. Then the

temperature distribution in the laser annealing process is investigated by finite element analysis. It confirms that CO₂ laser can effectively anneal NiTi films if the laser beam impinges from backside of Si wafer, and the high temperature zone is highly localized, almost within a circle with a radius of the laser beam spot diameter. The effective annealing zone is about the spot size of laser beam, which agrees well with previous experimental observation. Furthermore, effects of oxidation and interfacial layer are discussed. In addition, a theoretical analysis is carried out on direct laser annealing of NiTi thin films by different lasers.

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CHAPTER 1

Introduction

1.1 Fundamentals of shape memory alloys

Shape memory alloys (SMAs) have been used in a variety of applications due to their unique shape memory effect (SME). SME is a unique property of certain alloys exhibiting martensitic transformations. After deformed at a low temperature, a SMA can recover its original shape by the reverse transformation upon heating. This is called the SME [Fig. 1.1(a)]. On the other hand, another unique property, called the superelasticity (SE) [Fig. 1.1(b)], is that at a higher temperature, a large strain can be recovered upon unloading (Otsuka and Wayman 1998).

Figure 1.1 Typical behaviours of SMAs.

These two phenomena are associated with two different transformations at the crystal level: the phase transformation and martensite re-orientation. The change of crystal structure in NiTi alloy, a typical SMA, is between a body cubic central crystal at a high temperature austenite (A) phase and a low temperature martensite (M) crystal, typically monoclinic.

Figure 1.2 Illustrate the change of lattice structures of a SMA in the process of SME^{1.1}.

Normally, a SMA creates alternate bands upon cooling. One layer is tilted in one direction while the neighbouring layer is tilted in an opposite direction and so on. These alternate layers (twins) are able to balance the displacement of the "tilt" so that there is no net overall shape change. The essence of the SME is that the "tilted" (twinned) martensite can be flipped to the opposite "tilt" upon loading. That is, one can cause most of the martensite to "tilt" in the same direction rather than having equal amounts of alternate twins. Consequently, the material undergoes a shape change as a result of tilting. The actual shape memory arises when the alloy is heated and all the martensite twins must "untilt" back to the original crystalline structure (Huang 1998).

While phase transformation can be induced thermally or mechanically, martensite re-orientation can only be triggered by a stress. In both the SME and SE, the recoverable strain can be up to 7% in NiTi SMAs. In addition, it is possible to train a normal SMA with two-way shape memory (Huang and Toh 2000). Unlike one-way shape memory alloy (OWSMA), which can only remember the high temperature (austenite) shape, two-way

^{1.1} <http://smart.tamu.edu/overview/smaintro/detailed/detailed.html>.

shape memory alloy (TWSMA) remembers both the high temperature (austenite) and low temperature (martensite) shapes (Fig. 1.3).

Figure 1.3 Demonstration of TWSMA. M_f = martensite finish temperature, A_f = austenite finish temperature^{1,2}.

1.2 NiTi SMAs and applications in MEMS

In the past decades, considerable commercial and military interest in Micro-Electro-Mechanical Systems (MEMS) has developed. MEMS refer to devices, which have a characteristic length of less than 1 mm but more than 1 μm , that combine electrical and mechanical components and are fabricated using integrated circuit batch-processing technologies. MEMS promises to revolutionize the performance of a wide range of products by merging silicon-based microelectronics with 'micromachining' technologies, enabling complete systems-on-a-chip to be realized. MEMS enables the development of 'smart' products by augmenting the computational ability of microelectronics with the perception and control capabilities of microsensors and microactuators.

Among various fully integrated microactuation schemes of MEMS, including electrostatic, electromagnetic, piezoelectric, thermal bimorph, thermopneumatic, and SMAs, only

^{1,2} <http://www.mete.metu.edu.tr/Facilities/Research/SMA/smatext/Twm2.htm>

thermopneumatic and SMA actuators, both of them involve the phase transformation, are capable of generating large forces over long displacements. After a quantitative comparison of these microactuation schemes, the work-output per volume of SMA thin film microactuators exceeds that of the other microactuation mechanisms as shown in Fig. 1.4. In addition, a large achievable stress (500 MPa), and low driving voltage (<5 volts) of SMA thin films suggest a great potential as a primary actuating mechanism for mechanical devices with dimensions in the micron-to-millimeter range and large forces over long displacements.

Figure 1.4 Work per volume versus cycling frequency for various microactuators. Numbers refer to Table 1.1, which also gives details on the calculations. Ideal values, shown with unfilled diamonds, represent the energy available for actuation. Other values (filled diamonds) are based on actual microactuator data (Krulvitch *et al.* 1996).

As an actuator, SMA has some other unique advantages, such as, the sensing ability in operation due to the significant variation in resistance during actuation. This effect can be used to sense the position of an actuator. Actually, during the phase transformation in SMAs, many properties change, such as, the thermal conductivity, coefficient of thermal expansion, resistivity, and Young's Modulus (refer to Appendix A).

Since SMAs have the functions as actuators and sensors, they are promising candidates for micro devices. SMAs can fulfil simple, compact, and reliable mechanisms, which are useful in MEMS. A prototype of micro-robot utilizing SMA is presented in Fig. 1.5. The wireless heat-based SMA micro-robot has a gripper for 100 nm objects and "legs" for mobility. Twelve dots are targets heated by the e-beam or laser; they then conduct the heat to the SMA "muscles" in the legs and gripper to generate the programmed movement. The robot can be sized as small as 2 microns wide by 10 microns long.

Figure 1.5 Artist concept of wireless heat-based SMA micro-robot to the SMA "muscles" in the legs and gripper to generate the programmed movement. The robot can be sized as small as 2 microns wide by 10 microns long^{1,3}.

^{1,3} Technology Innovations, LLC and Innovation On Demand, Inc. July 17, 2003.

Actuator Type	W/V (J/m ³)	Equation	Comments
1. NiTi SMA	2.5×10 ⁷	$\sigma \cdot \varepsilon$	Max. one-time output: $\sigma = 500$ MPa, $\varepsilon = 5\%$
	6.0×10 ⁶		Thousands of cycles: $\sigma = 300$ MPa, $\varepsilon = 2\%$
2. Solid-Liquid Phase Change	4.7×10 ⁶	$\frac{1}{3} \left(\frac{\Delta V}{V} \right)^2 k$	k = bulk modulus = 2.2 GPa (H ₂ O) 8% volume change (acetamide)
3. Thermo-pneumatic	1.2×10 ⁶	$\frac{F \cdot \delta}{V}$	Measured values: F = 20 N, $\sigma = 50$ μ m, V = 4 mm × 4 mm × 50 μ m
4. Thermal Expansion	4.6×10 ⁵	$\frac{1}{2} \frac{(E_s + E_f)}{2} (\Delta \alpha \cdot \Delta T)$	Ideal, nickel on silicon, s = substrate, f = film, $\Delta T = 200^\circ\text{C}$
5. Electro-magnetic	4.0×10 ⁵	$\frac{F \cdot \delta}{V} \quad F = \frac{-M_s^2 \cdot A}{2\mu}$	Ideal, variable reluctance: V = total gap volume, $M_s = 1$ V·sec/m ²
	2.8×10 ⁴	$\frac{F \cdot \delta}{V}$	Measured values, variable reluctance: F = 0.28 mN, $\delta = 250$ μ m, V = 100 × 100 × 250 μ m ³ .
	1.6×10 ³	$\frac{T}{V}$	Measured values, external field: Torque = 0.185 nN·m, v = 400 × 40 × 7 μ m ³
6. Electrostatic	1.8×10 ⁵	$\frac{F \cdot \delta}{A \cdot gap} \quad F = \frac{\varepsilon V^2 A}{2\delta^2}$	Ideal: V = 100 volts, $\delta = \text{gap} = 0.5$ μ m
	3.4×10 ³	$\frac{F \cdot \delta}{V}$	Measured values, comb drive: F = 0.2 mN (60 volts), v = 2 × 20 × 3000 μ m ³ (total gap), $\delta = 2$ μ m
	7.0×10 ²		Measured values, integrated force array: v = device volume, 120 volts
7. Piezo-electric	1.2×10 ⁵	$\frac{1}{2} (d_{33} E)^2 E_f$	Calculated, PZT: $E_f = 60$ GPa (bulk), $d_{33} = 500$ (bulk), E = 40 kv/cm.
	1.8×10 ²		Calculated, ZnO: $E_f = 160$ GPa (bulk), $d_{33} = 12$ (bulk), E = 40 kv/cm
8. Muscle	1.8×10 ⁴	$\frac{1}{2} (\sigma \cdot \varepsilon)$	Measured values: $\sigma = 350$ kPa, $\varepsilon = 10\%$
9. Micro-bubble	3.4×10 ²	$\frac{F \cdot \delta}{V_b}$	Measured values: bubble diam. = 71 μ m, F = 0.9 μ N, $\delta = 71$ μ m

Table 1.1 Work per unit volume for various microactuators (Kruevitch *et al.* 1996).

So far, a number of alloy systems that exhibit the shape memory phenomenon have been found and investigated. Among them, CuZnAl should be the first choice, followed by CuAlNi, if the material cost is taken into consideration. CuZnAl is also the most suitable choice for damping related actuators (Huang 2002). However, the NiTi system has a much higher strength (actuation stress up to 500 MPa), larger recoverable strain (about 7%), and better corrosion resistance. Furthermore, NiTi has good biocompatibility, good wear resistance, high damping capacity and most importantly higher reliability (millions of cycles without loss of actuation properties (Johnson 1991). As a result, NiTi is the most widely investigated and used in the engineering applications. MEMS based on NiTi SMAs have been fabricated to create functional micro-grippers (Kruevitch *et al.* 1996), fluid flow valves (Kahn *et al.* 1997) and pressure regulators^{1,4}. Hence, in the course of this project, the focus is on NiTi only.

Although there have been extensive studies on the behaviour and applications of SMAs, up to date, the study on the microscopic behaviour is still rather limited (Cheng *et al.* 2001, Liu and Li 2001). In recent years, instrumented indentation technique has been used to study small scale mechanical properties (Liu *et al.* 1999, Gall *et al.* 2001) and the SME (Ni *et al.* 2002, Shaw *et al.* 2003) of SMAs. However, the TWSME at micro scale is still undeveloped. The TWSME may be utilized as a simple actuation mechanism for micro actuators, e.g., micro pumpers. Thus, the SME and TWSME behaviours in NiTi at micro scale are chosen as one of the objectives of this project.

In MEMS, NiTi is usually used in the form of thin film. Freestanding annealed NiTi thin films usually show intrinsic TWSME, with large displacement, but relatively small force in actuation. It is applicable in microsensors, microswitches or micropositioners. The nature of this TWSME could be due to intrinsic residual stress in NiTi films, compositional gradient through film thickness, existence of R-phase and hot shaping and aging of NiTi

^{1,4} <http://www.tinialloy.com/products.html>

film resulting in Ti_3Ni_4 precipitates (Fu *et al.* 2004). The constrained film/substrate actuators could provide large actuation force. The substrate may act as an effective biasing force, thus creating a TWSME.

Recently, a localized laser annealing method (He 2004) was proposed for crystallization of NiTi films in our group. In this method, only certain areas of a film are annealed by a laser beam to exhibit the SME, while the rest non-annealed areas remain amorphous. This method opens a new way for fabrication of NiTi SMA microdevices. The advantages of the localized laser annealing process include:

- (1) Precision in selection of the areas to be annealed, as small as in micron-meter;
- (2) Non-contact and efficient;
- (3) Free from restrictions on design and processing;
- (4) Full integration with the traditional MEMS processes.

However, the major drawbacks in this method are that the laser beam must shine from the backside, e.g., the silicon wafer side (He 2004), which is not so convenient from the application point of view, and the repeatability of the resultant shape memory thin film is still a problem. It should be significantly evaluated if amorphous NiTi thin films can be annealed directly and the reliability can be improved.

1.3 Objective of the project

The objective of this report is twofold. One is to study the micro scale properties of NiTi SMA by micro-indentation test and morphology/profile test, focus is on the development of TWSME. The other is to theoretically study the backside CO_2 laser annealing and direct laser annealing of NiTi thin films.

1.4 Scope of the project

The shape memory behavior at micro scale was studied on NiTi bulk samples. Micro-indentation experiments were performed using a CSEM Hardness Tester (CSEM) at different temperatures and different indentation loads. A Vickers indenter was used as spherical indenter cannot produce enough plastic deformation to induce the TWSME. Microscopic SME and TWSME of these indents were probed by a temperature controlled Atomic Force Microscope (AFM) and a WYKO 3-D Surface Interferometer (WYKO).

Theoretical study on backside CO₂ laser annealing and direct laser annealing was based on the previous experiments (He 2004). Four types of lasers, namely, CO₂ (10.6 μ m), HIPPO Nd:YAG laser (1064 nm), Green Nd:YAG laser (532 nm), AVIA Nd:YAG laser (355 nm), were investigated for direct annealing.

1.5 Outline of the report

Chapter 2 presents an extensive literature review to provide the background of SMAs and the equipments and techniques used in this project.

Chapter 3 is the preparation and characterization of materials for indentation tests. It is followed by a series of indentation experiments, which provide a platform for the investigation in Chapter 4.

Chapter 4 is an investigation on the SME and TWSME using AFM and WYKO.

Chapter 5 presents a theoretical study of backside CO₂ laser annealing of NiTi thin films.

Chapter 6 investigates direct laser annealing of NiTi thin films using different lasers.

Conclusions and future works are presented in Chapter 7.

CHAPTER 2

Literature Review

2.1 Basic Knowledge of SMAs

SMAs are quite fascinating materials characterized by the SME and SE, which ordinary metals and alloys do not have. This unique behavior was first found in a Au-47.5at% Cd alloy in 1951 (Otsuka and Wayman 1998), and was publicized by the discovery in a NiTi alloy by the U.S. Naval Ordnance Lab in 1963. Although a relatively wide variety of alloys are known to exhibit the SME, only those that can recover substantial amounts of strain and/or that generate significant force upon changing shape are of commercial interest. Table 2.1 lists a number of these systems. Among them, NiTi and a few of the copper-base alloys have received the most development efforts and commercial exploitations.

NiTi has very good electrical and mechanical properties, long fatigue life, and high corrosion resistance. As an actuator, it is capable of up to 7% strain recovery and 500 MPa restoration stress throughout many cycles (Johnson 1991). The advantages of NiTi become more pronounced as the size of the application decreases.

2.2 Phase transformation

As mentioned in Chapter 1, SME is associated with the phase transformation and reorientation of martensite variants. The martensitic transformation (from austenite to martensite) and its reverse transformation are lattice transformations involving a shearing deformation that results from cooperative atomic movements. Basically, this transformation is caused by the difference in free energy between the two phases as shown in Fig. 2.1 (Huang 1998).

Alloy	Composition	Range of transformation temperature (°C)	Transformation hysteresis (°C)
AgCd	44~49 at % Cd	-190 ~ 50	~ 15
AuCd	46.5~50 at % Cd	30 ~ 100	~ 15
CuAlNi	14~14.5 wt % Al 3~4.5 wt % Ni	-140 ~ 100	~ 35
CuSn	~15 at % X	-120 ~ 30	
CuZn	38.5~41.5 wt % Zn	-180 ~ -10	~ 10
CuZnX (X=Si,Sn,Al)	small wt % X	-180 ~ 200	~ 10
InTl	18~23 at % Tl	60 ~ 100	~ 4
NiAl	36~38 at % Al	-180 ~ 100	~ 10
NiTi	46.2~51 at % Ti	-50 ~ 110	~ 30
NiTiX (X=Pd,Pt)	50 at % Ni+X 5~50 at % X	-200 ~ 700	~ 100
NiTiCu	~15 at % Cu	-150 ~ 100	~ 50
NiTiNb	~15 at % Nb	-200 ~ 50	~ 125
NiTiAu	50 at % Ni+Au	20 ~ 610	
TiPdX (X=Cr,Fe)	50 at % Pd+X ~15 at % X	0 ~ 600	~ 50
MnCu	5~35 at % Cu	-250 ~ 180	~ 25
FeMnSi	32 wt % Mn, 6 wt % Si	-200 ~ 150	~ 100
FePt		~ -130	~ 4
FePd	~25 at % Pt	~ 50	
FeNiX (X=C,Co,Cr)	~30at % Pd small wt % X		

Table 2.1: Alloys with SME (Huang 1998).

Figure 2.1 Phase transformation in NiTi (Huang 1998).

Austenite is the high-temperature (high-energy) phase. In NiTi, it is Body-Centred Cubic (BCC) lattice, which has a B2 structure with $a_0 = 0.3015$ nm. The most common low-temperature (low-energy) phase, martensite, of NiTi is monoclinic 2H structure with $a = 0.2889$ nm, $b = 0.4120$ nm, $c = 0.4622$ nm, and $\beta = 96.8^\circ$. Refer to Fig. 2.1 for a schematic view of B2 and monoclinic 2H structures (Huang 1998).

In order to induce the austenite to martensite transformation, the chemical free energy of the martensite phase must be lower than that of the austenite phase. However, since the transformation requires also non-chemical free energy, such as transformation strain energy, friction energy, etc., the transformation can happen only when the difference between the chemical free energies of the two phases is greater than the necessary non-chemical free energy. Similarly, the transformation from martensite to austenite will occur only when the difference between the above energies, with the signs reversed, is sufficiently large. Thus, a distinguishing characteristic of SMAs is hysteresis, i.e. there is a difference between the forward and reverse transformation paths (Huang 1998). As shown in Table 2.1, the transformation hysteresis varies with the different alloys.

The change of martensite fraction against temperature is illustrated in Fig. 2.2, where the martensite fraction as the vertical axis is the volume percentage of martensite. Upon cooling, pure austenite starts to transform into twinned martensite at M_s (martensite start temperature). Upon further cooling, the martensitic transformation is completed at M_f (martensite finish temperature). Upon heating, the reverse transformation begins at A_s (austenite start temperature) and is completed at A_f (austenite finish temperature).

Figure 2.2 Martensite fraction vs. temperature (Huang 1998).

2.3 SME

At a low temperature, a SMA can be mechanically deformed. This deformation can be recovered by raising the temperature above A_f . Figures 2.3 (a)–(c) schematically illustrate the mechanisms of SME and SE, in which solid lines represent the SME path and dotted lines represent the SE path. Figure 2.3(d) is a series of photographs showing the SME: (1) the SMA wire is straight in the parent phase; (2) the wire is deformed in the martensite state; (3)–(5) the wire reverts to its original shape upon heating to a temperature above A_f .

Figure 2.3 (a)–(c) Schematic illustration of the mechanisms of SME and SE (Otsuka and Kakeshita 2002).

2.4 Two Way Shape Memory Effect

The ability of SMAs to recover a preset shape upon heating above its transformation temperatures and return to an alternate shape upon cooling is known as two-way memory. Two-way memory is unique in that the material "remembers" both the high temperature and low temperature shapes. This phenomenon is known as the two-way shape memory effect (TWSME). Much has been reported about this unique phenomenon in the literature and it has triggered many ideas in the minds of product designers. Some examples of these potential applications include reversible fasteners, temperature-sensitive actuators, retrievable medical implants, and toys and novelty items (e.g. Liu and McCormick 1990).

Creating two-way memory in SMAs involves a somewhat complex training process using one of the following approaches (e.g. Bellouard *et al.* 2003),

- Over-deformation while in the martensitic condition;
- Shape memory cycling (cool $\rightarrow$ deform $\rightarrow$ heat $\rightarrow$ repeat);

- Superelastic cycling (load → unload → repeat);
- Combined shape memory and superelastic cycling;
- Constrained temperature cycling of deformed martensite;
- Constrained aging for long periods of time (to yield the all-round SME which is different from TWSME in the fundamental mechanism), etc.

It is believed that through the training procedure anisotropic dislocation structures are developed in the austenitic matrix (Perkins and Sponholz 1984, Reyhani and McCormick 1986, Contardo and Guenin 1990, Liu and McCormick 1990). The dislocation structures create an anisotropic stress field in the matrix, which guides the formation of martensite into variants of preferential orientations in relation to the deformation adopted in the training procedure, thus resulting in a macroscopic shape change during subsequent thermal transformation cycles.

2.5 Stress vs. strain relationship

The mechanical behavior of SMAs is complicated. Corresponding to different type of transformation, SMA has different stress-strain curves. There are four types of relationships as schematically illustrated in Fig. 2.4 (Funakubo 1987). Figure 2.4(a) is the SME where the heating of SMA results in a full shape recovery after pre-straining and almost linearly unloading. The stress-strain curve of Fig. 2.4(b) is a combination of a superelastic effect and a SME. The stress-strain relation in Fig. 2.4(c) illustrates a complete superelastic effect where unloading of a SMA results in the total recovery of its initial position after going through a mechanical hysteresis, because at a temperature above A_f unstressed martensite is completely unstable in the absence of external stress. The stress-strain relation shown in Fig. 2.4(d) reveals that the SMA has been loaded to its plastic range, with some permanent deformation in crystal lattice resulted. Therefore, heating of the SMA may not restore the material back to its original position anymore.

Figure 2.4 Classification of stress-strain curves (Funakubo 1987).

In addition, tension and compression deformation behaviors of some SMAs can be significantly different as shown in Fig. 2.5. The compressive stress is found nearly 0.4 times higher than that in tension (Huang and Zhu 2002).

Figure 2.5 From tension to compression (NiTi). Dash-dotted line: tension (test); dashed line: compression (test); solid line: compression (prediction) (Huang and Zhu 2002).

2.6 Instrumented indentation technique

2.6.1 Indentation Hardness Testing

Indentation is a very common technique used to characterize hardness, which is a measure of wear resistance and ductility of materials. This technique is also commonly known as microhardness test. The purpose of microindentation hardness test is to study fine scale changes in hardness, either intentionally or accidentally. Microindentation was initially created as a means of quality control during metallurgical processing^{2,1}.

The hardness of a material is determined by forcing an indenter, such as a Vickers or Knoop indenter, into the surface of a material. Normally there are two kinds of shapes of indenters, namely, spherical and sharp. Each indenter has its own advantages and limitations. The indenter employed in the Vickers test is a square-based pyramid whose opposite sides meet at the apex at an angle of 136° (Vander Voort and Lucas 1998). The diamond is pressed into the surface of the material at a load ranging up to approximately 120 Kg with the size of the impression usually less than 0.5 mm. The Vickers number (HV) is calculated as (Vander Voort and Lucas 1998)

$$HV = 1.854 \frac{F}{D^2} \quad (2.1)$$

where F is the applied load (in kilograms-force) and D^2 the area of the indentation (measured in square millimeters). The applied load is usually specified when HV is cited. In this project, Vickers indenter, a sharp diamond indenter (Fig. 2.6) was used to probe the mechanical properties of NiTi.

^{2,1} <http://www.calce.umd.edu/general/Facilities/indent.htm>

Figure 2.6 Schematic diagram showing the shape of Vickers indenter and impression (Vander and Lucas 1998).

2.6.2 Instrumented indentation technique

More recently, instrumented indentation technique has become popular as it provides a continuous record of the variation of indentation load, P , as a function of the depth of penetration, h , into the indented specimen, from which mechanical properties such as hardness, elastic modulus, yield strength and strain hardening exponent can be estimated (Giannakopoulos and Suresh 1999, Venkatesh *et al.* 2000).

In an instrumented indentation test, the indenter is driven into a specific site of the material to be tested by applying an increased normal load [Fig. 2.7(a)]. Upon reaching a prescribed value, the normal load is removed. The position of the indenter relative to the sample surface is precisely monitored. For each loading/unloading cycle, the applied load is recorded against the corresponding position of the indenter [Fig. 2.7(b)]. The resulted load/depth curve provides data specific to the mechanical nature of the material under examination. Well established models can be used to obtain the hardness and modulus of

the material (VanLandingham 2003).

(a) Illustration of instrumented indentation test.

(b) Typical result.

Figure 2.7 Indentation for hardness and modulus measurements (VanLandingham 2003).

To study the mechanical properties of SMAs at a scale of micrometer, microindentation is preferred over nanoindentation at present as the deformation behavior may be affected by the size and orientation of crystal grains, since the grain size of NiTi is normally at a submicro level.

2.6.3 Basic knowledge

In this project, the Oliver-Pharr method (Oliver and Pharr 1992) was applied to acquire hardness and elastic modulus. Figure 2.8 schematically shows an indentation load-depth curve with a sharp indenter. The indentation load increases at a constant rate and leads to a nonlinear increase of the penetration depth. $h_{\max}$ is the maximum depth at the maximum load $P_{\max}$. The curve follows the Kick's law, i.e., $P = Ch^2$, where C is the indentation curvature. Kick's Law is not valid in the rate-dependent cases as the loading rate, and thus the material strength, varies during the impact. When the material response is rate-sensitive, C is not a constant and instead varies with the loading rate (Andrews *et al.* 2002). With a sharp indenter, the loading process is always elastic-plastic, while the unloading is basically elastic.

Figure 2.8 Typical indentation load depth curve (Giannakopoulos and Suresh 1999).

Hardness and some other material properties can be obtained from the load-depth curve. Hardness is normally defined as the mean contact pressure (Oliver and Pharr 1992) and is given as,

$$H = \frac{P_{\max}}{A_p} \tag{2.2}$$

where A_p is the projected contact area at the maximum load (Fig. 2.9). For a perfect Vickers indenter, $A_p = 24.5h_c^2$.

Another way to define hardness is through energy approach (Stilwell and Tabor 1961). The energy approach utilizes the area under the depth-load curve to acquire the elastic and plastic energies during indentation. It is a convenient method for extracting mechanical properties.

Figure 2.9 Schematic representation of the indentation process. h_c is the contact depth, h_s is the depth of the surface at the perimeter of contact and a is the radius of the contact circle defined by the indenter (VanLandingham 2003).

The energy approach was first proposed by Stilwell and Tabor (1961). They suggested that the conventional representation of hardness, Eqn. (2.3), is equivalent to the plastic work divided by the plastically deformed volume, i.e.,

$$\frac{P_{\max}}{A_p} = \frac{W_p}{V_p} \quad (2.3)$$

where W_p is the plastic work during the indentation process, V_p is the plastically deformed volume in the indented material. The right part of Eqn. (2.3) reflects the deformation extent of the indented materials and can be understood as the energy expenditure per unit volume during indentation. Tuck *et al.* (2001) reported that the energy approach method appears to be less sensitive than other definitions to the effects of pile-up observed in many materials. They also concluded that the plastic energy approach performs uniformly well for the full range of materials from soft and ductile to hard and brittle. The plastic work energy hardness is given by

$$H_p = \frac{\kappa P_m^3}{9W_p^2} \quad (2.4)$$

where $\kappa = 0.0378$ for Vickers indenter and W_p is the plastic work.

Elastic modulus can also be determined by an indentation test. According to Oliver-Pharr method (Oliver and Pharr 1992), the indentation modulus, E , can be calculated from the slope of the tangent of the unloading curve using a linear fit to the initial unloading data, i.e.,

$$E = \frac{1 - \nu_s^2}{\frac{1}{E_r} - \frac{1 - \nu_i^2}{E_i}} \quad (2.5)$$

where E_i is the elastic modulus of the indenter (1141 GPa for diamond), ν_i is the Poisson's ratio of the indenter (0.07 for diamond) and ν_s is the Poisson's ratio of the tested sample. The reduced modulus, E_r , is given by,

$$E_r = \frac{\sqrt{\pi}}{2\beta\sqrt{A}} \left(\frac{dP}{dh} \right) \quad (2.6)$$

where $S = dP/dh$ is experimentally measured stiffness of the upper portion of the unloading curve and β is a correction factor.

The hardness and elastic modulus derived from the Oliver and Pharr's method are apparent hardness and elastic modulus. However, for SMAs, conventional methods may not be applicable, since the indentation process is a combination of the stress-induced martensitic transformation, martensite reorientation and elastic/plastic deformation.

Figure 2.10 Total deformation energy and recovery deformation energy (high lighted).

(a) Total deformation energy; (b) recovery deformation energy.

Another important issue in the indentation technique is the energy recovery ratio (Liu *et al.* 1999). Refer to Fig. 2.10, W_t , the total deformation energy, is represented by the area enclosed by the loading curve and the maximum penetration depth, i.e.,

$$W_t = \int_0^{h_{\max}} P dh \quad (2.7)$$

where P is the applied load, h is the penetration depth and $h_{\max}$ is the maximum depth at the maximum load. The area enclosed by the unloading curve and the maximum penetration depth represents the recoverable deformation energy, i.e.,

$$W_r = \int_{h_r}^{h_{\max}} P dh \quad (2.8)$$

where h_r is the residual depth when the load is decreased to zero. The integration is

performed along the unloading curve. The ratio of the recovery (η) is defined as,

$$\eta = \frac{W_r}{W_t} \quad (2.9)$$

As the applied load reaches a prescribed value at time t_1 , it is maintained until time t_2 . $h_2 - h_1$ signifies the relative change of the indentation depth. The indentation creep, C_{IT} , defined as the relative change of the indentation depth whilst the applied load remains constant (Fig. 2.11), i.e.,

$$C_{IT} = \frac{h_2 - h_1}{h_1} \cdot 100 \quad (2.10)$$

Figure 2.11 Indentation creep C_{IT} .

2.6.4 Indentation size effect

A peculiar phenomenon known as the “indentation size effect” has been observed in a variety of materials (e.g., Nix and Gao 1998). For crystalline materials, wherein the hardness is observed to increase with the decrease of indentation size, large strain gradients inherent in small indentations lead to geometrically necessary dislocations that cause enhanced hardening. The hardness of a material depends on the characteristic length that

depends on the shape of the indenter. The relation between hardness and depth is given by Nix and Gao (1998) as

$$\frac{H}{H_0} = \sqrt{1 + \frac{h^*}{h}} \quad (2.11)$$

where

$$H_0 = 3\sqrt{3}\alpha\mu b\sqrt{\rho_s} \quad (2.12)$$

is the hardness that would arise from the statistically stored dislocations alone, in the absence of any geometrically necessary dislocations, and

$$h^* = \frac{81}{2}b\alpha^2 \tan^2 \theta \left(\frac{\mu}{H_0} \right)^2 \quad (2.13)$$

is a length that characterizes the depth dependence of the hardness. ρ_s is the density of statistically stored dislocations, μ is the shear modulus, b is the Burgers vector, α is a constant and θ is the angle between the surface of the conical indenter and the plane of the material surface.

2.6.5 Deformation at the tip of sharp indenter

Stress field caused by indentation is more complex than uniform uniaxial compression. During indentation the stress field is three-dimensional and has significant spatial gradients. Examination of the principal stresses for sharp indentation reveals that although tensile stresses are inevitable, the compressive stresses are nearly an order of magnitude higher (Lawn and Wilshaw 1975). Moreover, the largest compressive stress generates along a direction parallel to the surface normal, with the transverse tensile and compressive stresses having relatively small values.

Stress beneath the Vickers indenter during indentation process is very high. A general theoretical framework for sharp indentation has been proposed by Giannakopoulos and Suresh (1999). Results of experiment (e.g., Chaudhri 1998) and analysis (e.g., Giannakopoulos *et al.* 1994) show that there exists a unique characteristic equivalent plastic strain, which separates different modes of plastic deformation directly beneath the sharp indenter.

It was found that the average contact pressure, $P_{av} = P/A$, depends only on the inclined angle at the tip of the indenter, but not on the indentation load P or the true contact area A (Giannakopoulos *et al.* 1994, Chaudhri 1998). This average contact pressure is associated with the hardness H .

Figure 2.12 Schematic of different regimes of plastic flow at the tip of a sharp indenter (Giannakopoulos and Suresh 1999).

The innermost region comprises a zone where the material is “cut” by the sharp indenter. This cutting mode can be analyzed by means of the classical slip-line theories of rigid-perfect plasticity. Surrounding this region is a zone of strong gradients in plastic strain which is engulfed by an elastoplastic regime, where the so-called “cavity” model of

Johnson (1985) can be applied to extract the hemi-spherically shaped elastoplastic boundary. A unique characteristic strain separates the innermost “cutting” region from its surroundings. Although Tabor (1951) proposed a value of 0.08 for this characteristic plastic strain, more elaborate studies (e.g. Giannakopoulos *et al.* 1994, Chaudhri 1998) suggest a value in the range of 0.25 ~ 0.36.

2.6.6 “Pile-up” and “sink-in”

Pile-up and sink-in are the distinctive features in indentation experiments. The material around the contact area tends to deform upwards (pile-up) or downwards (sink-in) along the direction of the load (Fig. 2.13).

Figure 2.13 Schematic illustrations of (a) pile-up and (b) sink-in around a sharp indenter (Giannakopoulos and Suresh 1999).

Alcala *et al.* (2000) found that the deformation of pile-up or sink-in is correlated with the uniaxial strain hardening exponent. If the strain hardening exponent $n > 0.2$, sink-in is

dominant. Giannakopoulos *et al.* (1994) interpreted the deformation mode with computation results. They found that the pile-up or sink-in in a material around the indenter is primarily affected by the plastic properties of the material. Plastically displaced material tends to flow up to the faces of the indenter in a low-strain-hardening alloy due to the incompressibility of plastic deformation. The result is a “barrel-shaped” impression due to pile-up around the sharp polygonal indenter. On the other hand, for high-strain-hardening materials, the plastically deformed region is pushed out from the indenter with the imprint sinking below the initial surface level. The result is a “pin-cushionlike” impression around the sharp indenter. Methods, which are properly account for pile-up and sink-in around the indenter, are essential for the interpretation of the plastic properties of materials by recourse to instrumented indentation. It also influences hardness measurements as the true contact area between the indenter and the specimen increases in the case where pile-up predominates, and decreases in the event that sink-in occurs.

For convenience, Giannakopoulos and Suresh (Giannakopoulos *et al.* 1994, Suresh *et al.* 1997) proposed a new method which enables the determination of elastic and plastic properties of materials by employing instrumented sharp indentation. The method is named as a step-by-step method for sharp indentation tests as briefly described in Section 2.6.7.

2.6.7 Step-by-step method for sharp indentation test

According to the Oliver and Pharr method, the projected contact area for a perfect Vickers indenter is

$$A_p = 4h_c^2 \tan^2 \alpha = 24.5h_c^2 \quad (2.14)$$

The parameter α refers to the face angle of the Vickers indenter (68°) and h_c is the contact depth. Since the Oliver-Pharr method is based on elastic contact solutions and works well for hard ceramics, where sink-in predominates but fails with soft metals that display

extensive pile-up. When pile-up is significant, the Oliver-Pharr approach underestimates the true contact area by as much as 60%. This error in contact area then causes errors in hardness and modulus. Giannakopoulos and Suresh's method provides a new approach to determine the elastoplastic properties for sharp indentation tests without detecting contact area through visual observations (Giannakopoulos and Suresh 1999). This method also provides the correlation between penetration depth h and true contact area A and takes into account pile-up and sink-in. From the load-depth curve of an indentation test, the maximum indentation depth $h_{\max}$, the residual depth h_r , the indentation curvature $C = P/h^2$ and the initial unloading slope dP/dh can be determined.

The proposed method involves the following steps,

- Experimentally obtain $P - h$ curve using Vickers indenter.
- Identify $h_{\max}$ and h_r .
- Find $S (= P_{av}/E^*)$ from

$$S = \frac{P_{av}}{E^*} = (1 - \frac{h_r}{h_{\max}}) / d^* \quad (2.15)$$

where $d^* = 5$ for the Vickers pyramid indenter. S can also be estimated through the energy approach in Eqn.(2.15) as

$$S = (\frac{W_c}{W_t}) / d^* = (1 - \frac{W_p}{W_t}) / d^* \quad (2.16)$$

- Determine the true contact area at the maximum load $A_{\max}$.

$$A_{\max} = h_{\max}^2 \left[9.96 - 12.64(1-S) + 105.42(1-S)^2 - 229.57(1-S)^3 + 157.67(1-S)^4 \right] \quad (2.17)$$

- Calculate the effective elastic modulus of the indenter-specimen system, E^* , by

$$E^* = \frac{1}{c^* \sqrt{A_{\max}}} \left(\frac{dP}{dh} \right) \quad (2.18)$$

where $c^* = 1.142$ for the Vickers indenter.

- Find $(\sigma_{0.29} - \sigma_y)$,

$$\sigma_{0.29} - \sigma_y = 0.29E^* \left[1 - 0.142 \frac{h_r}{h_{\max}} - 0.957 \left(\frac{h_r}{h_{\max}} \right)^2 \right] \quad (2.19)$$

- With $P_{\max}$ and $h_{\max}$ identified from the $P - h$ curve, and $P_{\max} \approx Ch_{\max}^2$, C can be estimated. σ_y and $\sigma_{0.29}$ can be obtained by

$$C = \frac{P}{h^2} = M_1 \sigma_{0.29} \left\{ 1 + \frac{\sigma_y}{\sigma_{0.29}} \right\} \left\{ M_2 + \ln \left(\frac{E^*}{\sigma_y} \right) \right\}, \text{ for } 0.5 \leq \frac{P_{av}}{\sigma_y} \leq 3.0 \quad (2.20)$$

- The strain hardening exponent $n \approx \ln \{ \sigma_{0.29} - \ln(\sigma_y) \} / 5$.

2.6.8 Indentation behavior in SMAs

SMAs, in particular NiTi, have been tested by instrumented indentation technique in recent years to probe the wear resistance or erosion resistance (Liu and Li 2000, Cheng *et al.* 2001, Cheng *et al.* 2003). Gall *et al.* (2001) gave a brief review of instrumented microindentation on NiTi and proposed a schematic critical deformation mechanisms during indentation (Fig. 2.14).

The hardness of NiTi SMAs depends on the resistance of deformation due to dislocation motion (plastic deformation) and martensite formation/reorientation (Fig. 2.14). The area under the unloading portion of the indentation load–depth curve quantifies the recoverable energy. Deformation energy is recoverable through lattice relaxation or a reverse martensitic transformation. The area between the loading and unloading portions of the indentation load–depth curve quantifies the dissipated energy.

Liu *et al.* (1999) investigated the microscale superelastic behavior of a Ti-51at%Ni alloy by instrument indentation technique. It was demonstrated that superelastic behavior exists

during indentation that involves compressive stress and may be characterized by its recovered deformation energy. And the higher the degree of the superelastic effect (SE) is, the larger the recoverable deformation energy is. Ni *et al.* (2003, 2004) also observed the microscopic SE behavior of a NiTi alloy under complex loading conditions. Nanoscale SE behavior of indented NiTi films was reported by Ma and Komvopoulos (2003). Results revealed that SE behavior also exists at the nanoscale. The significance of normal load, nanoindenter tip radius and partial unloading on the transition from SE to elastic-plastic deformation of NiTi films was studied. The mechanisms of the reversible phase transformation and the energy dissipation in NiTi films exhibiting SE were subsequently interpreted.

Figure 2.14 Schematic diagram illustrating the different microstructural mechanisms leading to material hardness, energy dissipation and energy recovery during indentation of NiTi SMAs (Gall *et al.* 2001).

As for SME in indentation, Ni *et al.* (2002) have shown that thermally activated martensitic transformations allow recovery of microscale spherical or Vickers indentations in bulk NiTi. The same effect was observed in NiTi thin films on nanoscale by Shaw *et al.* (2003). Further study by Ni *et al.* (2004) showed the magnitude of deformation and recovery of NiTi alloys with pyramidal and spherical indenters. The results also suggest that the recovery ratios in both the SME and SE are independent on the depth for both Berkovich

and Vickers indenters.

2.6.9 Indentation rate

The indentation loading rate might be a factor that should be taken into consideration in SMAs. Leo *et al.* (1993) and Shaw and Kyriakides (1997) demonstrated that under mechanical cycling, the temperature in SMAs changes due to latent heat generated/absorbed during the phase transformation. The change of temperature during loading alters the stress-strain response and induces rate dependence as shown in Fig. 2.15.

Figure 2.15 Stress-strain curves of austenite (right) and martensite NiTiCu (left) (Kishi, *et al.* 2000).

2.7 Laser annealing of NiTi thin films

2.7.1 NiTi thin films

The first reported work on the integration of NiTi shape memory thin films into the silicon micromachining process is probably the one by Walker *et al.* (1990). They sputter-deposited NiTi films onto polyimide/gold coated substrates, patterned the NiTi films with a wet chemical etchant containing hydrofluoric and nitric acids, removed the polyimide/gold sacrificial layer, and then post annealed to produce free standing SMA thin

film springs. At almost the same time, A. D. Johnson vacuum-sputter-deposited NiTi shape memory films on heated substrates to fabricate valves which can be cycled at a rate of 20 Hz for more than two million times (Johnson 1991). These works have successfully demonstrated the possibility of producing micro-scale shape memory devices using IC processing techniques. After these pioneer works, intensive investigations on the deposition parameters, post-deposition heat treatment and micromachining techniques have been carried out to obtain optimum SMA thin films.

At present, there are several techniques to fabricate SMA films, namely, sputter deposition, pulse laser deposition, flash evaporation, ion beam sputter deposition and electron beam evaporation (He 2004). Among them, sputter deposition is widely used. Sputter deposition is a technology in which the materials are released from the sources at a much lower temperature than that of the evaporation. Various types of substrates, such as silicon, polyimide and glass, are placed in a vacuum chamber filled with gas (e.g., argon) at a low pressure, together with the source materials (targets). Gas plasmas are struck using an RF power source, causing the gas ionized. The ions are accelerated towards the surface of the targets, causing the atoms of the source materials to break off from the targets in vapor form and condense on the substrates for thin film deposition.

The properties of the deposited NiTi thin films have been investigated for some years. To name a few, Miyazaki and Ishida (1999) reported both the phase transformation and shape memory effect, Ishida *et al.* (1999) studied their mechanical properties, Surbled *et al.* (2001) investigated the effects of the composition and thermal annealing on the transformation temperatures, Fu and Du (2002) investigated the relaxation and stress recovery in the phase transformation, and Ishida *et al.* (1996) studied the stress-strain relations of sputtered NiTi thin films.

2.7.2 Laser annealing of NiTi SMAs

Laser annealing is a kind of laser surface treatment, which makes use of the rapid heating and cooling rates produced on metal surfaces exposed to scanning laser beams. This kind of laser heat treatment involves solid-state transformations. In laser annealing, the fraction of the beam power absorbed by a material is controlled by the absorptivity of the material surface. In many cases, the absorptivity is relatively low, especially for smooth surface and high electrical conductive materials. When the wavelength of a laser beam increases, the absorption normally decreases. Laser local annealing of cold-rolled NiTi shape memory thin sheets has been reported recently (Bellouard et al 1999, Bellouard et al 2000). A sample is shown in Fig. 2.16. The annealed part exhibits the shape memory effect, while the remaining non-annealed part is still elastic. Since cold-rolled sheets, which cannot be well integrated with the micro-machining process, have rougher surfaces than that of the sputter deposited films, a new technique has to be developed for annealing sputter deposited NiTi thin films, which have a surface roughness only about a few nanometers (He 2004).

Figure 2.16 SMA gripper: design and prototype (highlighted black area represents the partially annealed part). Dimensions: $1.4 \times 1.8 \text{ mm}^2$ (Bellouard *et al.* 1999).

2.7.3 Backside CO₂ Laser annealing of NiTi thin films (He 2004)

A continue-wave CO₂ laser (48-2 KWJ, SYNRAD) was used to anneal NiTi thin films

deposited by a DC/RF sputtering machine with an argon atmosphere of 1 mTorr. The experimental setup is schematically illustrated in Fig. 2.17. The laser beam was in TEM00 mode, 10.6 μm -wavelength, and 25 W. Figure 2.18 shows an annealed single line of about 120 μm in width. The investigation demonstrates that CO₂ laser is an effective technique for local annealing of NiTi thin films. However, further study should be carried out on the exact mechanism of laser annealing of NiTi thin films. This is critical in improving the repeatability and the consistency of the process, both are problems shown in He (2004).

Figure 2.17 Schematic illustration of backside CO₂ laser annealing (He 2004).

Figure 2.18 CO₂ laser annealed line (photo taken at room temperature, He 2004).

CHAPTER 3

Sample Preparation, Characterization and Indentation Test

3.1 Sample preparation and characterization

Specimens used in the present study were cut from a NiTi alloy ingot. They were machined into dimensions of 20×20×10 mm, and then heat-treated at 500°C for 60 minutes. The composition was determined by an Energy Dispersive X-ray (EDX) analysis as Ti-50.6at%Ni.

One of the most widely used technique to determine the phase transformation temperatures is Differential Scanning Calorimeter (DSC) test, which measures the heat flow into (endothermic) or out of (exothermic) a material as it undergoes a phase change. DSC test was carried out between –50°C and 120°C at a heating/cooling rate of 5°C per minute. As we can see in Fig. 3.1, upon cooling from the high temperature austenite phase, it begins to transform into martensite phase at about 27°C (M_s). The martensitic transformation finishes at about 12°C (M_f). Upon heating from the low temperature martensite phase, it starts to transform into austenite at about 14°C (A_s) and finishes at about 35°C (A_f). It is clear that the material can be of different phase at room temperature (about 23°C), depending on the thermal history. If the sample is cooled down to room temperature from a high temperature (above A_f), the majority of the sample is austenite. If the sample is heating up to room temperature from a low temperature (below M_f), both austenite and martensite exist in the material.

Figure 3.1 DSC curve of Ti-50.6at%Ni sample.

In order to get very smooth surface for later experiments, the samples were mechanically polished after heat treatment. Polishing was done in three steps. In the first step, the samples were grinded using #1000 sand papers. Subsequently, 3 μm polishing pads and 3 μm diamond paste were used for further polishing. In the last step, polishing was done at about 100°C using 1 μm polishing pads and 1 μm diamond paste. Referring to the DSC test in Fig. 3.1, the material is austenite at 100°C. After polishing, the samples were cleaned by water and alcohol. The average surface roughness, R_a , is less than 100 nm as measured by a Shimadzu 9800 AFM.

X-ray diffraction (XRD) test was used to determine the crystalline structures of the material. The XRD results at room temperature following different thermal histories are presented in Fig. 3.2.

(a)

(b)

Figure 3.2 XRD results. (a) Heated up to 130°C and then cooled down to room temperature; (b) cooled by liquid nitrogen and then heated to room temperature in air.

3.2 Indentation test

Indentation test was carried out and the basic mechanical properties, such as hardness and elastic modulus, of the NiTi SMA were obtained. The results of these tests serve as a foundation for further investigation of one-way and two-way shape recovery in Chapter 4.

3.2.1 Experimental Setup and Procedure

Two sets of experiments, namely, constant temperature test and constant load test, were performed. The constant temperature test aimed to study the load-dependence in indentation, while the constant load test was to investigate the temperature dependence in indentation. Same experimental setup was used for both sets of experiments.

- Experimental setup

Indentation experiments were conducted using a CSEM Hardness Tester from the CSEM Instruments with a displacement resolution of 0.3 nm and a force resolution of 0.1 mN. The Poisson coefficient of the diamond indenter is 0.07 and the Young's modulus is 1141 GPa. A Peltier effect heat pump was stuck to the bottom of the sample for temperature as illustrated in Fig. 3.3. The Peltier pump can cool or heat a sample within a temperature range from 0°C to 80°C. However, many dewes emerge on the sample surface at a temperature lower than 14°C.

- Constant temperature (room temperature) test

Before an indentation test, the NiTi sample was heated to 100°C and then cooled down to room temperature in air. DSC result reveals that austenite is dominant after this thermal process. Then, the test was carried out at different indentation loads and indentation rates. The indentation loads were selected from 100 mN to 1000 mN with a step of 100 mN. Three different loading rates, namely, 100 mN/min, 300 mN/min and 500 mN/min, were applied. In all tests, upon reaching the maximum indentation load, there was a 20 s holding

period before unloading at the same rate as that in loading. Hardness and elastic modulus were calculated from the measured P - h curve. Each test was repeated five times and their average was used in the analyses.

Additional tests were carried out at 11°C with maximum loads from 100 mN to 1000 mN. At each maximum load, the test was carried out only once. The results of these tests are not present here but will be used in Chapter 4.

Figure 3.3 Illustration of experimental setup.

- Constant load test

In these tests, a Peltier pump was used for cooling or heating samples. The temperature on the top surface of the sample was measured by a digital thermometer. Before each test, the indenter was held very closely to the surface of the sample for about 60 s in order to let the tip of the indenter has almost the same temperature as the tested sample.

In testing, the sample was first heated up from 11°C to 60°C and then cooled down to 11°C. During thermal cycling, indentation test was carried out at some selected temperatures under a fixed indentation load of 1000 mN and at a constant loading/unloading rate of 2000 mN/min. At each temperature, same indentation test was repeated five times.

3.2.2 Results

- Constant temperature test

Some typical results are presented in Fig. 3.4. The dashed lines are measured load-depth curves acquired directly from the CSEM microhardness tester. The solid lines are the average in respect to the applied load of five measured ones. The average load-depth curves are summarized in Fig. 3.5. These average curves are grouped under different loading rates in Fig. 3.6 for easy comparison.

- Constant load test

Upon thermal cycling, indentation test was carried out at some selected temperatures. A few typical results are presented in Fig. 3.7 for the heating process, while Fig. 3.8 is that of the cooling process. Some average results are shown in Fig. 3.9.

3.2.3 Analysis and discussion

The typical stress-strain relationships of a SMA of different initial phases, namely, austenite and martensite, upon loading at a constant temperature are illustrated in Fig. 3.10. Similar to Fig. 2.12, different phase regimes in a SMA at the tip of a sharp indenter can be schematically estimated as shown in Fig. 3.11.

As shown in Fig. 3.11(a), if the indentation test is performed at a low temperature ($<M_f$), the innermost regime is plastically deformed. Surrounding this regime is a zone of detwinned martensite. The outer regime is the twinned martensite. At a high indentation temperature ($>A_f$), the plastic zone is also surrounded by detwinned martensite, while the outer zone is austenite, Fig. 3.11(b). At an indentation temperature between A_f and M_f , austenite and twinned martensite may coexist in the outer region. Ignoring the contribution from small elastic deformation, upon unloading at the same high temperature ($>A_f$), only detwinned martensite in Fig. 3.11(b) recovers to austenite while the plastically deformed part remains.

Figure 3.4 Typical load-depth curves of constant temperature test.

(a)

(b)

(c)

(d)

(e)

(f)

Figure 3.5 Indentation results under different indentation loads of constant temperature test.

Solid line: 100 mN/min; dotted line: 300 mN/min; dashed line: 500 mN/min.

Figure 3.6 Average load-depth curves of different loads at different loading rates: (a) 100 mN/min, (b) 300 mN/min, (c) 500 mN/min.

Figure 3.7 Typical load-depth curves in heating of constant load test.

Figure 3.8 Typical load-depth curves in cooling of constant load test.

(a)

(b)

Figure 3.9 Average load-depth curves at different indentation temperatures in thermal cyclic test. Indentation load is 1000 mN. (a) Upon heating; (b) upon cooling.

Figure 3.10 Typical stress-strain curves of SMA upon loading at constant temperature.

Solid line: initial phase is austenite; dashed line: initial phase is martensite.

Figure 3.11 Illustration of phase regimes at the tip of a sharp indenter.

In both constant temperature test and constant load test, the measured load-depth curves disperse to some extent among the tested points (referring to Figs. 3.4, 3.7, 3.8). Previous experimental results have demonstrated that the crystal orientation has a strong influence on the indentation response in NiTi single-crystals (Gall *et al.* 2001). Gall *et al.* found that

the crystal with a surface normal oriented along [100] direction has the highest hardness value. This observation is consistent with the fact that, under the uniaxial stress state, specimens with an orientation close to [100] have the highest resistance to dislocation motion as compared with the other orientations (Sehitoglu *et al.* 2000). On the other hand, crystals with a [221] surface orientation consistently demonstrate the lowest hardness value (Gall *et al.* 2001). Hence, in a polycrystalline NiTi in which grains are oriented randomly, the indentation response may vary with the orientations of the grains under the indenter's tip. This is an important issue in nano-sized tips, but not in the current study.

- Constant temperature test

Effect of loading rate

As mentioned in Chapter 2, under a given stress state, the exact stress-strain relationship of a SMA is dependent on the applied strain rate partially due to the effects of latent heat in the phase transformation. According to the DSC result (Fig. 3.1), at room temperature, austenite is dominant in the material. During indentation, the stress-induced martensitic transformation and plastic deformation occur. As latent heat is released in the austenite to martensite transformation, sample is heated. Apart from that, plastic deformation also generates some heat, although it is relatively small as compared with the latent heat. In the martensite to austenite transformation upon unloading, which is somehow very much limited in our case, latent heat is absorbed. Thus, in theory, the indentation behavior of SMAs is supposed to be altered by the loading/unloading rate. However, Fig. 3.5 shows that there is not much difference among these curves at different loading rates in all applied loads. Figure 3.12 plots the average maximum indentation depth $h_{\max}$ and residual depth h_r against the maximum indentation load relationship. The curves at different loading rates overlap well. It also reveals that austenite NiTi is seemingly rate-independent in the tested loading rate range. This can be explained as the result that the heat generated around the indenter tip is transferred quickly into the surrounded bulk NiTi. As such, the influence of

loading rate is rather limited.

Figure 3.12 Average h_{max} and h_r under different loads of constant temperature test.

Apparent hardness

Indentation hardness of austenite NiTi is plotted in Fig. 3.13 against the depth at three loading/unloading rates, namely, 100 mN/min, 300 mN/min and 500 mN/min. It reveals that as a general trend, the hardness decreases with the increase of indentation depth and all curves more or less coincide.

Effect of indentation size

According to Eqn. (2.11), the square of the hardness plotted against the reciprocal of the indentation depth should result in a more or less linear relationship between them (Nix and Gao 1998). This is not so apparent in the tested NiTi samples as shown in Fig. 3.14.

Figure 3.13 Depth dependence of apparent hardness of austenite NiTi in constant temperature test.

Figure 3.14 Depth dependence of hardness in NiTi.

Apparent elastic modulus

Figure 3.15 presents the elastic modulus obtained using the Oliver-Pharr method against the indentation load relationship at different loading rates. It reveals that the changes in both indentation rate and maximum indentation load have no apparent influence on the elastic modulus. This is different from that reported in Liu and Xiang (1998) in which the

apparent elastic modulus of elasticity decreases with the increase of strain in both austenite and martensite NiTi upon uniaxial tensile loading. As the stress state in the sample under indentation test is rather complex, at this point, it is difficult to provide a direct link between the elastic modulus obtained by the Oliver-Pharr method in indentation test to that of the same material under uniaxial tension test.

Figure 3.15 Apparent elastic modulus of NiTi measured at different loads.

Indentation creep (C_{IT})

Indentation creep is a measure of the loading rate effect on creep penetration (Δh) and C_{IT} . Figure 3.16 plots the change of depth upon holding for 20 s at the maximum load. It appears that a higher loading rate results in a larger Δh , which means a higher creep strain rate. The relationship of C_{IT} vs. load at different loading rates is presented in Fig. 3.17. C_{IT} decreases with the increase of indentation load, which is consistent with the trend of hardness against indentation load relationship. A higher loading rate also results in a higher C_{IT} .

Figure 3.16. Depth change upon holding (20 s) at the maximum load.

Figure 3.17. C_{IT} at different loading rates.

Energy analysis

Fig. 3.18 plots the maximum indentation depth $h_{\max}$ and total deformation energy W_t at

different indentation loads. Both $h_{\max}$ and W_t increase with the applied load monotonously, but the former is from gradual to sharp as the applied load increases, while that of the latter is reversal. The recoverable deformation ratio (η) at different loads is shown in Fig. 3.19. Similar to the trend in apparent hardness, η decreases with the increase of load sharply at first and then turns to be seemingly stable. This is consistent with the result previously published in Gall *et al.* (2001). As explained by Gall *et al.* (2001), at a small indentation load, dislocations are inhibited from moving and the critical stress for inducing martensite is high. The low mobility of dislocations promotes high local stress and a large component of elastic strain, which is recoverable upon unloading. At a large indentation load, dislocations move more freely, resulting in permanent plastic strain and a loss of recoverability due to elastic relaxation.

Figure 3.18. Total deformation energy W_t and maximum indentation depth at different loads.

Figure 3.19 Recoverable deformation ratio (η) against load.

- Constant load test

Indentation depth

From Fig. 3.9, indentation load-depth curves upon heating and cooling, the maximum indentation depth h_{max} and residual depth h_r at some selected temperatures in a thermal cycle are obtained and plotted in Figs. 3.20 and 3.21, respectively. They are plotted together with the DSC result for easy comparison of the transformation temperatures. As shown, the difference between austenite and martensite is apparent, especially for h_r , but the transformation temperatures are not coincident with that from the DSC result. Both h_{max} and h_r are lower in the austenite phase. The major reason is because, according to the stress-strain curve of SMAs in Fig. 3.10, the total strain is lower at a lower temperature under the same stress.

Figure 3.20 Maximum indentation depth at some selected temperatures together with the DSC result.

Figure 3.21 Residual indentation depth at some selected temperatures together with the DSC result.

Ignoring the small elastic deformation, h_r is the result of plastic deformation plus the phase transformation at a low temperature. However, at a high temperature without any martensite at all, plastic deformation is the major contributor to the residual deformation.

Apparent hardness

Apparent hardness measured at some temperatures is shown in Fig. 3.22. Ordinary metals and alloys are hard at low temperature and soft at high temperature. SMAs are opposite as austenite is normally harder than martensite. Upon heating/cooling, the hardness increases/decreases smoothly. Note that in SMAs, W_p derived from the load-depth curves is not merely plastic work but including the work of the martensitic transformation and/or reorientation as well. To avoid error caused by pile-up or sink-in, the plastic work energy hardness defined by Eqn. (2.4) is calculated and presented in Fig. 3.23. It reveals that plastic work energy hardness has two apparent stages. However, the transition temperatures obtained from the DSC result and the hardness measurement are not coincident.

Figure 3.22 Apparent hardness at some selected temperatures together with the DSC result.

Figure 3.23 Nominal plastic work energy hardness at some selected temperatures together with the DSC result.

Apparent elastic modulus

Apparent elastic modulus measured at some selected temperatures under an indentation load of 1000 mN is shown in Fig. 3.24. It is clear that the apparent elastic modulus of martensite is significantly lower than that of austenite. Upon heating, elastic modulus increases at first and then keeps constant and increases again at a temperature above 50°C. Upon cooling, the elastic modulus gradually decreases all the way.

Indentation creep

Indentation creep test shows no distinct regularity (Fig. 3.25). C_{IT} is more or less a constant despite of some fluctuations.

Energy analysis

Figures 3.26-28 show the evolutions of total work energy (W_t), recovery work energy (W_r),

and the ratio of recovery energy (η) in constant load tests against temperature respectively, together with the result of DSC test.

Figure 3.24. Apparent elastic modulus at some selected temperatures together with the DSC result.

Figure 3.25 Indentation creep at some selected temperatures together with the DSC result.

Figure 3.26 W_t at some selected temperatures together with the DSC result.

Figure 3.27 W_r at some selected temperatures together with the DSC result.

Figure 3.28 η at some selected temperatures together with the DSC result.

It appears that W_t and W_r do not provide much useful information about the general trend in terms of their relationship with temperature in the constant load test, while η against temperature relationship is clearer, despite of the difference in the transformation temperatures as in comparison with that obtained from DSC test.

3.3 Remarks

At this point, it is concluded that the phase transformation process determined by the constant load indentation test in terms of the studied material properties does not match that determined by the DSC test. This may be partially explained as follows. What a DSC test measured is the thermally induced phase transformation, while that in an indentation test is the stress-induced phase transformation, in which the stress state is rather complex. Hence, the phase transformation temperatures determined by them may not be the same.

CHAPTER 4

Two-way Shape Memory in NiTi SMA Micro Indents

In Chapter 3, micro indentation tests were carried out on a NiTi SMA. Mechanical properties, e.g., hardness and elastic modulus etc., were investigated. In this chapter, the shape memory effect (SME) and two-way shape memory effect (TWSME) are investigated by two surface topography measurement techniques, namely, AFM and WYKO interferometer. To the best knowledge of this author, TWSME has not yet been reported in the literature.

4.1 Experimental setup and procedure

Heat pumps based on the Peltier effect were integrated into a Shimadzu AFM and a WYKO 3-D Surface Interferometer for temperature control as illustrated in Figs. 4.1 and 4.2, respectively.

Two groups of indents mentioned in Chapter 3 were investigated. Indents of Group I were produced in the cooling course of the constant load test. The constant load test reported in Chapter 3 was carried out at some selected temperatures in a heating and then cooling process. In the heating course, the indents at lower temperatures were heated up so that their original shapes were partially recovered due to SME. As such, only those indents that were obtained in the cooling course were candidates for current investigation. At one temperature, one indent was arbitrarily chosen among five indents produced under the same conditions. Indents of Group I were measured by WYKO. Indents of Group II were the results of the additional constant temperature tests, which were carried out at 11°C under indentation loads ranging from 100 mN to 1000 mN. Only one indentation test was carried out at each load. Indents of Group II were measured by AFM.

Figure 4.1 Temperature controllable AFM.

Figure 4.2 Temperature controllable WYKO interferometer.

Both groups of indents went through thermal cyclic test for the SME and TWSME. Depth was taken as a parameter in measuring the SME and TWSME. First, samples were tested upon heating from room temperature to 50°C. Subsequently, samples were tested upon cooling from 50°C to room temperature. After that, samples went through one more thermal cycle between 14°C and 50°C to study the TWSME. At a temperature lower than 14°C, the sample surface was immediately covered by a lot of dew under the testing environment. Hence, 14°C was the lowest temperature used in the course of this study. Finally, more thermal cyclic tests were performed to study the stability of the TWSME.

4.2 Results

4.2.1 SME

Some typical topographies and profiles of indents of Group I before thermal cycling are presented in Fig. 4.3. It shows that martensite indents (indentation temperature $< M_f$) tend to be sink-in [Fig. 4.3(a-d)], while austenite indents (indentation temperature $> A_f$) tend to be pile-up [Fig. 4.3(g-h)]. Figure 4.4 is the 3-D views and profiles (WYKO) of a typical sink-in indent of Group I before and after heating. Figure 4.5 presents a typical indent of Group II at different temperatures (AFM). Despite that all martensite indents of Group II before heating are sink-in, after heating, indents of both groups are pile-up.

4.2.2 TWSME

TWSME experiments were followed after the SME experiments. Figure 4.6 shows the top views and profiles of a typical indent of Group I at 21°C and 50°C in a new thermal cycle (by WYKO), while Fig. 4.7 presents the result of a typical indent of Group II (by AFM). Results of other indents resemble Figs. 4.6 and 4.7, and are not presented here.

(a)

(b)

(c)

(d)

Figure 4.3 Typical topographies and profiles of indents of Group I. Indentation load was 1000 mN, measured at 17°C.

Figure 4.4 3D views and profiles of a typical sink-in indent of Group I before and after heating. Measured at 17°C. The indentation temperature was 13.4°C; indentation load was 1000 mN.

Figure 4.5 3-D views of a typical indent of Group II at different temperatures. The indentation temperature was 11°C; indentation load was 1000 mN.

Figure 4.6 Topographies and profiles of a typical indent of Group I at two different temperatures in the second thermal cycle. Indentation temperature was 13.4°C; indentation load was 1000 mN.

Figure 4.7 3-D views of a typical indent of constant temperature test in the second thermal cycle. The indentation was performed at 11°C; indentation load was 1000 mN.

4.3 Analysis and discussion

As the indentation tests were carried out in one laboratory, while AFM and WYKO tests were done in another laboratory, the NiTi samples were put into iced water during transportation. Thus, some indents that were not produced at room temperature might be subjected to some level of the phase transformation. Figure 4.8 presents the residual indentation depths measured by the indentation test and WYKO interferometer test. Two curves are slightly different. This means the influence of the transportation can be neglected. As such, in the following discussion, residue depth, h_r , obtained from the WYKO interferometer is taken as the residual depth of Group I and used in the following analysis. Similarly, h_r , measured by AFM is used as the residual depth of Group II.

Figure 4.8 A set of residual indentation depths of Group I measured by indentation tests and WYKO. WYKO tests were done at room temperature (17°C).

• Pile-up/sink-in

Figure 4.3 reveals that martensite indents tend to be sink-in and austenite indents tend to be pile-up. As mentioned in Chapter 2, previously investigation reveals that the type of deformation, either pile-up or sink-in, is associated with the uniaxial strain hardening

exponent n . The strain-hardening exponent may have a value from $n = 0$ (perfectly plastic solid) to $n = 1$ (elastic solid). For a low strain hardening alloy, pile-up tends to occur due to the incompressible plastic deformation. High strain hardening materials are on the contrary. To study the pile-up/skin-in phenomenon in NiTi, the step by step method proposed by Giannakopoulos and Suresh (1999) was used to calculate n . The resultant indentation parameters, elastic modulus and strain hardening exponent are listed in Table 4.1. It reveals that pile-up/sink-in phenomenon is not seemingly solely dependent on the strain-hardening exponent in this material. E determined from all three approaches, namely, the depth approach, the energy approach and from the machine output, increases with the increase of the indentation temperature. It is consistent with the fact that the elastic modulus of austenite NiTi is higher than that of martensite. The strain hardening exponent also increases slightly when the indentation temperature is higher than A_f and thus the austenite indent should be more like sink-in than martensite indent. However, the actual experimental results are in contrary. All the austenite indents are pile-up. It seems that these methods used to estimate the elastic modulus may not be applicable in analyzing the pile-up/sink-in deformation of SMAs. This is very likely to attribute to the complex deformation mechanism in SMAs.

The stress-strain relationship of SMAs at different temperatures may provide a partial explanation. Recalling Fig. 3.10, we can see that in Stage II, the strain hardening exponent of austenite is almost zero (known as *plateau* in the literature). Hence, the indent is in a pile-up shape as illustrated in Fig. 3.11(b). The high strain hardening martensite NiTi is on the contrary, which results in sink-in as shown in Fig. 3.11(a).

Indentation temperature (°C)	$h_p/h_{\max}$	W_i (nJ)	W_r (nJ)	W_e/W_i	S		$A_{\max}$ (μm^2)		dP/dh (mN/ μm)	E (GPa)			n
					$h_p/5h_{\max}$	$W_e/5W_i$	$S= h_p/5h_{\max}$	$S= W_e/5W_i$		$S= h_p/5h_{\max}$	$S= W_e/5W_i$	CSEM	
11	0.73	1916.201	1916.147	0.251526	0.054	0.050305	606.668024	616.4148876	1390	42.21576	41.89441	48.96	0.582379
12.8	0.7352381	1947.572	1947.519	0.242054	0.052952	0.048411	671.875286	685.1959339	1437	41.50155	41.11247	47.73	0.579926
13.4	0.72888016	1938.483	1938.429	0.243778	0.054224	0.048756	628.099205	643.1057442	1456	43.40646	42.91843	50.01	0.591832
15.8	0.79867257	1909.046	1909.005	0.244774	0.040265	0.048955	526.252641	506.6974306	1377	44.7849	45.60271	48.02	0.572442
17.5	0.72727273	1929.946	1929.892	0.241	0.054545	0.0482	647.102988	665.0806267	1376	40.53334	40.00336	46.73	0.574426
19.9	0.71150097	1919.625	1919.567	0.251712	0.0577	0.050342	628.567016	648.7806421	1349	40.32809	39.71949	46.34	0.573862
23.2	0.684	1831.917	1831.854	0.27945	0.0632	0.05589	583.283689	601.7615431	1273	39.53754	38.9491	45.35	0.574051
27	0.64893617	1743.235	1743.165	0.326855	0.070213	0.065371	500.370918	510.6735182	1214	40.66268	40.26667	46.64	0.586688
32	0.65517241	1702.454	1702.385	0.34239	0.068966	0.068478	490.236125	491.2415311	1254	42.36096	42.31939	48.74	0.570949
38.3	0.64203233	1607.378	1607.306	0.377154	0.071594	0.075431	422.24221	415.5447422	1294	46.88291	47.24182	54.13	0.595294
41.9	0.61707317	1614.369	1614.293	0.372172	0.076585	0.074434	370.791663	374.1175985	1268	48.9222	48.71464	56.72	0.608683
50	0.6372315	1628.847	1628.775	0.335458	0.072554	0.067092	393.796452	402.9225633	1321	49.43014	48.89408	57.27	0.634258

Table 4.1 Indentation parameters, elastic properties of Group I, where $S= h_p/5h_{\max}$ is used in the depth approach, $S= W_e/5W_i$ is used in the energy approach. E of CSEM is the output from the equipment.

- Some definitions

A schematic illustration of the depth change in an indentation test and following thermal cycling is presented in Fig. 4.9. Here, $h_{\max}$ is the maximum indentation depth in an indentation test, h_r is the residual depth after unloading, which may include two contributors, namely the elastic recovery and the recovery mainly due to the superelasticity in SMAs at a high temperature. The TWSME depth, h_{tw} , is the depth at the low temperature after the first heating cycle; h_p represents plastic deformation which is measured at a high temperature, where only austenite exists. The difference between h_p and h_{tw} is the result of the TWSME, while the difference between h_{tw} and h_r is that of the SME. Depth is obtained as the average of four sides of an indentation in the course of this study.

Figure 4.9 Schematic illustration of the load-depth curve upon loading/unloading and in the subsequent thermal cycling.

Here, we define the recovery ratio in the SME $\eta_s = \frac{h_r - h_{tw}}{h_r}$, and the recovery ratio in

$$\text{TWSME } \eta_{tw} = \frac{h_{tw} - h_p}{h_{tw}}.$$

Referring to Figs. 3.12 and 3.13, the phase regime of an indent (indentation temperature $< M_f$) in the first heating course is illustrated in Fig. 4.10.

Figure 4.10 Illustration of phase regime of an indent in the first heating course.

Figure 4.11 shows the phase regime of an indent upon cooling back to a low temperature. The difference in depth between high temperature and low temperature is a direct measure of the TWSME. In both Figs. 4.10 and 4.11, the subscripts, + and -, represent the extrusive and concave parts of the indent relative to the flat sample surface, respectively.

Figure 4.11 Illustration of phase regime of an indent in a thermal cycling.

• SME and TWSME study

Group I

Figure 4.12 presents the residual depth-temperature curve of a typical sink-in indent in

the first thermal cycle. Figure 4.13 shows the cross-section of an indent in the first thermal cycle. The change in depth reveals the SME due to the reverse transformation. After heating, all the sink-in indents become pile-up in shape as a result of SME and all pile-up indents are still pile-up. This is a phenomenon not reported before.

The variation of the indentation depth of all indents in the first thermal cycle is given in Fig. 4.14. It shows that h_r increases with the decrease of indentation temperature. h_{p+} , h_{p-} and h_p seem to be constants, which means the plastic deformation under a given indentation load is more or less temperature independent. This can be explained by the stress-strain relationship in Fig. 3.10. Given a load that is high enough for the SMA to reach its plastic stage (exactly the case when a sharp indenter is used), the plastic deformation is a constant, regardless of the exact initial phase. Indentation temperature only affects the shape and size of the indent. After thermal cycling, all indents of the same load are more or less the same in both shape and size.

Figure 4.12 Residual depth in the first thermal cycle (together with DSC result). The indent was done at 13.4°C at an indentation load of 1000 mN.

Figure 4.13 Profiles of a typical sink-in indent of Group I in the first thermal cycle. The indentation temperature was 13.4°C and indentation load was 1000 mN.

Figure 4.14 h_r , h_p , and h_{tw} against indentation temperature together with the DSC result. h_{p+} and h_{tw+} are more or less overlapped. h_{r-} is zero when indentation temperature is lower than 27°C which means sink-in.

Recovery ratios of Group I are plotted in Fig. 4.15. Since h_{p+} and h_{tw+} are almost identical, the recovery ratio (η) of the concave part is also plotted for comparison. Here,

$$\eta_{s-} \text{ is defined as } \eta_{s-} = \frac{h_{r-} - h_{tw-}}{h_{r-}}, \text{ and } \eta_{tw-} \text{ is defined as } \eta_{tw-} = \frac{h_{tw-} - h_{p-}}{h_{tw-}}.$$

Figure 4.15 η_s , η_{s-} , η_{tw} and η_{tw-} against indentation temperature together with the DSC result.

In the SME, η_s of the pure martensite indentations is virtually a constant. So is that of the pure austenite indentation, but its magnitude is only one third of that of the pure martensite. Between pure martensite and pure austenite, η_s increases sharply from about 10% to around 40% with the decrease of indentation temperature from 36°C to 23°C. However, the transformation temperatures are higher than that of the DSC result.

The temperature dependence of η_s can be explained by the stress-strain relationship of SMAs as shown in Fig. 3.10 together with the phase regime under an indenter (Fig. 3.11). For simplicity, ignore the deformation associated with the elastic stress field induced by the plastic deformation upon loading since it is relatively small. As explained before, under a given load that is large enough to ensure the material reaching its plastic deformation range, the plastic deformation is more or less the same regardless the exact initial phase. Thus, the plastic deformation has no significant contribution to

the difference in the SME at different indentation temperature. As the TWSME is resulted by the plastic deformation, it may be roughly considered as independent on the indentation temperature as well, i.e., h_{tw} is more or less a constant, and so are η_{tw} and η_{tw-} in the TWSME. At a high temperature, less detwinned martensite may be produced upon indentation, and part of the detwinned martensite reverses back to the austenite upon unloading, while at a low temperature the detwinned martensite produced upon indentation is more and it remains almost untouched upon unloading. Thus, the depth of the indent (h_r) increases with the decrease of the indentation temperature. Based on the definition of η_s , it is clear that η_s is smaller at a high indentation temperature.

Group II

The indentation tests were carried out at 11°C and the resultant indentations were sink-in. Thus, h_{r+} is always zero and $h_r = h_{r-}$. After heating, they were pile-up. h_r , h_p and h_{tw} of Group II are plotted in Fig. 4.16. h_r , h_p and h_{tw} increase almost linearly with the indentation load. It means that both the deformations due to the SME and TWSME increase with the increase of indentation load. However, the bulge part of an indentation (for both h_{p+} and h_{tw+}) only increases slightly with the increase of the load.

The recovery ratios in the SME and TWSME of Group II are presented in Fig. 4.17. It reveals that these ratios also increase linearly with the indentation load. This is in contradiction to that reported in Ni *et al.* (2002), in which the recovery ratio in SME is found to be load independent in a load range from 50 mN to 2500 mN. We can easily explain our results referring to the discussion about Fig. 4.15. It is expected that h_r increases with the increase of the indentation load. If the plastic deformation is strongly dependent on the indentation load (roughly in a linear manner), the deformation in the TWSME should be a linear function of the indentation load as well. Thus, the recovery ratios in the SME and TWSME should increase with the indentation load in a roughly linear manner.

The TWSME has been found in all tested samples of both Groups I and II. Depending on the applied indentation load, η_{tw} can be up to 14% as shown in Fig. 4.17. The volume

change in the TWSME can be up to about $50\text{ }\mu\text{m}^3$ under an indentation load of 1000 mN. This might be a promising actuation mechanism for micro-pumps.

Figure 4.16 h_r , h_p , and h_{tw} against indentation load.

Figure 4.17 Recovery ratios in the SME and TWSME at different indentation loads.

Stability of TWSME

Thermal cyclic tests have been carried out using the temperature controllable AFM to study the reproducibility and stability of the TWSME. Experimental results of four indentations selected from Group II are shown in Figs. 4.18-20.

Figure 4.18 h_r and h_p , h_{tw} of the second and tenth thermal cycles.

Figure 4.19 h_r , h_p and h_{tw} of the second and tenth thermal cycle.

Figure 4.20 η_{tw} of Group II after 10 thermal cycles.

It is clear that the TWSME still exists even after 10 thermal cycles. The depth recovery ratio in the TWSME is about 10%. It appears quite stable during thermal cycling. More thermal cyclic test is necessary to check the long-term stability after, say millions of cycles.

4.4 Remarks

Thermal cyclic tests were carried out to study the SME and TWSME in some of indents produced previously (in Chapter 3). All indents after thermal cycling appear to be in a pile-up shape and show the TWSME. The dependence of the pile-up/sink-in phenomenon on the indentation temperature is identified and explained. It is found that the depth recovery ratios in the SME and TWSME are almost linearly dependent on the indentation load while independent on the indentation temperature. The TWSME exists after 10 thermal cycles. The TWSME produced by this method may be use in micro actuators.

CHAPTER 5

Laser Annealing I: Theory and Backside CO₂ Laser Annealing of NiTi Thin Films

A new annealing approach, CO₂ laser annealing, for NiTi thin films, has been reviewed in Chapter 2. The films annealed by CO₂ laser are crystallized and with shape memory. This chapter presents a theoretical study of laser annealing of NiTi thin films, so that one can have a better understanding of this annealing technique. First, a basic laser irradiation model for multilayer structure is presented. Subsequently, CO₂ laser annealing of NiTi thin films is investigated in details.

5.1 Absorption of laser irradiation

Fresnel Equations¹

To estimate the amount of laser energy that couples into a film, Fresnel equations can be used. Fresnel equations give the ratio of the amplitude of the reflected electric field over that of the initial electric field for electromagnetic radiation incident on a dielectric material. In general, when a wave reaches a boundary between two materials with different dielectric constants, part of the wave energy is reflected and the remaining is transmitted. Since electromagnetic waves are transverse, there are separated coefficients in the directions perpendicular to and parallel to the surface of the dielectric. We may denote the coefficient for reflection of the transverse electric field (TE) as r_s , and the coefficient for reflection of the transverse magnetic field (TM) as r_p . In addition to the reflection amplitude coefficients, reflection intensity coefficients are often defined as the square of the corresponding amplitude coefficients as

¹ <http://scienceworld.wolfram.com/>

$$R_s = |r_s|^2 \quad (5.1)$$

$$R_p = |r_p|^2 \quad (5.2)$$

Figure 5.1 Schematic plot of TE radiation.

For TE radiation shown in Fig. 5.1, one has

$$r_s = \frac{E_r}{E_i} = \frac{\frac{n_1}{\mu_1} \cos \theta - \frac{n_2}{\mu_2} \cos \theta'}{\frac{n_1}{\mu_1} \cos \theta + \frac{n_2}{\mu_2} \cos \theta'} \quad (5.3)$$

where n_1 is the refraction index of the first medium, n_2 is that of the second, θ is the angle to the normal of the first medium, θ' is the angle to the normal of the second medium (which is different from θ due to refraction), μ_1 is the magnetic permeability of the first medium, and μ_2 is the permeability of the second medium. In general, $\mu_1 \approx \mu_2 \approx 1$. Hence,

$$r_s = \frac{n_1 \cos \theta - n_2 \cos \theta'}{n_1 \cos \theta + n_2 \cos \theta'} \quad (5.4)$$

The relationship between θ and θ' follows the Snell's law, i.e.

$$n_1 \sin \theta = n_2 \sin \theta' \quad (5.5)$$

Figure 5.2 Schematic plot of TM radiation.

For TM radiation illustrated in Fig. 5.2, one has

$$r_p = \frac{E_r}{E_i} = \frac{\frac{n_2}{\mu_2} \cos \theta - \frac{n_1}{\mu_1} \cos \theta'}{\frac{n_2}{\mu_2} \cos \theta + \frac{n_1}{\mu_1} \cos \theta'} \quad (5.6)$$

If $\mu_1 \approx \mu_2 \approx 1$, it is reduced to

$$r_p = \frac{n_2 \cos \theta - n_1 \cos \theta'}{n_2 \cos \theta + n_1 \cos \theta'} \quad (5.7)$$

In the case of normal incidence (i.e., $\theta = 90^\circ$), the reflection amplitude, r_n , can be expressed as

$$|r_n| = |r_s|_{90^\circ} = |r_p|_{90^\circ} = \left| \frac{n_2 - n_1}{n_2 + n_1} \right| \quad (5.8)$$

and the intensity reflectance, R_n , can be expressed as

$$R_n = |r_n|^2 = \left| \frac{n_2 - n_1}{n_2 + n_1} \right|^2 \quad (5.9)$$

For absorbent materials, whose complex indexes of refraction are $m_1 = n_1 - i k_1$ and $m_2 = n_2 - i k_2$, from Eqns. (5.4) and (5.7), it can be deduced that (Ward 1994)

$$r_s = \frac{(n_1 - i k_1) \cos \theta - (n_2 - i k_2) \cos \theta'}{(n_1 - i k_1) \cos \theta + (n_2 - i k_2) \cos \theta'} \quad (5.10)$$

$$r_p = \frac{(n_2 - i k_2) \cos \theta - (n_1 - i k_1) \cos \theta'}{(n_2 - i k_2) \cos \theta + (n_1 - i k_1) \cos \theta'} \quad (5.11)$$

At $\theta = 90^\circ$, the intensity coefficient for reflection can be expressed as

$$R_n = |r_n|^2 = \left| \frac{(n_1 - i k_1) - (n_2 - i k_2)}{(n_1 - i k_1) + (n_2 - i k_2)} \right|^2 \quad (5.12)$$

Absorption of laser radiation by metals

When laser strikes a metal surface, the energy is absorbed within a thin layer near the surface. The absorption follows

$$I(z) = I_0 \exp(-\alpha z) \quad (5.13)$$

where I_0 is the incident intensity, $I(z)$ is the intensity reaching depth z from the surface, and α is the absorption coefficient. The optical penetration depth is defined as (Ready *et al.* 2001)

$$l = \frac{1}{\alpha} = \frac{\lambda}{4\pi k} \quad (5.14)$$

where λ is the wavelength of incident light. For metals with a value of k of an order of 10, a layer in a thickness of an order of 100 nm may be considered as opaque (Ready *et al.* 2001). In practice, the optical penetration thickness is very small as compared with the

thickness of metallic films. Thus, the absorption of metals is customary to speak of absorption by a “surface”, although a thin surface layer is implied.

For an opaque metal impinged by laser in the air, the fraction of incident radiation absorbed is

$$A = 1 - R \quad (5.15)$$

The reflective at normal incidence can be calculated from Eqn. (5.12) as

$$R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2} \quad (5.16)$$

where $n_I = 1$, $k_I = 0$ in Eqn. (5.12) for air. The complex indexes of refraction of a metal is $m = n - i k$.

Thus, the absorptivity of metals is

$$A = \frac{4n}{(n+1)^2 + k^2} \quad (5.17)$$

Absorption of laser radiation by semiconductors

Now we consider the absorption of laser in an isotropic slab of finite uniform thickness, h , and infinite extension in the xy -plane. For a semi-infinite slab, i.e., optical penetration depth is smaller than the thickness ($l < h$), absorptivity can be calculated by Eqn.(5.17). In the case of moderate to weak absorption ($l \geq h$), multiple reflections within the slab cannot be ignored. The absorptivity becomes dependent on the thickness of the slab, i.e., $A = A(h)$.

Due to energy conservation, the absorptivity, A , is related to the reflectivity, R , and the transmittivity, D , by

$$A + R + D = 1 \quad (5.18)$$

For a slab with finite thickness and in the case of weak absorption ($l \gg h$) and $k \ll 1$, one has (Bäuerle 2000)

$$R = \frac{(1 - n^2)^2 \sin^2(\beta h / 2)}{\xi} (1 - A) \quad (5.19)$$

$$A = 2k \frac{(1 + n)\beta h - (1 - n)\sin(\beta h)}{\xi} \quad (5.20)$$

$$D = \frac{4n^2}{\xi} (1 - A) \quad (5.21)$$

where $\xi = 4n^2 + (1 - n^2)^2 \sin^2(\frac{\beta h}{2})$, and $\beta = 4\pi n / \lambda$.

Absorption of laser energy in multilayer structures

Discontinuity in material properties occurs at the interface of multilayer structures as shown in Fig. 5.3. Define the complex indexes of refraction of layers 1 and 2 as $m_1 = n_1 - i k_1$ and $m_2 = n_2 - i k_2$. Hereinafter, subscripts 1 and 2 stand for the layer 1 and layer 2, respectively.

Figure 5.3 Laser irradiation on a multilayer structure.

Consider that $h_2 \gg l_2$ (l_2 is the optical penetration depth of layer 2), layer 2 can be considered semi-infinite in terms of its optical behavior. Because $D = 0$, we have

$$A + R = 1 \quad (5.22)$$

where A ($A_1 + A_2$), is the total absorptivity of the system. For surface absorption ($h_1 \geq l_1$), $A = A_1$. For weakly absorbing films ($h_1 < l_1$), due to interferences, the total absorptivity changes with film thickness, h_1 . The heat generated in layers 1 and 2 can be expressed as (Bäuerle 2000)

$$Q_1 = I_0 f_1(z) \quad (5.23)$$

$$Q_2 = I_0 f_2(z) \quad (5.24)$$

where $f_1(z)$ and $f_2(z)$ describe the attenuation of the laser beam in z -direction. The functions $f_1(z)$ and $f_2(z)$ can be written as (Bäuerle 2000)

$$f_1(z) = \alpha_1 (1 - R_1) \left| \frac{r_{12} \exp(-i\varphi) + \exp(-i2\psi_1) \exp(i\varphi)}{r_{M1} r_{12} + \exp(-i2\psi_1)} \right|^2 \quad (5.25)$$

and

$$f_2(z) = \alpha_2 n_2 \left| \frac{(1 + r_{M1})(1 + r_{12})}{r_{M1} r_{12} + \exp(-i2\psi_1)} \right|^2 \exp(\alpha_1 h_1) \exp[-\alpha_2 (z - h_1)] \quad (5.26)$$

with

$$1 - R_1 = \frac{4n_1}{(1 + n_1)^2 + k_1^2},$$

$$\varphi = \frac{2\pi z(n_2 + ik_2)}{\lambda},$$

$$r_{M1} = \frac{n_M + ik_M - n_1 - ik_1}{n_M + ik_M + n_1 + ik_1},$$

$$r_{12} = \frac{n_1 + ik_1 - n_2 - ik_2}{n_1 + ik_1 + n_2 + ik_2},$$

$$\psi_1 = \frac{2\pi h_1(n_1 + ik_1)}{\lambda}.$$

The energies absorbed within the film and the substrate are

$$A_1 = \int_0^{h_1} f_1(z) dz \quad (5.27)$$

and

$$A_2 = \int_{h_1}^{\infty} f_2(z) dz \quad (5.28)$$

The oscillation in the absorptivity as shown in Eqns. (5.27) and (5.28) is due to the interference of laser light within layer 1. The period is (Bäuerle 2000)

$$\Delta h = \frac{\lambda}{2n_1} \quad (5.29)$$

5.2 Backside CO₂ laser annealing of NiTi thin films

Considering the case reported in He (2004), NiTi thin films were deposited on 4-inch (100) silicon wafers (with a thickness of 450 μm). The thickness of NiTi films was measured as 3.4 μm . The composition of the amorphous thin films is Ni_{51.7}Ti_{48.3} (at.%).

Figure 5.4 Schematic illustration of backside CO₂ laser annealing.

A continue-wave CO₂ laser (48-2 KWJ, SYNRAD) was used for annealing NiTi thin films. The experimental setup is schematically illustrated in Fig. 5.4. The laser beam was in the TEM₀₀ mode, 10.6 μm-wavelength, and 25 W. The laser beam was focused onto the Si wafer surface. The diameter of the focused beam spot was about 100 μm. An X-Y stage (M-UTM150CC1HL, Newport) carrying the samples moved horizontally at a speed of 3 mm/s. In real practice, a laser beam scans over a sample at a given speed following a pre-determined path by moving the stage carrying the sample horizontally. Normally relative speed of the laser beam (i.e., the moving speed of the stage carrying the sample) is not fast, for simplicity we may consider both laser and sample are fixed while let the annealing time be a variable. For example, with a laser beam spot radius as 50 μm, 0.03 second annealing time roughly corresponds to a scanning speed of 3 mm/s.

For optical properties of Si and NiTi, one may refer to Table 5.1.

Material	n	k	l (optical penetration depth, $l = \frac{\lambda}{4\pi k}$)
Air	1	0	N/A
Si	3.4215	1.27×10^{-4}	33 mm (Bäuerle 2000)
NiTi (estimation)	$7.568 \left(\frac{n_{ni} + n_{ti}}{2} \right)$	$28.339 \left(\frac{k_{ni} + k_{ti}}{2} \right)$	0.03 μm
SiO ₂	2.184	2.205×10^{-2}	41.15 μm
TiO ₂	1.445	0.063	13.39 μm

Table 5.1 Selected optical properties of crystalline Si and amorphous NiTi (Palik 1985, Palik 1991).

5.2.1 Absorption of Si/NiTi multilayer

NiTi can be considered as a semi-infinite substrate in terms of its optical behavior. Thus $A+R=1$. Since $h_{si} < l_{si}$ (33 mm), where subscript *si* stands for Si wafer, the absorption behavior of Si/NiTi multilayer is weak absorption. Both Si wafer and NiTi thin film absorb laser energy. Figure 5.5 shows the distribution of absorptivity near the Si/NiTi interface calculated by Eqns (5.25) and (5.26).

Figure 5.5 Distribution of absorptivity near the Si/NiTi interface ($h_{si} = 450 \mu\text{m}$).

By integrating absorptivity through respective material in its thickness direction, we get the absorptivity of Si and NiTi as $A_{si} = 28.1\%$, $A_{niti} = 24.5\%$ and the total absorptivity $A = A_{si} + A_{niti} = 52.6\%$. Here, subscript *niti* stands for NiTi. The average absorptivity of Si is $0.06\%/\mu\text{m}$ over its thickness (450 μm). NiTi thin film absorbs laser energy within a thickness less than 300 nm.

Distribution of absorptivity also changes with h_{si} . Figures 5.6 and 5.7 show the variation of the absorptivity distributions in Si and NiTi when h_{si} is gradually reduced from 450 μm to

Figure 5.6 Distribution of absorptivity in Si of different thicknesses of Si (only the distance range from 200 μm to 202 μm is shown).

Figure 5.7 Distribution of absorptivity in NiTi at different thickness of Si.

The total absorptivity ($A=A_{si}+A_{niti}$) also changes with h_{si} in a period of $1.55\text{ }\mu\text{m}$ due to the interference (Fig. 5.8).

Figure 5.8 Total absorptivity of Si/NiTi system vs. different Si thickness. The period of oscillation is $\frac{\lambda}{2n_{si}} = 1.55\text{ }\mu\text{m}$. (a) Overall view; (b) zoom-in view of the highlighted zone in

(a).

5.2.2 Temperature distribution

A few analytical models have been developed for laser surface treatment. Some of the early works are analytic solutions of one-dimensional heat conduction. Later on both analytic and numerical methods were applied to investigate temperature distribution. In the case of multilayer structures as described here, a few analytical models have been developed (e.g., Burgener and Reedy 1982, Calder and Sue 1982). However, these models are steady state

solutions under many conditions and assumptions. As such, finite element analysis is applied in the course of this project.

Obviously, in laser annealing, the density of solid NiTi is almost a constant, but many other material properties are not. Figure 5.9 shows the temperature dependent thermal conductivities and specific heats of Ni, Ti and Si. Since the temperature dependent thermal properties of NiTi are still unknown, and according to Fig. 5.9, the thermal properties of Ni and Ti do not vary tremendously within the temperature range of $300\text{ K} \leq T \leq 1500\text{ K}$, the thermal conductivity and specific heat of NiTi are considered as constants in this study for simplicity.

Figure 5.9 Temperature dependent thermal properties of Si, Ni and Ti (Incropera and DeWitt 1996).

Physical parameters in laser annealing and properties of NiTi and Si are listed in Tables 5.2 - 5.4 (He 2004).

Symbol	Description	Unit	Value
P	laser power	W	22.4
w_0	laser beam spot radius	μm	50
T_0	environment temperature	K	300
V	scanning speed	mm/s	3

Table 5.2 Physical parameters in the laser annealing experiment.

Symbol	Description	Unit	Value
ρ	mass density	kg/m^3	6450
c_p	specific heat	$\text{J}/(\text{kg}\cdot\text{K})$	837
κ	thermal conductivity	$\text{W}/(\text{m}\cdot\text{K})$	13.3
T_m	melting temperature	K	1573

Table 5.3 Properties of NiTi at $T = 300\text{ K}$ (SMA Inc.).

Symbol	Description	Unit	Value
ρ	mass density	kg/m^3	2330
c_p	specific heat	$\text{J}/(\text{kg}\cdot\text{K})$	712 (300 K), 790 (400 K), 867 (600 K), 913 (800 K), 946 (1000 K), 967 (1200 K)
κ	thermal conductivity	$\text{W}/(\text{m}\cdot\text{K})$	148 (300 K), 98.9 (400 K), 61.9 (600 K), 42.2 (800 K), 31.2 (1000 K), 25.7 (1200 K)
T_m	melting temperature	K	1685

Table 5.4 Properties of Si at $300\text{ K} < T < 1500\text{ K}$ (Incropera and DeWitt 1996).

ANSYS is used for numerical simulation in this study, following the previous works by Dr Gao Xiangyang and Mr He Qiang. The geometry for investigation is illustrated in Fig. 5.4. The thickness of silicon substrates is a variable, and the thickness of NiTi film is fixed as 4 μm . The sample is chosen in a disk shape with a radius of 8000 μm , and the model is

axi-symmetric. The upper surface and the lower surface have heat convection with the environment (air). The coefficient of thermal convection is chosen as $H = 20 \text{ W/m}^2\text{K}$. Refer to Tables 5.2 - 5.4 for the physical parameters and thermo-mechanical properties of NiTi and Si. Note that the properties of silicon at a given temperature are determined from the properties of the two nearby temperatures by linear data fitting. A typical mesh for finite element simulation is plotted in Fig. 5.10. The energy absorption for crystallization and phase transformation is ignored.

Figure 5.10 Finite element model (ANSYS).

The intensity of a laser beam generally follows the Gaussian distribution, in the transverse direction of the beam, one has

$$I(r) = I_0 \exp\left(-\frac{r^2}{w_0^2}\right) \quad (5.30)$$

where I_0 is the laser intensity at the center of the beam (maximum laser intensity), r is the distance away from the center of the laser beam, and w_0 is the focused spot radius of the beam. Figure 5.11 is a graphical expression of the relationship. To get a better approximation of Gaussian distribution, the area within $2w_0$ is finer meshed [Fig. 5.10 (b)].

In this simulation, eight zones are divided equally along the radius of the beam spot according to the following expression

$$f(r_1, r_2) = \frac{\int_{r_1}^{r_2} 2\pi r I_0 \exp\left(-\frac{r^2}{w_0^2}\right) dr}{I_0 (\pi r_2^2 - \pi r_1^2)} \quad (5.31)$$

where f is the average laser power distribution ratio between different distances (r_1 and r_2) from the center of the laser beam, the average power distribution ratios for respective zones are 0.969391, 0.856599, 0.668857, 0.461493, 0.281365, 0.151581, 0.0721583 and 0.030352.

Figure 5.11 Gaussian distribution of laser beam intensity.

Heat in silicon directly generated by the laser beam is assumed to be uniformly distributed (A_{si}/h_{si}) within thickness direction in the radiation zone, while the NiTi film is directly heated uniformly at the interface of Si/NiTi. The heat sources in silicon substrate and NiTi film follow Gaussian distribution within the radiation zone.

If the laser power is 25 W, the thickness of NiTi film is 4 μm and the thickness of Si wafer is 450 μm , the highest temperature is 922 K at an annealing time of 0.01 second [Fig. 5.12 (a)]. The investigation of the relationship between the highest temperature and a slight variation in Si thickness is carried out with different Si thicknesses, namely, 450 μm , 449.94 μm , 449.785 μm , 449.63 μm , 449.475 μm , 449.32 μm , 449.165 μm , 449.01 μm , 448.855 μm , 448.7 μm , 448.545 μm and 448.39 μm . One may refer to Fig. 5.8 for their respective absorptivity.

Figure 5.12 shows the temperature distribution at 0.01 second annealing time as simulated using *Ansys* for a few Si thickness. We can see that the high temperature zone is located in a small area around the Si/NiTi interface. It is noticed that in Fig. 5.12(a), the radius of high temperature zone above 773 K is about 56 μm , which is higher than the NiTi crystallization temperature (Johnson 1991). Hence, the effective annealing zone should be about 112 μm in width. This is consistent with the measured width of the annealed line, which is about 120 μm (He et al. 2004). In other cases, the high temperature zone is also around 110 μm .

The relationship between the highest temperature and Si thickness is plotted in Fig. 5.13. It is obvious that a slight variation in thickness of Si wafer has a strong influence on the result of CO₂ laser annealing.

(a) $h_{si} = 450 \mu\text{m}$, $A_{si} = 28.06\%$ and $A_{niti} = 24.52\%$.

(b) $h_{si} = 449.940 \mu\text{m}$, $A_{si} = 31.3\%$ and $A_{niti} = 27.35\%$.

(c) $h_{si} = 449.785 \mu\text{m}$, $A_{si} = 18.79\%$ and $A_{niti} = 16.4\%$.

(d) $h_{si} = 449.630 \mu\text{m}$, $A_{si} = 9.06\%$ and $A_{niti} = 7.93\%$.

(e) $h_{si} = 449.475 \mu\text{m}$, $A_{si} = 5.51\%$ and $A_{niti} = 4.82\%$.

(f) $h_{si} = 449.320 \mu\text{m}$, $A_{si} = 4.17\%$ and $A_{niti} = 3.65\%$.

Figure 5.12 Temperature distribution at 0.01 second.

Figure 5.13 Highest temperature and absorptivities of Si and NiTi against thickness of Si.

5.2.3 Effects of oxidation and interfacial layers

Up to this point we have assumed that the material is pure and homogeneous, and its surface is isotropic and optically smooth. However, during intense laser irradiation, even an initially ideal material may have its surface composition and quality altered. Laser induced high temperature may cause strong oxidation and/or other chemical reaction, and produce a surface layer of a material different from the original. In He (2004), the backside of Si wafer is rather rough. The root-mean-square roughness, R_q , of backside (without polishing) of the single-side Si wafer is about 0.85 μm , while R_t (maximum peak-to-valley height of roughness) can be up to 7.6 μm as measured by a WYKO interferometer. It means the thickness of Si wafer may vary around 7.6 μm within a small area. For simplification, we may only consider the specular loss caused by R_q ($<1.55 \mu\text{m}$) and ignore the absorptivity change induced by R_t ($>1.55 \mu\text{m}$). On the other hand, it is well known that even at room

temperature, a thin native oxide layer can be formed on the surface of Si wafer in air. Native oxide layer is typically 1~10 nm thick (e.g. Bäuerle 2000). During laser processing, laser-enhanced oxidation occurs, which alters the absorption behavior of Si/NiTi multilayer system. In the following investigation, we ignore oxidation during laser processing, but concentrate only on the influence of different thickness in native oxide layer. In addition, diffusion may occur at the interface between Si and NiTi at a high temperature. The following discussion addresses the influence of surface roughness, surface oxidation and interfacial layer on the radiative properties.

Effect of surface roughness

A surface is “optically smooth” if the average length scale of surface is much less than the wavelength of the electromagnetic wave. A common measure of surface roughness is given by R_q . In general, with the increase of roughness, a surface will become less reflective, less specular and more diffusive. This behavior may be explained through geometric optics. In view of this, a laser beam hitting a rough surface may undergo two or more reflections off local peaks and valleys (resulting in increased absorption), after which it leaves the surface into an off-specular direction.

In order to count the loss in specular reflectance due to surface imperfections, one can estimate the effect of surface roughness by *IMD* (Windt 1998), a commercial software developed for calculating specular and non-specular (diffuse/roughness) optical functions of any arbitrary multilayer structure. As a typical result, Fig. 5.14 reveals the change of total absorptivity due to the variation in roughness at backside Si wafer.

Figure 5.14 Absorptivity ($A = A_{si} + A_{niti}$) and reflectivity of Si/NiTi multilayer vs. roughness of backside Si wafer. $h_{si} = 450 \mu\text{m}$, $\lambda = 10.6 \mu\text{m}$.

The change in total absorptivity of Si/NiTi multilayer seems to be in contradiction to the common sense, i.e., a rough surface should result in an increase in absorption. It may be explained as follows: in a single crystalline Si wafer, the absorptivity increases with the increase of roughness due to more reflection. The absorptivity (refer to Fig. 5.14) changes from 3.6% to 35.8% as the roughness is increased by 1 μm . In a Si/NiTi multilayer, the rough surface of Si wafer absorbs more light than a smooth surface and subsequently less light can reach the NiTi thin film. Thus, the interference becomes weaker than that of smooth Si surface, which results in a decrease in the total absorption.

Effect of oxide layer

Both Si and NiTi have native oxide layer if one leaves them in air even at room temperature. The oxide layers of Si and NiTi have different optical properties. In the case of backside

laser annealing of NiTi thin films (deposited by sputtering in vacuum), for simplicity, consider only the oxidation of Si and ignore the oxidation of NiTi. To study the influence of oxide layer in Si, a simple approach is to treat the oxide as a thin SiO₂ layer atop of Si. Figure 5.15 presents the total absorptivity of SiO₂/Si/NiTi multilayer (calculated by *Macleod*²). It shows that a thin oxidation layer (thickness < 100 nm) does not change the total absorptivity very much.

Interfacial layer

If a Si/NiTi interfacial layer does exist (normally generated in a high temperature process), the total absorptivity of multilayer may alter. The interface layer may be up to about 120 nm (Fu *et al.* 2003). This effect is estimated by *IMD* as shown in Fig. 5.16. It reveals that the total absorptivity of the multilayer increases from 52.6% to 55.3% with a 120 nm interface layer, while the reflectivity decreases from 47.4% to 44.7%.

Figure 5.15 Total absorptivity of SiO₂/Si/NiTi multilayer. $\lambda = 10.6 \mu\text{m}$.

² *Macleod* is a commercial software for computing optical properties of multilayer systems.

Figure 5.16 Effect of Si/NiTi interface layer. $h_{si} = 450 \mu\text{m}$, $\lambda = 10.6 \mu\text{m}$.

5.3 Remarks

Now we may conclude that the exact thickness of Si wafer (in a 1.55 μm period) has significant influence in CO₂ laser annealing of NiTi films. Since the tolerance in the thickness of Si wafer is about $\pm 25 \mu\text{m}$ (JA Inc.), special attention is required for precise control of the wafer thickness. In the annealing process, the high temperature zone is highly localized within a zone with a radius about two times of the focused beam spot radius. As demonstrated, the width of effective annealing zone ($T > 773 \text{ K}$) is about the same size as the diameter of the laser beam spot, which agrees well with the experimental observation reported previously. The effects of surface roughness, oxide layer and interface layer may induce instability in laser annealing and should be taken into consideration. Double-side polished wafer is preferred for backside annealing.

CHAPTER 6

Laser Annealing II: Direct Laser Annealing of NiTi Thin Films

Laser annealing of NiTi thin films from the back Si wafer side does not fully compatible with many MEMS fabrication processes. Sputtering a thin Si layer atop of NiTi thin films may be a solution, which makes direct laser annealing possible. After annealing, the sputtered Si layer can be easily etched away by a standard MEMS process. This chapter investigates the required conditions for direct laser annealing following this idea. A typical situation of laser direct annealing is schematically illustrated in Fig. 6.1. Table 6.1 lists the refractive indexes of Si, NiTi, SiO₂ and TiO₂ at different wavelengths.

Figure 6.1 Schematic illustration of direct laser annealing.

6.1 Absorption of Si/NiTi/Si multilayer¹

Similar to the backside annealing, NiTi is considered as a semi-infinite substrate in terms of its optical behavior and $A+R=1$ for the Si/NiTi/Si multilayer. Since no light passes to Si wafer, Si wafer can be excluded from the calculation of absorption, i.e., only the sputtered Si layer and NiTi thin film absorb laser energy. Figures 6.2 and 6.3 show the total

¹ Absortivity is calculated by *Macleod*.

absorptivity of the multilayer impinged by four different types of lasers, namely, CO₂, HIPPO, AVIA and Green lasers.

	<i>n</i>				<i>k</i>			
Wavelength(nm)	10600	1064	532	355	10600	1064	532	355
	(CO ₂ laser)	(Nd:YAG, HIPPO)	(Nd:YAG, Green)	(Nd:YAG, AVIA)	(CO ₂ laser)	(Nd:YAG, HIPPO)	(Nd:YAG, Green)	(Nd:YAG, AVIA)
Si	3.74	3.597	4.428	3.728	0	0	0.878	2.771
NiTi ² (estimation)	$\frac{7.568 + n_{Si}}{2}$	1.03	1.019	2.231	$\frac{28.339 + k_{Si}}{2}$	4.49	1.729	1.049
SiO ₂	2.184	1.45	1.547	1.476	2.205×10^{-2}	0	0	0
TiO ₂	1.445	2.74	3	4.023	0.063	0	0	0.173

Table 6.1 Refractive indexes of Si, NiTi, SiO₂ and TiO₂ at different wavelengths (Palik 1985, Palik 1991).

Figure 6.2 Total absorptivity of sputtered Si/NiTi multilayer. $\lambda = 10.6 \mu\text{m}$ (CO₂ laser).

² From *TFCompanion*, Semiconsoft, Inc.

Figure 6.3 Total absorptivity of sputtered Si/NiTi multilayer. λ is 1064 nm (HIPPO Nd:YAG laser), 532 nm (Green Nd:YAG laser) and 355 nm (AVIA Nd:YAG laser).

Figure 6.2 reveals that the first peak in absorptivity of CO₂ laser ($\lambda = 10.6 \mu\text{m}$) annealing is at around $0.72 \mu\text{m}$. The absorptivities of Si and NiTi are calculated as $A_{si} = 0.07\%$ and $A_{niti} = 33.5\%$, respectively. Figure 6.3 shows the absorptivity of other three lasers. The absorptivities of 1064 nm and 532 nm laser oscillate with a period of $\frac{\lambda}{2n_{si}}$. For the 355 nm

laser, if the thickness of sputtered Si exceeds the optical penetration depth l_{si}

($l_{si} = \frac{\lambda}{4\pi k_{si}} = 9.35 \text{ nm}$), the absorption of sputtered Si becomes strong and interference

disappears. Thus, the absorbed laser power tends to be stable. Absorptivity of different thickness of sputtered Si in Table 6.2 proves that the laser power is mainly absorbed by the sputtered Si layer when $h_{si} > l_{si}$.

ANSYS results reveal that the highest temperature in the case of a 0.72 μm Si layer atop of NiTi film is 1032 K for CO₂ laser ($\lambda = 10.6 \mu\text{m}$) (Fig. 6.4). Hence, we may conclude that the minimal thickness of sputtered Si layer for CO₂ laser annealing is about 0.72 μm .

Absorptance (%)	$h_{si} = 20 \text{ nm}$	$h_{si} = 45 \text{ nm}$	$h_{si} = 90 \text{ nm}$
A_{si}	34.83	41.9	42.35
A_{niti}	3.95	0.28	0.002
$A = A_{si} + A_{niti}$	38.78	42.18	42.352

Table 6.2 Absorptivity of different thickness of sputtered Si. $\lambda = 355 \text{ nm}$.

Figure 6.4 Temperature distribution of Si/NiTi/Si multilayer at 0.01 s. Laser power is 25 W, 0.72 μm sputtered Si layer, 4 μm NiTi layer and 450 μm Si wafer. $A_{si} = 0.07\%$ and

$$A_{niti} = 33.5\% .$$

Above analysis shows that the thickness of sputtered Si is still a dominant factor. The 355 nm laser may be a good candidate for annealing due to its insensitivity to the thickness of Si as long as $h_{si} > 45$. However, since the sputtered Si is relatively thin, the effects of oxidation in sputtered Si (SiO_2) and interfacial layer should not be ignored. Assuming the Si layer is deposited right after NiTi film in the same vacuum chamber, the oxidation in NiTi may be neglected. The effect of roughness can also be ignored since in general the average roughness is only around a few nanometers in sputtered amorphous NiTi thin films (He 2004).

6.2 Effects of oxidation and interfacial layer

Using the same software as mentioned in Section 5.2.3, a study on the effects of oxidation and interfacial layers is carried out. Figures 6.5-6.8 show the thickness dependence of $\text{SiO}_2/\text{Si}/\text{NiTi}$ multilayer at different wavelengths. As shown in Figs. 6.5-6.8, the total absorptivity is mainly dependent on the thickness of sputtered Si.

Figure 6.5 Total absorptivity of $\text{SiO}_2/\text{Si}/\text{NiTi}$ multilayer. $\lambda = 10.6 \mu\text{m}$ (CO_2 laser).

Figure 6.6 Total absorptivity of SiO₂/Si/NiTi multilayer. $\lambda = 1.064 \mu\text{m}$ (HIPPO Nd:YAG laser).

Figure 6.7 Total absorptivity of SiO₂/Si/NiTi multilayer. $\lambda = 532 \text{ nm}$ (Green Nd:YAG laser).

Figure 6.8 Total absorptivity of SiO₂/Si/NiTi multilayer. $\lambda = 355\text{ nm}$ (AVIA Nd:YAG laser).

Figures 6.9-6.12 present the thickness dependence of Si/NiTi interface layer of four different wavelengths. The total absorptivity increases with the increasing thickness of the Si/NiTi interface layer. As compared with that in backside annealing, the effects of oxidation layer and interfacial layer are more significant.

Figure 6.9 Total absorptivity of Si/NiTi multilayer with a Si/NiTi interfacial layer. $\lambda = 10.6\text{ }\mu\text{m}$ (CO₂ laser).

Figure 6.10 Total absorptivity of Si/NiTi multilayer with a Si/NiTi interfacial layer. λ =1.064 μm (HIPPO Nd:YAG laser).

Figure 6.11 Total absorptivity of Si/NiTi multilayer with a Si/NiTi interfacial layer. λ =532 nm (Green Nd:YAG laser).

Figure 6.12 Total absorptivity of Si/NiTi multilayer with a Si/NiTi interfacial layer. $\lambda = 355$ nm (AVIA Nd:YAG laser).

6.3 Remarks

Above-theory study reveals that direct laser annealing of NiTi thin films is possible. The influence of oxidation and interfacial layer is more significant than that in backside CO₂ annealing. However, experimental verification is necessary, but has not yet carried out due to time limit.

CHAPTER 7

Conclusions and Future Works

7.1 Conclusions

This thesis presents studies on two novel techniques for the fabrication of NiTi SMA micro devices. One is to utilize the SME and TWSME at micro scale generated by indentation, and the other is laser annealing of NiTi thin films.

Micro indentation study of NiTi SMA

Microscopic behavior of SMAs has been investigated in recent years due to its great potential in MEMS. For instance, the motion generated by either SME or TWSME in indentation can be a promising actuation mechanism for micro devices.

A series of micro indentation tests were carried out at different temperatures and different loads. Subsequently, the SME and TWSME in the indents were investigated by AFM and WYKO. Some important mechanical properties of NiTi SMAs, such as, hardness and elastic modulus, were studied by the indentation tests. Hardness was found to be dependent on the indentation load and temperature. At a constant indentation temperature, hardness is affected by the indentation size. While under a constant load, different from normal metals, hardness is higher at a higher temperature. Elastic modulus is independent on the indentation load but affected by the indentation temperature. Elastic modulus of martensite is lower than that of austenite. Energy analysis was also carried out. It was found that energy approach does reveal the difference between martensite and austenite in many aspects, but still cannot match the transformation temperatures with the result of DSC test. This might be attributed to the complex stress state in indentation test.

Pile-up/sink-in phenomenon was studied after indentation tests. The step-by-step method

proposed by Giannakopoulos and Suresh (1999) was found inadequate to explain this phenomenon in SMAs. A schematic explanation, which combines the stress-strain relationships of SMAs at different temperatures and the phase regime under the tip of indenter upon loading, was proposed. It can interpret the pile-up in the austenite samples (due to low-strain-hardening) and sink-in in the martensite samples (caused by high-strain-hardening). However, after a thermal cycle, all indents were pile-up.

The SME results obtained in the course of this project show some difference as compared with that previously reported in the literature. Ni et al. (2004) and Shaw et al. (2003) reported that the recovery ratio of SME in martensite indents of Vickers indenter is a constant. Our experiment revealed that the recovery ratio of SME in martensite indents increases with the indentation load. And the recovery ratio of SME is also dependent on the indentation temperature, i.e., a lower indentation temperature leads to a higher recovery ratio.

The TWSME was found in all indents, which is attributed to the severe plastic deformation under a sharp indenter. At a given indentation load, the plastic deformation was found to be a constant, and thus the recovery ratio of TWSME was independent on the indentation temperature. On the other hand, with the increasing indentation load, plastic deformation increases and the recovery ratio of TWSME also increases accordingly. In addition, thermal cyclic tests showed that the TWSME still exists even after 10 cycles.

Laser annealing of NiTi thin films

Previous experiments showed that CO₂ laser annealing of sputter deposited NiTi thin films through silicon wafer side resulted in the crystallization of NiTi films, which show shape memory but are lack of stability in processing. A theoretical study on the process of CO₂ laser annealing was carried out. Laser energy absorptivity was determined based on the

interference phenomenon. It was found that the exact thickness of Si wafer is a dominant factor in absorptivity. Temperature distribution in the laser annealing process was investigated by finite element analysis. It revealed that CO₂ laser can anneal NiTi films if the laser beam impinges from the back silicon side, and the high temperature zone is highly localized. The effective annealing zone is about the spot size of the laser beam, which agrees well with the previous experimental observation.

The effects of surface conditions and interfacial layer on CO₂ laser annealing were discussed. It was found that surface roughness, oxide layer and interfacial layer may induce instabilities in laser annealing and should be considered seriously. For CO₂ laser annealing from the back Si wafer side, double-side polished wafer is preferred.

Furthermore, a more adaptable approach, direct laser annealing, by sputtering a thin Si layer atop of NiTi was proposed. Absorptivity analysis and FEM simulation of lasers with different wavelengths were performed. The results showed that the required minimal thickness of sputtered Si thin layer depends on the wavelength of the laser. For instance, a sputtered Si layer of 700 nm in thickness on a NiTi thin film is adequate for CO₂ laser annealing, while for 1064 nm Nd:YAG laser, the thickness is around 40 nm. It also showed that 355 nm lasers are good candidate, as they have a stable absorptance as long as the Si layer is thicker than 40 nm.

7.2 Future works

- A study on the long-term stability of TWSME in micro indents of NiTi SMAs is necessary.
- Experimental investigation is necessary to verify the theoretical study of direct laser annealing of NiTi thin films in Chapter 6.

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APPENDIX A

SELECTED PROPERTIES OF TYPICAL SMAs¹

		NiTi	CuZnAl	CuAlNi
Specific heat (J/Kg°C)		450-620	390-400	373-574
Thermal conductivity (at 20°C) (W/mK)		8.6-18	84-120	30-75
Density (Kg/m ³)		6,400-6,500	7,540-8,000	7,100-7,200
Latent heat (J/Kg)		19,000-32,000	7,000-9,000	7,000-9,000
Electrical resistivity (10 ⁻⁶ Ωm)		0.5-1.1	0.07-0.12	0.1-0.14
Thermal expansion coefficient (10 ⁻⁶ /K)		6.6-11	17	17
Maximum recovery stress (Mpa)		500-900	400-700	300-600
Normal working stress (Mpa)		100-130	40	70
Fatigue strength (N=10 ⁶) (Mpa)		350	270	350
Maximum transformation strain (%)	N=1	6-8	4-6	5-6
	N<10 ²	6-8	4	4
	N<10 ⁵	2-4 (3)		
	N<10 ⁷	0.5		
Normal number of thermal cycles		>10 ⁵	>10 ⁴	> 5×10 ³
Young's Modulus (Gpa)		28-83	70-100	80-100
Shape memory transformation temperature (°C)		-200-200	-200-150	-200-200
Hysteresis (°C)		2-50	5-20	20-40
Maximum overheating temperature (°C)		400	150	300
Damping capacity (SDC%)		15-20	30-85	10-20
Grain size (µm)		1-100	50-150	25-100
Melting, casting and composition control		difficult	fair	fair
Forming (rolling, extrusion)		difficult	easy	difficult
Cold-working		fair	restricted	very difficult
Machinability		difficult	very good	good
Cost ratio		10-100	1-10	1.5-20

¹ (Huang 2002)

APPENDIX B

SELECTED DATA FROM PHILIPS XRD DATABASE

Element	Structure	2 θ (°)	Int. (%)	h k l	Remark
NiTi	Cubic	42.803	100	1 1 0	Austenite(B2)
NiTi	Cubic	61.978	40	2 0 0	Austenite(B2)
NiTi	Cubic	78.147	60	2 1 1	Austenite(B2)
NiTi	Monoclinic	45.187	26	0 2 1	Martensite(B19')
NiTi	Monoclinic	50.924	12	$\bar{1}$ 1 2	Martensite(B19')